Frontispiece: Battery buildings of the Woodstock Goldmining Company, Karangahake, 1897. Watercolour by Christopher Aubrey (floruit 1876 - 1906). Alexander Turnbull Library.

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FLUID INCLUSIONS, STABLE ISOTOPES AND GEOCHEMISTRY
OF PORPHYRY COPPER AND EPITHERMAL VEIN DEPOSITS
OF THE HAURAKI GOLD - SILVER PROVINCE,
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ABSTRACT

Tertiary epithermal Au-Ag-Pb-Zn-Cu vein, and porphyry copper deposits occur in the Hauraki Province.

The epithermal deposits were extensively mined for gold and silver in the late 1800's, and early 1900's and produced approximately 300 million grams (10 million ounces) of gold and 1,000 million grams (30 million ounces) of silver. They occur in Jurassic greywacke suite rocks, lower Miocene-Pliocene andesites and dacites, and upper Miocene-Pleistocene rhyolites although the deposits in the andesites and dacites produced most of the gold and silver mined.

Base metal assemblages of the epithermal deposits are dominated by pyrite, sphalerite, galena and chalcopyrite, whereas acanthite and native gold (electrum) are the most common precious metal minerals. Tellurides (e.g. hessite) and seleniferous - selenide minerals are locally important. Gangue minerals are mainly quartz and calcite.

Near neutral or slightly alkaline fluid pH is indicated for the epithermal fluids by the occurrence of sericite and/or adularia in wall rock alteration mineral assemblages. Acidic fluids, forming kaolinite, are characteristic of late stages or near surface environments.

Fluid inclusion filling temperatures, and sulphur isotope temperatures from sphalerite-galena pairs, indicate that base metal deposition occurred mainly between 320 and 280°C, precious metal assemblages predominantly in the range of 280 - 200°C and late stage barite, in some deposits, generally below 200°C. There is fluid inclusion evidence for boiling during mineralisation in some deposits.

Apparent salinities of the epithermal fluids, determined from fluid inclusion freezing temperatures, range from 0 - 6.1 eq. wt. % NaCl. No consistent difference in average apparent salinity was recognised between the different types of epithermal deposits, although the highest recorded values were from the base metal deposits.

The absence of liquid CO_2 in fluid inclusions limits the maximum possible concentration of CO_2 to approximately 3 mole %. Extraction and measurement of CO_2 from some samples indicates an average concentration of approximately 1 mole %. Corrections for dissolved CO_2 required to transform apparent salinities to true salinities indicate that CO_2 is the major solute in low salinity inclusions and that its concentration varied widely during mineral deposition in most deposits.

Thermodynamic models of the geochemical environments of mineral deposition indicate that the large gold-silver deposits were formed by solutions in which sulphur occurred predominantly in reduced form, whereas many other deposits formed from solutions with approximately equal concentrations of oxidised and reduced aqueous sulphur species.

Mineral deposition resulted from several different processes including: changes in fluid pH accompanying reactions with the wall rocks, mixing with other types of fluids, boiling, and variations in the concentration of CO_2 in solution. These various processes acted separately in different parts of the hydrothermal system and general deposited characteristic mineral assemblages.

Deuterium/hydrogen ratios of water extracted from fluid inclusions indicate that most hydrothermal fluids were originally meteoric water.

Sulphur isotope ratios of sulphide and sulphate minerals, in association with the thermodynamic relations of the mineral assemblages, indicate that the sulphur was derived from at least two different sources; sedimentary sulphate and magmatic SO_2 , the relative importance of each varying from one deposit to another.

Two types of hydrothermal systems are postulated for the formation of the epithermal deposits. During andesitic volcanism in the Miocene-early Pliocene, hydrothermal fluid convective cells were generated by heat from near surface small intrusive bodies of magma, whereas during rhyolitic volcanism in the late Miocene-Pleistocene the heat sources were larger plutons at greater depth.

Porphyry copper deposits are associated with quartz diorite stocks intruded into Jurassic greywacke suite rocks and Miocene andesites. They are "diorite" model hypabyssal and volcanic types. The major minerals are quartz, pyrite, chalcopyrite and sphalerite. Additional minerals differ between the different deposits and define two contrasting geochemical environments of deposition, one characterised by low fS_2 , fO_2 and ΣS , indicated by the presence of pyrrhotite, and the other of moderate to high fS_2 , fO_2 and ΣS , indicated by the occurrence of bornite, magnetite or hematite. Associated hydrothermal alteration is generally propylitic although limited phyllic and "potassic" (defined by secondary biotite) types also occur in some deposits.

Fluid inclusion and sulphur isotope studies of the Miners Head porphyry copper deposit suggest that copper mineralisation occurred at a temperature of approximately $425^{\circ}C$ from fluids with apparent salinities up to 15.5 eq. wt. % NaCl and containing sulphur of magmatic origin, predominantly as H_2S .

PREFACE

The principal aim of this thesis is to determine and compare the physicochemistry of mineralisations from several areas of Great Barrier Island and the Coromandel Peninsula (Hauraki Gold - Silver Province). A secondary aim is to formulate a model of mineral genesis.

The writers experimental work consisted of four major projects: 1. electron microprobe analyses of selected sulphide minerals, 2. fluid inclusion heating and freezing studies, 3. fluid inclusion chemical and isotopic (hydrogen) analyses, and 4. sulphur isotope analyses of sulphide and sulphate minerals. In addition a brief study was made of the ore petrography of some deposits.

The geology and hydrothermal alteration of the deposits were not investigated by the writer because they have been studied in detail within the last fifteen years by other workers. However much of this information is currently unpublished and is only available in mineral exploration reports and theses. Williams (1974), the most recent comprehensive review, includes material up to only 1971 and therefore it is appropriate to incorporate an up-to-date review in this thesis.

A description of the individual deposits, incorporating the writers work and a review of previous studies, is presented in Volume 2. Because this thesis is primarily a comparative study of the deposits, the former section is presented as an appendix (Appendix I) rather than as a separate part within the main section. However, it contains most of the geological and physicochemical data, and interpretation, on which the thesis is based and is therefore not a "subsidiary addition" in the strict sense of the word appendix (as defined by the Concise Oxford Dictionary; Sykes, 1976).

The choice of areas studied and the detail of information presented in this thesis is influenced by the accessibility of the individual deposits. Mining in the province was mainly

confined to the late 1800's and early 1900's and most of the workings are now partly or fully collapsed. Many of the mines, including the largest, Waihi, were mined from shafts and are now flooded. Samples originating from some of these mines were obtained from mine dumps and museum, university and private collections. The precision with which their original location within the mine can be determined depends on the care taken in their original collection, collation and storage.

The deposits in the Thames - Tapu, Kapowai and Golden Cross areas (Fig. 1-1) were not investigated (although reviewed in Appendix I). Merchant (1978), concurrently with the early part of this thesis work, studied the mineralisation and fluid inclusions of the Thames - Tapu area and Dr. B.W. Robinson of the Institute of Nuclear Sciences has investigated the stable isotopes (unpublished). Although some underground workings are accessible at Kapowai, mineralisation is rare and the vein material generally unsuitable for fluid inclusion work (chalcedonic quartz and quartz pseudomorphs after calcite). The workings at Golden Cross are inaccessible.

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ABBREVIATIONS FOR MINERALS

The abbreviations used for mineral names in this thesis, follow the scheme listed below, unless stated otherwise.

Metallic ("Ore") Minerals

ac	acanthite
agu	aguilarite
apy	arsenopyrite
bi	bismuthinite
bo	bornite
cal	calaverite
cb	cinnabar
cc	chalcocite
cv	covellite
el	electrum
en	enargite
gn	galena
hm	hematite
mc	marcasite
mg	magnetite
mo	molybdenite
nm	naumannite
pb	polybasite
pg	pyrargyrite
po	pyrrhotite
ptz	petzite
sb	stibnite
sch	scheelite
sp	sphalerite
syl	sylvanite
thd	tetrahedrite
wo	wolframite

Gangue Minerals

ad	adularia
ak	ankerite
an	anhydrite
ba	barite
ca	calcite
carb	carbonate
cl	chlorite
do	dolomite
fl	fluorite
qtz	quartz
mu	muscovite
pym	pyromanganite
rho	rhodochrosite
sc	sericite
sd	siderite

CHAPTER 1

INTRODUCTION

LOCATION OF STUDY

The area of study is termed here the Hauraki Gold - Silver Province and comprises Great Barrier Island and the Coromandel Peninsula as far south as Te Puke (Fig. 1-1).

ECONOMIC HISTORY

Epithermal vein type deposits were extensively mined in the late 1800's and early 1900's, establishing the area as a gold - silver province with gold production comparable with the most successful gold mines in other parts of the world at that time. Between 1852 and 1952 approximately 300 million grams (10 million ounces) of gold and 1,000 million grams (30 million ounces) of silver were produced from the centres shown in Figs 1-1 and 1-2.

Porphyry copper mineralisation at Miner's Head (Fig. 1-1) yielded 2,300 tonnes of copper ore between 1857 and 1867.

Initially, primitive ore treatment and extraction methods caused large quantities of gold and silver to be lost in the tailings. This problem was mostly overcome by the introduction of cyanidation in the 1890's.

The most successful mines were at Waihi (the largest mine in New Zealand, Figs 1-3 and 1-4) and Karangahake (Fig. 1-5 and Frontispiece), where gold and silver values, although not outstanding, were consistent throughout most of the production period of the mines (72 and 60 years respectively). In contrast, mines at Coromandel and Thames had boom and bust periods due to the occurrence of gold and silver in restricted bonanzas. Other mining centres were generally only marginally economic or were failures due to low gold values and unsuitable treatment methods.

Deposits at Te Aroha, Maratoto and Thames have been mined recently. Tui Mine (Te Aroha) was re-opened in the mid 1960's by Norpac Mining Company and produced lead, zinc and copper concentrates for export. Declining concentrate prices, mercury contamination and increasing overheads caused it's closure in 1974. Consilver re-opened the Maratoto mine in 1968 and produced small quantities of silver and gold but this venture also ceased in 1973. Several small syndicates are presently mining at Thames on a weekend basis (e.g. Roberts family operating the Reuben Parr - Caladonian mine).

Figure 1-1: Location of mineral deposits and past mining centres in the Hauraki Gold-Silver Province.

Figure 1-2: Bullion (gold plus silver) production from the main mining centres. Values are grams $\times 10^6$.

Figure 1-3: Waihi in the early 1900's. Waihi township in the left background, Waihi Company's Union Battery in left and centre foreground, Martha Hill and opencut in centre background and Grand Junction Battery in right background. Alexander Turnbull Library.

Figure 1-4: Waihi Gold Mining Company's 200-stamp battery and treatment plant at Waihi. Alexander Turnbull Library.

Figure 1-5: Karangahake 1914, showing the buildings of the Talisman Consolidated Company: battery and treatment plant in left foreground and centre middle distance, powerhouse in centre and right foreground. The mines are in Karangahake Mountain in the background. Price Collection, Alexander Turnbull Library.

Figure 1-6: The prospecting opencut in Martha Hill, Waihi, 1978. The vein material (e.g. white rock in bank behind truck at right) was processed in a mill erected on the site of the old Waihi Company's Union Battery (see Fig. 1-3).

Mineral exploration activity in the province rapidly increased with the rise in gold prices in the late 1970's. In 1976 AMOCO started a detailed exploration program beginning with a low level aeromagnetic survey followed by systematic geochemical sampling and geological mapping. They have since investigated and diamond drilled a number of deposits. Gold Mines of N.Z., Goldfields, Mineral Resources Ltd - Otter Minerals, AMAX, CRA and BP have also been active in the area. Following Mineral Resources (N.Z.) Ltd - Waihi Mining and Development's large "prospecting" cut on the old Waihi Mine (Fig. 1-6) AMAX are presently drilling deeper levels.

PREVIOUS GEOLOGICAL WORK

During the main period of mining in the late 1800's and early 1900's a number of geological reports and bulletins were written by members of the Geological Survey and Mines Department. The most important works of this period were the series of bulletins describing the geology of the various subdivisions of the Coromandel Peninsula (Fig. 1-7A): Fraser & Adams (1907), Fraser (1910), Bell & Fraser (1912), Henderson & Bartrum (1913) and Morgan (1924) and a book by Downey (1935) detailing the history and production of the individual mines.

The geology from these early reports and bulletins was compiled and updated in the DSIR 1:250,000 scale geological maps (Fig. 1-7B), Barrier (Thompson, 1960), Auckland (Schofield, 1967) and Rotorua (Healy et al, 1964).

The renewed mining and exploration activity in the late 1960's spawned a second phase of geological literature consisting of theses at Auckland University and publications resulting from them (both referenced in Fig. 1-8), publications by DSIR staff (Fig. 1-9) and mineral exploration company reports (Fig. 1-10). A recent DSIR 1:63,360 scale geological map of the northern part of the Coromandel Peninsula (Skinner, 1976; Fig. 1-7C) has completely revised the regional stratigraphy from that in earlier works.

Most of the authors referenced above and in Figs 1-8, 1-9 and 1-10 described the geology, hydrothermal alteration and mineralisation of one or more of the individual mining centres, but recently there has been a trend to include investigations of the physicochemical conditions of mineralisation in their studies. Robinson (1974) studied stable isotopes of the mineralisation at Tui Mine, whereas Merchant (1978), Torkler (1978), Robson (1979) and Erceg (1981) included some fluid inclusion work in their studies of Thames - Tapu, Neavesville, Coromandel, Whangapoua and Te Ahumata respectively. Robinson & Christie (1980) combined stable isotope and fluid inclusion studies in their investigation of the Maratoto Mine.

A

EARLY DSIR GEOLOGICAL BULLETINS

B

DSIR GEOLOGICAL MAPS AT 1:250,000 SCALE.

C

RECENT DSIR GEOLOGICAL MAPS AT 1:63,360 SCALE

Figure 1-7: Bulletins and maps of the geology of the Hauraki area, published by the N.Z. Geological Survey.

Figure 1-8: Geological theses and associated publications relating to the mineral deposits of the Hauraki Gold-Silver Province.

Figure 1-9: Recent publications by DSIR staff relating to the mineral deposits of the Hauraki Gold-Silver Province.

Figure 1-10: Reports by mineral exploration companies.

CHAPTER 2

REGIONAL GEOLOGY

INTRODUCTION

The following account of the geology of the Coromandel Peninsula and Great Barrier Island is a synthesis of previous work (theses and published material) and current thinking by exploration and academic geologists.

STRATIGRAPHY

The stratigraphy presented in the following sections is illustrated in Figs 2-1 and 2-2 and summarised in the synopsis at the end of the chapter. Only a brief account is given here of selected formations as more detailed descriptions are given by Skinner (1976) and other referenced works.

Manaia Hill Group

The oldest rocks of the Coromandel Peninsula and Great Barrier Island are greywacke and argillite of the Manaia Hill Group. Rare fragmented fossils indicate an upper Jurassic (Ohauan - Puaruan) age (Stevens, 1970).

Skinner (1972, 1976) subdivided the group into Moehau Formation and Tokatea Hill Formation.

Moehau Formation consists of slope-deposited turbidites characterised by a lithic volcanic greywacke and subgreywacke suite (argillite, siltstone, sandstone, chipwacke and conglomerate) derived from calc-alkaline volcanic and plutonic rocks and minor sedimentary rocks.

In contrast the Tokatea Hill Formation consists of a feldspathic greywacke suite (mudstone, siltstone and sandstone) almost devoid of volcanic detritus except near the base, derived from a more mature calc-alkaline plutonic landmass with minor sedimentary rocks. The lower members of the formation are slope-deposited turbidites, whereas the upper part resulted from stable deposition in deeper water.

Te Kuiti Group

Torehina Formation

The Torehina Formation consists of a series of limestones, calcareous siltstones (some fossiliferous: Gigantostrea wollastoni), carbonaceous sandstones, conglomerates and thin coal seams (Kear, 1955; Skinner, 1976).

Foraminifera indicate a Duntroonian (mid-Oligocene) age (Hornibrook, in Kear 1955).

Figure 2-1: Regional geological map.

Figure 2-2: Stratigraphic column.

Coromandel Group

Introduction

Thompson (1960) and Schofield (1967) grouped the andesites (and some dacites) of Great Barrier Island and the Coromandel Peninsula into the Beesons Island Volcanics (synonymous with the First and Second Period Volcanics of the early writers). Subsequent geological studies of these areas followed their example until Skinner (1976) formally restricted Beesons Island Volcanics to a specific group of rocks, at present identified only from Tapu north to Colville. The Beesons Island Volcanics of Thompson and Schofield are now termed Coromandel Group. This group includes Skinner's Beesons Island Volcanics Formation in addition to several other formations of volcanic and intrusive rocks formerly included in the Beesons Island Volcanics.

Published detailed mapping of the Coromandel Group (i.e. Skinner, 1976) cover only the northern part of the Coromandel Peninsula, north of the town of Coromandel, and therefore formal subdivision of the Coromandel Group is confined to this area. However, several informally defined formations described in Auckland University M.Sc. and Ph.D. theses, and some presently being mapped by Skinner, are also included here.

Volcanic Rocks

Table 2-1 lists some of the formally and informally defined formations of volcanic rocks included here in the Coromandel Group. Their distribution is shown in Fig. 2-3.

Volcanic rocks of the Coromandel Group range in age from lower Miocene to late Pliocene. A compilation of K - Ar ages is shown in Fig. 2-4. Skinner (pers. comm.) considers that these K - Ar ages, together with palynological dates, indicate that the Coromandel Group comprises three distinct phases of andesitic volcanism as illustrated in Fig. 2-5. These began in the north and centres were then sited progressively further south. The first two phases were separated by a period of volcanic quiescence, whereas the second and third phases were separated by a period of rhyolite volcanism (Whitianga Group, see later section).

TABLE 2-1: Some formations of volcanic rocks included in the Coromandel Group. Only the formations listed under Northern Coromandel Peninsula, including the Beesons Island Volcanics (also listed under Central Coromandel Peninsula), have been formerly defined. The formations are listed within each group in a general order of increasing age.

NORTHERN COROMANDEL PENINSULA (Skinner, 1976)

Mahinapua Andesite:

hornblende andesite with hypersthene, and minor augite and biotite; pyroclastics, flows, sediments and intrusives.

Te Tutu Andesite:

2 pyroxene (hypersthene dominant) basic andesite; pyroclastics.

Parakete Formation:

hornblende dacite with hypersthene; pyroclastics, volcanic (epiclastic) sediments and rare flows.

Materangi Andesite:

foliated coarsely porphyritic hornblende andesite to quartz andesite with hypersthene and augite; flows, pyroclastics and intrusives.

Whangapoua Andesite:

2 pyroxene (hypersthene dominant) basic andesite; flows and pyroclastics.

Beesons Island Volcanics:

hornblende-bearing hypersthene andesites (generally with either augite or quartz plus biotite); volcanic (epiclastic) sediments, pyroclastics and minor flows and plugs.

Tuateawa Andesite:

2 pyroxene (hypersthene dominant) andesite; flows pyroclastics and sediment.

Te Karaka Andesite:

2 pyroxene (hypersthene dominant) andesite; flows and breccias.

Kokumata Dacite:

ranges from biotite-hornblende dacite, through biotite-hornblende-augite andesite to hornblende pyroxene quartz andesite; flows, pyroclastics and sediments.

Omoho Formation:

rhyodacite and quartz porphyry; tuffs and sediments.

Port Charles Andesite:

hornblende-pyroxene, pyroxene-hornblende-quartz and pyroxene andesites; flows, breccias and tuffs.

CENTRAL COROMANDEL PENINSULA (Skinner et al. 1979; pers.comm.)

Omahia Andesite (=Taurauikau Andesite at Table Mountain):

dark strongly porphyritic, feldspathic, basic andesite (varieties containing augite, hornblende, hypersthene, olivine and quartz c.f. Schofield, 1967; Main, 1971; Rabone, 1971; Hayward, 1974) Omahia Andesite of the Waitawheta area was K-Ar dated at 3.78my by Stipp (1968).

Taurahuehue Andesite:

fine grained glassy pyroxene andesite.

Maumaupaki Volcanics:

hornblende bearing felsic andesite to dacite.

Beesons Island Volcanics: (see previous section).

HOT WATER BEACH - TAIRUA (Ovens, 1976)

Tapuaetahi Andesite:

hypersthene-augite andesite; flows, breccias, tuffs and dikes.

THAMES (Fraser, 1910)

Premier Andesite:

hypersthene augite andesite flows.

Tararu Andesite: (writer's term)

pyroxene, hornblende-pyroxene, hypersthene and hornblende andesites and dacites; flows, breccias & dikes.

WAITEKAURI (Rabone, 1975)

Jubilee Andesite:

hypersthene andesite flows and minor breccias.

Ohinemuri Andesite:

quartz-hypersthene andesite flows.

Puketawa Andesite:

augite-hypersthene andesite flows.

TE AROHA (Cochrane, 1969)

Summit Andesite:

augite-hypersthene andesite flows.

Ruakaka Quartz Andesite:

quartz andesite flows, breccias and tuffs.

Tui Andesite:

augite-hypersthene andesite flows. K-Ar dated at 16.2m.y. by Adams et al (1974).

Figure 2-3: Formally and informally defined formations of volcanic rocks, included in the Coromandel Group (see Table 2-1 for descriptions).

Figure 2-4: Compilation of K-Ar ages for volcanic rocks of the Coromandel Group.

a = Adams & others (pers. comm.)

b = Adams *et al* (1974)

c = Stipp (1968)

Figure 2-5: Phases of andesitic volcanism distinguished by Dr D.N.B. Skinner (pers. comm.).

Intrusive Rocks

(a) Oroville Quartz Porphyrite

Ramsay (1971) and Ramsay & Kobe (1974) mapped a small intrusive body (approximately 500 m in diameter) in Coromandel Group andesites of the Te Ahumata area and named the unit Oroville Quartz Porphyrite. It consists of a "porphyritic to panidiomorphic, granular quartz-hypersthene-augite rock with plagioclase phenocrysts" (Ramsay & Kobe, 1974 p145). Contacts with surrounding andesites are not exposed.

(b) Paritu Plutonics

A composite pluton intruding both Moehau Formation (greywacke suite rocks) and Port Charles Andesite at the northern end of the Coromandel Peninsula was named Paritu Plutonics by Black (1972). The predominant rock type is quartz diorite (Skinner, 1976), however granodiorite and tonalite are also major constituents. K - Ar ages range from 16.0 to 17.1 m.y. (Richards et al, 1966).

(c) Kai-iti Porphyrites

Kai-iti Porphyrites are andesitic and dacitic intrusive bodies in Manaia Hill Group and Coromandel Group rocks which are neither clearly the intrusive equivalent of any volcanic eruptive formation, nor fall within a mappable geographic - compositional association (Skinner, 1976).

Kai-iti Porphyrites have been mapped in the northern part of the Coromandel Peninsula (north of the town of Coromandel) by Skinner (1975, 1976), in the Petote Stream area (south-east of the town of Coromandel) by Edwards (1979), and in the Manaia Valley by Stevens (1980). The latter authors recommended abandoning the term porphyrite and renaming the formation Kai-iti Intrusives.

A quartz diorite cemented breccia pipe at Miners Head and various quartz diorite porphyry dikes to the north of this locality, intruding greywacke suite rocks on Great Barrier Island, have not been formally named. They are informally included within the Kai-iti Porphyrites in this Thesis. Similarly, various intrusives in greywacke or Coromandel Group volcanics noted by Fraser & Adams (1907) from the Tokatea and Opitonui Mines and by Brathwaite (1980) from the Waihi Mine are also here included in the Kai-iti Porphyrites.

The Miners Head intrusive was K - Ar dated at 18.1 ± 0.2 m.y. (Dr C.J.D. Adams & Prof. P.M. Black, pers. comm.).

(d) Whangapoua Intrusives

Stocks of hornblende diorite porphyry and hornblende microdiorite porphyry emplaced in Coromandel Group andesites of the Whangapoua area were named Whangapoua Intrusives by Robson (1979). The hornblende diorite porphyry stock is cut by several dikes of andesite porphyry.

(e) Tainui Intrusives

Merchant (1978) recognised several high level intrusive stocks of quartz diorite porphyry and dacite porphyry, and deeper level leucocratic quartz diorite intruding Coromandel Group andesites of the Tapu - Thames area. He collectively named them Tainui Intrusives.

K - Ar ages range from 9.3 to 12.6 (- 19.9 ?) m.y. (Dr C.J.D. Adams & Dr R.J. Merchant pers. comm.).

Waitawheta Dacites

Waitawheta Dacites, named by Healy et al (1964, c.f. Briggs 1973), occur predominantly south of Waikino although a few small isolated occurrences were mapped in the area between Coromandel and Whitianga by Schofield (1967). Skinner (1979) has suggested that the dacitic rocks of the Waitekauri area, mapped by Rabone (1971, 1975) as Whitianga Group (see next section), may also be Waitawheta Dacites.

Waitawheta Dacites comprise dacitic to andesitic lava flows, pyroclastics (ignimbrites and non-welded types) and sediments. In their type area they occur between Coromandel Group andesites and Whitianga Group rhyolites and ignimbrites but they have not been formally assigned to either of these groups.

Stipp (1968, p 215) determined a K - Ar age of 3.90 ± 0.07 m.y. for Waitawheta Dacites at the western end of the Kaimai Tunnel.

Whitianga Group

The Whitianga Group (synonymous with the Third Period Volcanics of the early writers) consists of rhyolite pyroclastics and epiclastic sediments, ignimbrites and flow banded, spherulitic and lithoidal rhyolites. The stratigraphy and geology, with emphasis on the pyroclastic flow units, were reviewed by Briggs (1973).

Thompson (1966) classified the Whitianga Group into two "contemporaneous" subgroups: Minden Rhyolite (flow banded, spherulitic and lithoidal rhyolite) and Coroglen Ignimbrite (ignimbrites, pyroclastics and sediments). Hayward (1974) suggested that the latter should be

termed Coroglen Subgroup rather than Coroglen Ignimbrite because it is not entirely composed of ignimbrite. The terms Minden Rhyolite Subgroup and Coroglen Subgroup are used in this thesis.

Harvey (1967), Rutherford (1970, 1978), Hayward (1971, 1973, 1974), Rabone (1971, 1975), Ramsay (1971), Ramsay & Kobe (1974), Moore (1976, 1979), Ovens (1976), Merchant (1978), Torckler (1978), Barker et al (1980) and Erceg (1981) investigated individual areas of Whitianga Group rocks in detail and their results indicate a complex stratigraphic succession involving sequences of alternating Coroglen Subgroup and Minden Rhyolite Subgroup formations. Skinner (in Skinner et al, 1979) suggested that each dome complex and flow sheet must be treated as a separate formation. Correlation from one area to another is therefore difficult.

The most complete exposed sequence has been described from the Table Mountain area (Fig. 2-6) by Hayward (1971, 1973, 1974) and is summarised in Fig. 2-7. Hayward (1974) considered that a volcanically - quiescent period of erosion took place between the Coromandel Group andesitic eruptions and the start of the Whitianga Group rhyolite activity, forming a moderately dissected landscape and depositing pockets of talus breccia.

The first rhyolitic eruptions were a short explosive phase followed by a quiescent period of sedimentation in small lakes (Wainora Formation). Major tephra eruptions which buried the land beneath a thick blanket of ash and lapilli shower deposits, hot pyroclastic flows, and lahars terminated the Wainora sedimentation. Although the lakes soon became infilled, deposition of fluvial, subaerial, and minor lacustrine sediments continued in the valleys during the first half of this eruptive phase, after which all Coroglen sediments and ignimbrites were subaerial.

As the explosive tephra eruptions waned, Minden Rhyolite domes were intruded and extruded, possibly along some of the pre-existing vents. Two phases of domes occur at Table Mountain and these are interbedded with Coroglen Subgroup pyroclastics and epiclastics.

The following descriptions of other Whitianga Group sequences are listed in geographical order from north to south (c.f. Fig. 2-6).

Great Barrier Island

Whitianga Group rocks are exposed on Great Barrier Island at Mt Hobson, Te Ahumata (Whitecliffs) and Okupu (Fig. 2-6).

The Hobson Rhyolite (Thompson, 1960) of Mt Hobson consists of

Figure 2-6: Rhyolitic rocks of the Hauraki Gold-Silver Province.

MINDEN RHYOLITE
SUBGROUP

COROGLLEN SUBGROUP

WHITIANGA GROUP

COROMANDEL GROUP

Atuatumoe, Waiwawa,
Kauaeranga, and Moyles
(oldest) rhyolite
domes.

Omahia Andesite

Subaerial deposits:
dominantly pyroclastic,
several thin poorly
welded ignimbrites

undifferentiated

Waterlaid pyroclastics:
interlensing fine-
coarse grained
sediments, with
andesite, pumice &
rhyolite blocks

not

exposed

not

exposed

Wainora Fm.

Fine grained highly
carbonaceous
epiclastic lake
sediments with leaf
impressions and
mussel fossils.
Preceded by pre-lake
pyroclastics with
andesite and rhyolite
clasts.

Undifferentiated
andesite flows
and epiclastic
sediments.

100 m
50 m
0

Figure 2-7: Stratigraphic column for the Table Mountain area compiled from descriptions by Hayward (1974a; 1974b).

rhyolite lavas and minor breccia and tuff which may be part of an eroded dome (Thompson, 1960). A rhyolite dome also occurs at Okupu (Erceg, 1981).

The Ahumata Sinter Formation (Ramsay & Kobe, 1974) at Te Ahumata is a lacustrine sequence of siliceous sinter, rhyolite pyroclastics and carbonaceous shales (Ramsay & Kobe, 1974).

Whitianga

The area east of Whitianga (Fig. 2-8) was described by Harvey (1967) and Ovens (1976) and comprises 10 domes, numerous small associated pumice breccias and two ash flow (ignimbrite) sheets of the Whitianga Group. Harvey (1967) considered that dome formation began by exogenous growth involving the effusion of flow rhyolites and pumice breccias. Subsequent endogenous dome building produced the main dome with spherulitic outer and crystalline inner phases. Sometime late in this sequence at least two domes erupted fragmental material forming ash flow sheets. Ovens (1976) postulated that the Whitianga Ash Flow was erupted from a vent sited in what is now Whitianga Harbour, whereas the Hot Water Beach Formation (ignimbrite) was considered to have originated from a breach in the Whenuakite Dome. The Hot Water Beach Formation occurs at the margin of the Whitianga Group and unconformably overlies Tapuaetahi Andesite Formation (Coromandel Group).

Based on the geomorphology, Ovens concluded that the Whenuakite Dome was considerably younger than the other domes in the area.

Paku Island

The Minden Rhyolite dome comprising Paku Island (Fig. 2-6) was described by Rutherford (1970). It consists of a steep to vertical flow layered perlitic to glassy spherulitic, obsidian rich outer zone surrounding a core or plug of inward dipping flow banded lithoidal rhyolite. Eruptions of ignimbrites and pumice breccias occurred prior to endogenous dome building.

Broken Hills

The sequence at Broken Hills, described by Moore (1976, 1979), consists of a 100m thick series of flow banded rhyolites (Minden Rhyolite), unconformably overlying Coromandel Group volcanics, followed by Coroglen Subgroup pyroclastics.

Figure 2-9: Fission track ages of Whitianga Group rocks: a = Minden Rhyolite Subgroup, determined by Rutherford and b = Coroglen Subgroup, determined by Kohn (1973). Areas of rhyolite rocks (Whitianga Group and other units) are shaded.

Thames

Only pyroclastics and ignimbrites of the Coroglen Subgroup are present in the Lookout Rocks of the Thames area, described by Merchant (1978). He correlated them with the Whitianga Group sequence at Table Mountain, 10 km to the north-east.

Neavesville

Minden Rhyolite is also absent from the Neavesville area described by Torckler (1978) and Barker et al (1980). At this location the Coroglen Subgroup consists of pyroclastics followed by lacustrine sediments and a further phase of subaerial rhyolitic pyroclastics.

Waitekauri

In the Waitekauri area Rabone (1971, 1975) mapped units of fine grained dacite breccias, massive hornblende dacite flows, lithoidal rhyodacites and rhyolite. The dacitic rocks predominate.

Skinner (in Skinner et al, 1979) suggested that all the dacitic - rhyodacitic rocks of the Waitekauri area may be units of the Waitawheta Dacites.

Waitekauri - Waihi

In the south-eastern section of the Waitekauri area and over much of the Waihi Plains the Whitianga Group consists of spherulitic rhyolite overlain by two ignimbrites; the Owharoa Ignimbrite Formation (Rabone, 1975), formerly known as Owharoite or Wilsonite, and the Tridymite Rhyolite (c.f. Ewart & Healy, 1965 and summary by Briggs, 1973).

Age of the Whitianga Group

Rutherford (1978) dated Minden Rhyolite obsidians from five locations (Fig. 2-9) using the fission track method. His results (8.3 m.y. to 2.3 m.y.) generally support the hypothesis that rhyolite volcanism began in the north and progressed southwards.

Kohn (1973) dated Owharoa Ignimbrite Formation at 2.89 m.y. and Tridymite Rhyolite at 1.5 m.y. also using the fission track method.

Papamoa and Waiteariki Ignimbrites

The rhyolite pyroclastic units in the southern part of the region were mapped by Healy et al, (1964) as Papamoa Ignimbrite and Waiteariki Ignimbrite. Although Briggs (1973), in her review,

included them as part of the Whitianga Group they have not been formerly assigned to this group and are therefore considered separately here.

Waiteariki Ignimbrite is dacitic in composition, whereas Papamoa Ignimbrite is dacitic to andesitic. The units are similar in appearance and stratigraphic position and may be correlatives. Healy *et al* (1964) assigned them a Miocene age, however paleomagnetic evidence suggests that the age of Waiteariki Ignimbrite (and Papamoa Ignimbrite?) may be mid-Pleistocene (c.f. Briggs, 1973).

Papamoa Ignimbrite is separated from older Coromandel Group andesites by Te Puke Breccias, a sedimentary unit consisting of pumice breccias and tuffs, with interbedded freshwater siltstones and sandstones (Healy *et al*, 1964).

Kerikeri Volcanic Group

Mercury Basalts

Mercury Basalts are a series of "extrusives, intrusives, pyroclastites and epiclastites belonging to a saturated high alumina, calc-alkaline basalt suite of tholeiitic parentage" (Skinner, 1976 p 15). They were mapped by Skinner from the eastern tip of the Kuaotunu Peninsula, Red Mercury Island and several nearby islands. He considered that they were younger than lower Pliocene (Skinner, 1976) and probably of mid or late Pleistocene age (Skinner, in Skinner *et al*, 1979).

STRUCTURE

Introduction

The structure of the province is dominated by the NW - NNW trend of the Coromandel Peninsula and fold axes of the greywacke basement (Manaia Hill Group). Subsequent faulting was predominantly longitudinal (NW - NNW) or transverse (NE - ENE) to this trend, however Skinner (1976) considered that where there is thick Cenozoic rock cover the faults trend more NW and NE.

Hauraki Depression

The western margin of the Coromandel Peninsula is bounded by the Hauraki Depression, defined by the Hauraki Plains and the Firth of Thames. Hochstein & Nixon (1979) suggested that the Hauraki Depression was part of a rift structure, the Hauraki Rift, which extends for approximately

300 km from the Taupo Volcanic Zone, through the Hauraki Gulf, to Whangarei (Fig. 2-10). These authors considered that the rift was initiated in the upper Miocene and that recent activity is indicated by active faulting, shallow earthquakes and the presence of numerous hot springs (e.g. Te Aroha).

Coromandel Depression

O'Leary (1978) made a gravity survey of the eastern part of the Coromandel Peninsula and interpreted his results to indicate the existence of a graben between Whitianga and Whangamata (Figs 2-10 and 2-11) filled with Whitianga Group rocks. He named the structure the Whitianga Graben. He proposed that the graben was offset at some locations by WSW - ENE cross faults dividing it into a number of blocks. In cross-section (Fig. 2-11) the western margin of this graben has a shallow dip, whereas the eastern margin dips steeply. The graben was considered to be approximately 2.5 km deep.

Hochstein (1980) grouped the Whitianga Graben with similar grabens to the north and south (the latter termed the Waihi Graben) as parts of a structure he named the Coromandel Depression (Fig. 2-10).

RELATION OF VOLCANISM TO PLATE TECTONICS

Regional Setting

Ballance (1976) related the upper Cenozoic volcanism in the northern part of New Zealand to a series of six successive magmatic arcs formed as a result of subduction of the Pacific Plate beneath the Indian Plate. The igneous rocks of the Coromandel Peninsula and Great Barrier Island may be correlated with four of these arcs as follows:

Northland Arc (c.a. 18 m.y. to c.a. 15 m.y.): Early to mid Miocene Coromandel Group quartz diorite and granodiorite intrusives (e.g. Miners Head and Paritu) and andesite volcanics.

Coromandel Arc (c.a. 15 m.y. to 6 m.y.): Upper Miocene Coromandel Group andesite volcanics and intrusives (e.g. Tainui Intrusives).

Whitianga Arc (c.a. 6 m.y. to 3 m.y.): Pliocene Whitianga Group rhyolite volcanics, Waitawheta Dacites and Coromandel Group andesitic and dacitic volcanics and intrusives (e.g. Omaha Andesite).

Tauranga Arc (c.a. 3 m.y. to 0.75 m.y.): Whitianga Group ignimbrites (e.g. Owaharoa Ignimbrite Formation and Tridymite Rhyolite), Papamoa Ignimbrite, Waiteariki Ignimbrite and Mercury Basalts (Kerikeri Volcanic Group).

FIGURE 2-10A

FIGURE 2-10B

Figure 2-10: The Hauraki Rift and Coromandel Depression: Fig. 2-10A, map (after Hochstein & Nixon, 1979; Hochstein 1980; O'Leary, 1978) and Fig. 2-10B, cross section (modified from Hochstein & Nixon, 1979 Fig.10).

Figure 2-11: Cross sections of the Whitianga Graben (Fig. 2-10). (From O'Leary, 1978 Figs 3, 4 and 5.)

The evolution of the magmatic arcs in relation to the position and form of the Indian Plate/Pacific Plate boundary was discussed by Cole & Lewis (1981).

Magma Genesis

The genesis of the magmas which produced the intrusive and extrusive rocks of the Coromandel and Whitianga Groups is probably similar to that presently forming andesitic and rhyolitic volcanism in the Taupo Volcanic Zone, the latter representing a later stage in the evolution of the New Zealand Magmatic Arc (Ballance, 1976; c.f. Cole & Lewis, 1981).

The models advanced by Cole (1981) for the genesis of the volcanic rocks of the Taupo Volcanic Zone are considered by the writer to be also applicable to the Coromandel and Whitianga Groups. He suggested that andesite magmas were formed by partial melting of amphibolite in the subduction zone, whereas hydration of the lower crust, causing partial melting of the greywacke suite rocks, produced the rhyolite magmas.

SYNOPSIS

The basement rocks of Jurassic greywacke and argillite (Manaia Hill Group) were intensively deformed, uplifted and folded approximately along the axis of the peninsula during the Rangitata Orogeny (Jurassic to Cretaceous). A long period of peneplanation followed, culminating in a mid Tertiary marine transgression with the deposition of a succession of fresh water, estuarine and marine sediments (Torehina Formation) around the periphery of the Coromandel Ranges.

A volcanic arc (Northland Arc of Ballance, 1976) was initiated in the lower Miocene by the formation of a westward dipping subduction zone intersecting the surface east of the Coromandel Peninsula. Plutonic and hypabyssal acid and intermediate magmas intruded the greywacke (e.g. Paritu Plutonics and Kai-iti Porphyrites) and were associated with widespread andesitic volcanism (lower Coromandel Group) between 19 and 16 m.y.. Volcanic episodes began in the northern part of the region and migrated southward with time.

A period of volcanic quiescence occurred over most of the area between 16 and 12 m.y. to be followed by a second period of intrusion (e.g. Tainui Intrusives) and andesitic volcanism between 12 and 6 m.y. (Coromandel Arc of Ballance, 1976). Sometime during this period the site of subduction began migrating south-eastward to form successively the Tauranga Arc and the Taupo Arc. The changing tectonic pattern caused tensional faulting and the development of the Coromandel Depression into

which rhyolite volcanics (Whitianga Group) were intruded and erupted between 9 and 3 m.y. (c.a. Whitianga Arc).

Andesitic and dacitic volcanism (e.g. Omaha Andesites and Waitawheta Dacites) proceeded concurrently with, but in different areas to, the rhyolite volcanism.

Volcanism culminated with the eruption of large pyroclastic flow deposits (e.g. Owharoa Ignimbrite Formation and Tridymite Rhyolite) and basalts (Mercury Basalts).

A zone of rifting currently occurs to the west of the Coromandel Peninsula, in the Hauraki Depression, and is related to the present site of the magmatic arc in the Taupo Volcanic Zone.

CHAPTER 3

HYDROTHERMAL ALTERATIONINTRODUCTION

An understanding of the style of hydrothermal alteration of the country rocks is important to the study of mineralisation for the interpretation of both the physicochemistry and genesis.

This chapter reviews the types of hydrothermal alteration identified in the province by previous writers.

HYDROTHERMAL ALTERATION MINERAL CHECKLIST

The hydrothermal alteration minerals identified from the various areas studied by previous writers are listed in Table 3-1.

NOMENCLATURE

Some brief notes on a few hydrothermal alteration minerals are included here to rationalise the nomenclature used in their identification by the different authors referenced in later sections.

Kaolin, Kaolinite and Kaolinite Group

The term kaolin was used by the early writers for all hydrothermal clays and does not necessarily imply a kaolinite composition. Therefore it is abandoned here and the term hydrothermal clay is used instead. the term kaolinite is used for the mineral species kaolinite and is distinct from the term kaolinite group which includes all clays with a kaolinite 2 layer type structure (e.g. kaolinite, dickite, nacrite and halloysite).

Sericite

Sericite is a term used to define fine grained white mica, either muscovite ($K_2Al_4[Si_6Al_2]O_{20}[OH]_4$) or paragonite ($Na_2Al_4[Si_6Al_2]O_{20}[OH]_4$). Only the potassium form is considered here.

K-sericites tend to have higher SiO_2 , MgO and H_2O and lower K_2O than muscovites and as such are illites ($K_{0-2}Al_4[Si_{8-6}Al_{0-2}]O_{20}[OH]_4$), clays of intermediate composition and structure between muscovite and montmorillonite ($Al_4Si_8O_{20}[OH]_4$).

X-ray diffraction studies of sericites of the Hauraki Gold - Silver Province have identified their composition as illite, and in some cases interlayered illite - montmorillonite, the latter regarded by some authors also as illite (c.f. Krauskopf, 1979). The general term sericite is used

TABLE 3-1: (Continued)

	Miners Head	Te Abumata	Partitu	Kuactuanu	Petote Stream	Whangapoua	Manala	S - E Whittanga	Boat Harbour	Pumkdn Hill, Tairua	Broken Hills	Tapu-Thames	Thames Andesites	Thames Lookout Rocks	Andesite	Rhyolite	Karatoto	Waitekawiri	Waihi	Karangahake	Tui Mine
Heulandite												10		23	9						
Laumontite																					
Lepidocrocite						17				22	11										
Kaolinite	11	14		14		17	17	7	13	22	11	10	10	10			9	15	12		
Magnetite						17						10			23						
Montmorillonite		14							13	22	11	10									
Mordenite										11											
Orthoclase	18																				
Prehnite	6																				
Pyrite	16	25	14	4	17	21	13	22	11	10	10	10	10	10	23	23	9	15	12	8	24
Pyrophyllite										22		10	10								
Quartz	6	16	25	14	4	17	21	7	13	22	10	10	10	10	23	23	9	15	12	8	24
Sericite	6	16	25	14	4	17	21	13	22	11	10	10	10	10	23	23	9	15	12	8	24
*2	a,b	a,b	a,b	a,b	a,b	a,b	a,b			a,b											
Stilbite												10									
TiO ₂ minerals	25					17	21			22	11	10			23	23				3	8
Uralite	25																				
Wairakite																					
Zeolite - undifferentiated	6

TABLE 3-1: (Continued)

1.	Barker <u>et al</u> (1980)	9.	Main (1971)	17.	Robson (1979)
2.	Black (pers. comm.)	10.	Merchant (1978)	18.	Skinner (1967)
3.	Braithwaite (1980)	11.	Moore (1976)	19.	Skinner (1968)
4.	Edwards (1979)	12.	Morgan (1924)	20.	Skinner (1975)
5.	Erceg (1981)	13.	Ovens (1976)	21.	Stevens (1980)
6.	Gregg <u>et al</u> (1970)	14.	Parkinson (1980)	22.	Swindale & Hughes (1968)
7.	Harvey (1967)	15.	Rabone (1975)	23.	Torckler (1978)
8.	Henderson & Bartrum (1913)	16.	Ramsay & Kobe (1974)	24.	Weissberg & Wodzicki (1979)
		25.	Wodzicki (1970)		

*¹ Rock type

A = andesite
D = dacite
G = greywacke
Q = quartz diorite
R = rhyolite

*² Sericite composition

a = illite
b = interlayered
illite-montmorillonite

TABLE 3-2: Hydrothermal alteration mineral assemblages identified in greywacke suite rocks of the Hauraki Gold - Silver Province by previous studies.

Location Classification	Petote Stream Area (Edwards, 1979)	Manaiia (Stevens, 1980)	Kuaotunu (Parkinson, 1980)
Propylitic	Pyrite, epidote, chlorite, secondary quartz, calcite and clays	chlorite, pyrite, epidote sericite (illite type clays)	Secondary quartz, chlorite, calcite, sericite (illite and interlayered illite - montmorillonite), montmorillonite and zeolites
Sericitic	Sericite and quartz		
Quartz-sericite	quartz and sericite	pyrite, chlorite, sericite, (interlayered illite - montmorillonite & illite), interlayered chlorite - montmorillonite	
Sillicic	quartz, pyrite, minor sericite, chalcopryrite and covellite		

here but is qualified by the more specific compositional terms of illite and interlayered illite - montmorillonite where known.

TiO₂ Polymorphs and Leucoxene

Leucoxene and the polymorphs of TiO₂; anatase, brookite and rutile, have each been noted as hydrothermal alteration products (or vein minerals) in the rocks of the Hauraki Gold - Silver Province. However, there is some confusion in the literature regarding the composition of leucoxene and its relation to the TiO₂ polymorphs. Deer, Howie & Zussman (1966 pp 412 - 413) considered that leucoxene "is normally finely crystalline rutile, but leucoxene composed of finely divided brookite is also known", whereas Kerr (1979) and Heinrich (1965) considered leucoxene to be an amorphous hydrated form of TiO₂.

Authors of early literature on the province appear to report all TiO₂ alteration minerals as leucoxene, therefore using it as a general term, whereas some recent authors have differentiated the TiO₂ polymorphs rutile, anatase and brookite from leucoxene (e.g. Merchant, 1978; Edwards, 1979; Robson, 1979). Stevens (1980) incorrectly considered leucoxene synonymous with anatase and rutile (c.f. Stevens, 1980 p 46).

Anatase, brookite, rutile and leucoxene are considered as separate forms of TiO₂ in this thesis and are reported as such wherever possible.

STYLE OF HYDROTHERMAL ALTERATION IN SPECIFIC ROCK TYPES

Greywacke Suite Rocks of the Manaia Hill Group

The hydrothermal alteration of greywacke suite rocks in the Hauraki Gold - Silver Province has been described in detail from only three areas (Table 3-2): Kuaotunu (Parkinson, 1980), Petote Stream area (Edwards, 1979) and Manaia (Stevens, 1980). Earlier authors (e.g. Fraser & Adams, 1907; Smale, 1962; Skinner, 1976) used general terms such as "pyritised" and "silicified" to describe the alteration of the greywacke rocks.

Edwards (1979) and Stevens (1980) subdivided the altered rocks of the Petote Stream and Manaia areas respectively into various ranks based on the hydrothermal mineral assemblages (Table 3-2). Parkinson's (1980) description of the alteration at Kuaotunu suggests that it is very similar, except that epidote is absent and the clay minerals exhibit the depth related distribution, in order of increasing depth, of: kaolinite, sericite (illite) $\pm$ kaolinite, and sericite (illite).

Figure 3-1: Style of hydrothermal alteration of Coromandel Group andesites determined by previous studies. (From Edwards, 1979 Figs. 3-1 and 3-2.)

Andesites and Dacites of the Coromandel Group

Some different types of hydrothermal alteration described from the Coromandel Group andesites and dacites are illustrated in Fig. 3-1. The alteration is typically propylitic producing a green rock containing a basic mineral assemblage of quartz, sericite, carbonate (mainly calcite but siderite and dolomite are often present), chlorite and pyrite. There are differences in additional alteration products between the various areas. For example, the following plagioclase alteration products have been identified in some areas (c.f. Table 3-1): secondary albite, adularia, prehnite and the zeolites; heulandite, laumontite, stilbite and wairakite. Similarly, propylitic alteration of pyroxenes and hornblende has also produced epidote, biotite and uranalite at some locations (c.f. Table 3-1).

Progressive propylitic alteration generally follows the sequence of: (1) alteration of the groundmass and phenocrystic hypersthene to chlorite ($\pm$ epidote), (2) alteration of augite and hornblende to chlorite and calcite ($\pm$ epidote), and (3) alteration of plagioclase to sericite and calcite ($\pm$ adularia, $\pm$ secondary albite and $\pm$ zeolites).

With increasing intensity the alteration changes from propylitic to intermediate argillic alteration (or a clay - sericite equivalent) developing an assemblage of quartz, clay and pyrite. Examples were reported by Ramsay & Kobe (1974) from Te Ahumata (quartz, sericite, kaolinite and rare non-expanding chlorite and pyrite); Robson (1979) from Whangapoua (sericite, chlorite, quartz, pyrite and sphene); Merchant (1978) from Tapu - Thames (sericite, pyrite, quartz, kaolinite and chlorite); Main (1971) from Maratoto (quartz, kaolinite and pyrite) and Rabone (1975) from Waitekauri (quartz, kaolinite, sericite, chlorite and pyrite). The specific composition of the sericite in some of these areas is listed in Table 3-1.

The most advanced type of hydrothermal alteration in the andesites and dacites is quartz - sericite (equivalent to phyllic). Examples were described by Robson (1979) and Merchant (1978) from the Whangapoua and Tapu - Thames areas respectively. This type of alteration produces an assemblage of quartz, sericite and pyrite.

Alteration of a different style to that described above occurs associated with a number of small unmineralised (except for pyrite) sinter deposits in the andesites north of Tairua (Tapuaetahi Andesite). Most of the deposits probably represent former sites of hot springs and fumeroles although Ovens (1976) suggested that some (e.g. Pumpkin Hill, also known as Pukepaukeua, about 1.5 km north of Tairua) are in fact vein deposits formed at depth. The types of alteration that occur are silicification,

TABLE 3-3: Hydrothermal alteration mineral assemblages identified from intrusive rocks of the Mauraki Gold - Silver Province by previous studies.

Location	Paritu	Manaia	Tapu - Thames
Classification	(Wodzicki, 1970; Skinner, 1975)	(Stevens, 1980)	(Merchant, 1978)
Propylitic	chlorite, epidote, calcite, sericite, secondary quartz, adularia, pyrite, leu- coxene, secondary albite, sphene, "Kaolin type clay" (Skinner 1975)	chlorite, pyrite, magnetite, calcite, secondary quartz, epidote and leucoxene.	chlorite, calcite, epidote, secondary albite, secondary quartz, sericite, pyrite, zeolite and montmorillonite.
Silicification	quartz and pyrite		
Clay-sericite (argillic)		Secondary quartz, pyrite, Sericite, pyrite, quartz, sericite (illite and kaolinite and chlorite. illite-montmorillonite), chlorite, interlayered chlorite, montmorill- onite and kaolinite	
Quartz-sericite (phyllic)		Secondary quartz, sericite, Quartz, sericite and pyrite, chlorite, inter- layered chlorite - montmorillonite	pyrite
Alkali silicate (Potassic)	Orthoclase		Biotite, magnetite and secondary albite

intermediate argillic alteration and advanced argillic alteration. The predominant assemblage is quartz and kaolinite (Ovens, 1976) although Swindale & Hughes (1968) described the following minerals from Pukepaukeua: secondary quartz, kaolinite, pyrophyllite, dickite, diaspore, montmorillonite, sericite, epidote, pyrite and leucoxene.

Intrusive Rocks of the Coromandel Group

The nature of the hydrothermal alteration of intrusive Coromandel Group rocks has been described from Paritu (Wodzicki, 1970; Skinner, 1975), Manaia (Stevens, 1980) and Tapu - Thames (Merchant, 1978). The hydrothermal alteration minerals occurring at these locations and their associations are listed in Table 3-3.

The various intrusive centres in the Tapu - Thames area (Tainui Intrusives) exhibit a zonal distribution of hydrothermal alteration in the order of quartz - sericite, argillic and propylitic from core to margin, whereas at Manaia the largest intrusive body (a member of the Kai-iti Porphyrites) is zoned in a reverse direction with a central core of advanced propylitic alteration surrounded by successive zones of clay - sericite (argillic) and quartz - sericite alteration. Zonal patterns of alteration have not been recognised in the Paritu Plutonics with the various phases exhibiting different degrees of alteration. For example, Skinner (1975) noted that hydrothermal alteration varied from slight in the quartz diorite to intense in the granodiorite. The alteration is generally propylitic although Skinner (1967) noted druses of secondary orthoclase in the igneous rocks of the coastal section which may constitute a limited development of potassic alteration.

Some phases of the Paritu Plutonics and Kai-iti Porphyrites at Paritu have also been effected by pre-hydrothermal alteration stages of metamorphism (production of tourmaline and epidote) and deuteritic uraltisation (alteration of hornblende and some pyroxene to uraltite). Similar uraltisation was reported from intrusive rocks (Kai-iti Porphyrites) of the Petote Stream area by Edwards (1979).

Rhyolites of the Whitianga Group

Hydrothermal alteration of the Whitianga Group rocks occurs spatially related to veins and sinter deposits. The major types of alteration are silicification and intermediate argillic alteration although advanced argillic and alkali silicate types also occur.

Silicification occurs in most areas of altered Whitianga Group rhyolites, particularly the domes of Minden Rhyolite Subgroup (c.f. Harvey, 1967; Hayward, 1974; and Ovens, 1976).

Intermediate argillic alteration has been described from Te Ahumata (Erceg, 1981), the area south-east of Whitianga (Harvey, 1967; Ovens, 1976), Broken Hills (Moore, 1976, 1979) and Thames (Merchant, 1978). Quartz, kaolinite, sericite and pyrite are the predominant minerals produced although the assemblage in the Lookout Rocks of Thames is quartz, dickite and pyrite. The accessory minerals at Te Ahumata are metahalloysite, siderite and adularia, whereas adularia, halloysite and mordenite occur at Broken Hills.

Advanced argillic alteration occurs in the Lookout Rocks. Merchant (1978) identified two different assemblages: (a) natroalunite and quartz with minor hematite, barite and kaolinite, and rare pyrite, and (b) pyrophyllite and dickite, $\pm$ diaspore, $\pm$ quartz.

In contrast to the style of alteration described above, Torckler (1978) found that the rhyolite rocks at Neavesville were altered to potassium silicate assemblages. These predominantly consisted of quartz and adularia.

Figure 3-2: Map of the Coromandel Group Volcanic rocks, illustrating Schofield's (1967) differentiation of "areas more extensively propylitised than others".

intrusive centres (although the pattern at Manaia is complicated by reverse zoning within the main intrusive body).

- (4) Regional zonation: The 1:250,000 scale geological map of Auckland (Schofield, 1967), differentiated "areas more extensively propylitised" within the andesite terrain (Coromandel Group rocks). Two, or possibly three (if Waihi is included), parallel N - S trending zones of regional alteration occur (Fig. 3-2) separated by less altered rocks. The trends may be a function of time (altered andesites are older and the hydrothermal alteration predates the younger andesites), erosion level (the hydrothermally altered andesites represent deeper levels) or spatially restricted intrusive activity.

CHAPTER 4

MINERALISATION

INTRODUCTION

This chapter compares the mineralised deposits of the Hauraki Gold - Silver Province described individually in Appendix I.

Porphyry copper and epithermal deposits occur in the Province. The term epithermal is used here in the sense of Schmit (1950) and Sillitoe (1977) to describe mineralisations formed at shallow depth without the implication of low temperature as originally suggested by Lindgren (c.f. Lindgren, 1933).

CHECKLISTS OF PRIMARY MINERALS

The primary metallic minerals identified from the individual deposits are listed in Table 4-1, whereas the gangue minerals are listed in Table 4-2.

PORPHYRY COPPER DEPOSITS

Porphyry copper deposits occur at the northern end of Great Barrier Island (the Needles and Miners Head), Paritu, Manaia and between Tapu and Thames (Fig. 4-1 and Table 4-3). They are of Miocene age (Fig. 4-1) and are associated with dikes, stocks and plutons of predominantly quartz diorite to granodiorite composition (and their volcanic equivalents), which intrude Jurassic greywacke suite rocks and/or Miocene andesites. In terms of Nielsen's (1976) depth classification the Tapu - Thames deposits are volcanic, whereas the others are hypabyssal.

Pyrite and chalcopyrite are the major metallic minerals (Table 4-3) and occur disseminated, infilling shears or in quartz veinlets. In some cases the veinlets form stockwork patterns cementing brecciated country rock. Sphalerite, molybdenite, pyrrhotite and magnetite are the main accessory minerals although the following minerals have also been identified from individual deposits: argentian pentlandite, arsenopyrite, bornite, cassiterite, galena, gold, hematite, marcasite, rutile, tourmaline and wolframite.

All of the deposits described have been investigated by mineral exploration companies (including drilling in the case of Paritu and the Ohio Creek deposit in the Tapu - Thames area) and their results to date suggest that the deposits are small and presently uneconomic. However, further exploration work is being conducted.

TABLE 4-1: Checklist of Primary Metalliferous Minerals

1.	This Study	9.	Main (1971)	17.	Ramsay (1971)
2.	Barker et al (1980)	10.	Merchant (1978)	18.	Robinson (1974)
3.	Bell & Fraser (1912)	11.	Moore (1976)	19.	Robson (1976)
4.	Black (1970)	12.	Moore (1979)	20.	Skinner (1967)
5.	Erceg (1981)	13.	Morgan (1924)	21.	Stevens (1980)
6.	Fraser (1910)	14.	Parkinson (1980)	22.	Torckler (1978)
7.	Fraser & Adams (1907)	15.	Rabone (1971)	23.	Weigel (1978)
8.	Henderson & Bartrum (1913)	16.	Ramdohr (1980)	24.	Wodzicki & Weissberg (1970)

? Uncertain identification

* Syngenetic

TABLE 4-1: (Continued)
Colville
Gt Barrier Is Peninsula

Colville Gt Barrier Is Peninsula																													
TABLE 4-1: (Continued)																													
	Needles	Miners Head	Te Ahumata	Partiu	Tanglaro Stm	Kuatunu	Tokatea	Kauri Block	Kapanga	Petote Stm Area	Whangapoua	Manata	Kapowai	Boat Harbour	Broken Hills	Tapu-Thames	Thames	Andesites	Rhyolites	Maratoto	Golden Cross	Komata	Waitekauri	Wahiti, Martha	Wahiti, Rosemont	Karangahake	Tui Mine	Waiorongomai	
Electrum		17	20	7	7	7	7	7	7	7	21	3	3	11	6	6	6	2	22	3	3	3	3	3	3	8	8	AuAg	
Enargite															6													Cu ₃ AsS ₄	
Famatinite		5									19				6													Cu ₃ SbS ₄	
Ferrimolybdenite															6													Fe ₂ (MoO ₄) ₃	
Freibergite		5									19				6	6	22			9	73	15	3	3	3	8	24	8	PbS
Galena	23	17	20	20	7	20	20			20	19	21			10													Au	
Gold (Native)															10														
Hematite							7								10			*22							3	18	18	Fe ₂ O ₃	
Hessite							714	1							6	6	22			3					10	8	8	Ag ₂ Te	
Kobellite															10	10												Pb ₂ (BiSb) ₂ S ₆	
Mackinawite		723																										(FeNiCo)S	
Magnetite												21			10													Fe ₃ O ₄	
Marcasite		17	20	20	14						19	21		11	6	6	6			9		15			8	24		FeS ₂	
Molybdenite			20								12	21			6		2							13				MoS ₂	
Meneghinite																710												CuPb ₁₃ Sb ₇ S ₂₄	
Miargyrite		5									19				10													AgSbS ₂	
Nagyagite															16													Pb ₅ Au(TeSb) ₄ S ₅₋₈	
Naumannite		17												11														Ag ₂ Se	
Petzite															10	10												Ag ₃ AuTe ₂	
Polybasite-Pearceite		17													10													Ag ₁₆ Sb ₂ S ₁₁ - Ag ₁₆ As ₂ S ₁₁	

TABLE 4-1: (Continued)

Gt Barrier Is Colville Peninsula																													
	Miners Head	Te Ahumata	Paritu	Tangiaro Stm	Kuautunu	Tokatea	7 Kauri Block	Kapanga	Petote Stm Area	Whangapoua	Manata	Kapowai	Boat Harbour	Broken Hills	Tapu-Thames	9 Thames	Andesites	Rhyolites	Maratoto	Golden Cross	Komata	Waitekauri	3 Waihi, Martha	3 Waihi, Rosemont	Karangaahake	Tui Mine	Watorongomai		
Pyrargyrite	17														10	6	6	22	*22	3	3	3	15	3	3	8	24	8	Ag ₃ SbS ₃
Pyrite	23	17	20	20	7	7	7	7	20	19	21	3	11	6	6	6	22	*22	3	3	3	3	15	3	3	8	24	8	FeS ₂
Pyrrotite	23	5	20	14						12	21			10								1							FeS
Robinsonite															10														Pb ₇ Sb ₁₂ S ₂₅
Seleniferous Tellurobismutite														10															Bi ₂ (SeTe) ₃
Sphalerite	23	23	17	20	20	7	20	20	20	19	21			6	6	22	9	9	9	9	9	15	3	8	24	8			ZnS
Stephanite														710															Ag ₅ SbS ₄
Stibnite	17						7			19				6	6														Sb ₂ S ₃
Stutzite														10	10														Ag ₅ Te ₃
Sylvanite														10	10														AuAgTe ₄
Titanomagnetite																													(FeTi) ₃ O ₄
Tellurium (Native)														16															Te
Tennantite																									1				Cu ₁₂ As ₄ S ₁₃
Tetradymite														10												1			Bi ₂ Te ₂ S
Tetrahedrite	17		20							19				10	10							1			24	1			Cu ₁₂ Sb ₄ S ₁₃
Tschemannite													11																AgAsS ₂
Wolframite	723		20																							723			(Fe Mn) WO ₄

Figure 4-1: Location of porphyry copper style deposits in the Hauraki Gold - Silver Province. Ages are K-Ar dates on the host intrusive rocks (after Richards et al., 1966 and Dr C.J.D. Adams and others, pers. comm.).

TABLE 4-3: Porphyry copper style mineralisations of the Hauraki Gold-Silver Province.

Location	Major Minerals	Minor Minerals	Form of Mineralisation	Reference
Needles (Great Barrier Island)	Quartz, chalcopyrite and bornite	Pyrite, sphalerite, galena, and Ag-Ge-Se sulphosalts	Mineralised breccia and pebble dikes intruding greywacke suite rocks	Weigel (1978)
Miners Head (Great Barrier Island)	Quartz, chalcopyrite and pyrite	Sphalerite, pyrrhotite, argentian pentlandite and galena	Pipe of quartz diorite cemented argillite breccia. Mineralisation concentrated in breccia dike separating breccia pipe from non- brecciated porphyritic dike and argillite	Gregg et al. (1970) Weigel (1978)
Paritu (Northern Colville Peninsula)	Quartz, pyrite and chalcopyrite	Sphalerite, molybdenite, pyrrho- tite, arsenopyrite wolframite, marcas- ite and cassiterite	Disseminated mineralisation in biotite quartz diorite phase of pluton. Minor disseminated and vein mineralisation at margins of pluton and in adjacent horn- felsed greywacke	Skinner (1967) Wodzicki (1970)
Manaia	Quartz, pyrite, magnetite and chalcopyrite	Sphalerite, galena, pyrrhotite, molybden- ite and marcasite	Rare sulphide mineralisation infilling joints and shears and in quartz veinlets occurring in small quartz diorite stock and surrounding greywacke	Stevens (1980)
Tainui (Tapu - Thames)	Quartz, pyrite, chalcopyrite, magnetite and hematite	Molybdenite, gold, rutile, sphalerite, tetrahedrite, pyrrhotite	Mineralisation found dissemin- ated, infilling joints and shears and in quartz veins within quartz diorite stocks intruding andesite	Merchant (1978)

EPITHERMAL DEPOSITS

Introduction

Some aspects of the epithermal deposits are summarised in Table 4-4 and their locations are shown in Fig. 4-2. They occur in all but the youngest rocks of the province (Pleistocene ignimbrites and basalts) and range in age from Miocene to Pleistocene.

The mineralisation occurs predominantly in veins formed as fault fissure fillings, although some replacement mineralisation of wall rocks adjacent to the veins and in vein breccias of wall rock also occurs. Disseminated mineralisation in country rocks away from the veins is minor.

The faults are mostly tensional features, predominantly normal and dextral with mineralisation deposited in the resulting dilatent zones (c.f. Main, 1979). Bonanza mineralisation at Coromandel and Thames and silver mineralisation at Maratoto occurred at the intersection of a younger fault pattern, in some instances sinistral and/or reverse, with the pre-existing normal dextral patterns.

Practically all major faults strike in the north quadrant (NW to NE), a feature which can be equated to the arc - subduction tectonic system operating at the time. At some locations (e.g. Waiorongomai) a north-east trending fault pattern is superimposed on earlier north trending faults.

The size and type of veins are dependant on the competency of the host rocks, which can be ordered in decreasing competency as: greywacke, andesite, dacite and rhyolite. Large composite veins are mainly found in greywacke and andesite, whereas small veins as vein systems are typical in the dacites and interlacing networks of veinlets in the rhyolites.

Brecciation and crustification are common vein textures. In the former case the mineralisation cements the breccia fragments (Fig. 4-3) which are either of wall rock or early vein material and may be up to a metre or so in size. Crustification usually takes the form of symmetrically or assymmetrically banded veins (Figs 4-4, 4-5 and 4-6). Good examples of cockade structure (Fig. 4-7) are rare. Comb structure and deposition in vugs (Figs 4-8 and 4-9) characterise the late stages of vein filling.

The predominant metallic minerals are pyrite, sphalerite, galena, chalcopyrite, acanthite and electrum (Table 4-1) and these occur in a gangue mineral assemblage of mainly quartz and calcite (Table 4-2). Gold - silver selenide and telluride minerals occur in some deposits and these are characteristic components of some deposits, for example the mines between Tapu and Thames are notable for their telluride minerals.

TABLE 4-4: Bullion production, host rock, associated hydrothermal alteration and mineral content of some of the epithermal vein deposits.

Location	$\frac{EAu+Ag}{x10^6}$	$\frac{EAu+Ag}{tonne}$	EAU equiv. $x10^6$	$\frac{Au}{Ag}$	Host Rock	Associated Hydrothermal Alteration	Metals	Form	Gangue	Mineral Assemblages
Te Ahumata	1.3	80	0.3	0.03 (0.2)	A, R	Pr Ar	Ag, Sb, (Cu, Pb, Zn, minor Au)	S^{2-}, Se^{2-} sulphosalts (el)	Q, QPC	2,4,9,10
Northern Coville negligible Peninsula	-	-	-	(Tangiaro Stream <0.01)	G, A, QD	Pr	Pb, Zn, Cu (minor Ag, Au)	S^{2-} (minor el)	Q (C)	
Kuaotunu	2.8	30	1.7	(1.2)	G	Pr Ar	Au, Ag (minor Pb Zn, Cu)	el (minor S^{2-})	Q, QPC	2,5,7
Tokatea	3.9	130	2.6	(1.7)	G, A	Pr	Au, Ag, As, Pb, Zn, Cu	el, S^{2-} (minor Te^{2-})	Q (C)	4,5,7,8
Kauri Hock and Kapanga	7.4	100	5.3	(2.2)	A	Pr Ar	Au, Ag, As	el, S^{2-}	Q (very minor C)	8
Petote Stm Area negligible	-	-	-	-	G	Pr Qs S	Pb, Zn, Cu	S^{2-}	Q	2,4
Whangapoua	1	20	0.5	(Opitonui: 0.9)	A	Pr Ar Qs	Pb, Zn, Cu, Sb, (minor Ag, Au)	S^{2-} , sulphosalts, el	Q	2,4,6,7,10
Kapowai	0.2	30	0.1	(1.1)	R	S	Au, Ag	el	Q	(7, no acanthite ?)
Broken Hills	1.7	40	0.6	(0.6)	R	Ar S (Pr)	Au, Ag	el, Se^{2-}, S^{2-} sulphosalts	Q, Ba	9,11
Tapu-Thames	6.5	40	2.1	(0.3)	A	Pr Ar Qs As	Pb, Zn, Cu, Ag, Au, (minor Bi Sb)	S^{2-}, Te^{2-}, Se^{2-} , el	Q	1,2,3,4,5,6,9,11,12
Thames	69	50	44	(0.6)	A	Pr Ar	Au, Ag, Sb (Pb, Zn, Cu)	el, sulphosalts S^{2-} (Te^{2-}, Se^{2-})	Q (Ba)	3,4,5,6,8,9,10,11,12
Neavesville	0.9	40	0.4	(0.5)	A, R	Pr Ps (Ar Qs)	Au, Ag (very minor Zn, Pb, Cu and Mo)	el, $S^{2-}, (Te^{2-})$	Q (A, Br)	5, (7, no acanthite ?)
Maratoto	4	50	0.3	(0.01)	A	Pr Ar	Ag, Cu, Pb, Zn (minor Au)	S^{2-}, Te^{2-} (el)	Q, C, QPC	2,5
Golden Cross	12	80	2.9	(0.3)	A	Pr	Au, Ag (Pb, Zn, Cu)	el, S^{2-}	Q, QPC, C	5 7 ?
Konata	16.6	80	3.4	(0.2)	A	Pr	Au, Ag	el, S^{2-}	Q, C, QPC	7 ?
Waitekauri	1.4	40	0.6	(0.7)	A	Pr Ar Ps	Pb, Zn, Cu, Au, Ag	S^{2-} el	Q, QPC, (C, A)	2,4,7 ?
Waihi	1,100	90	211	0.2	A	Pr (Qs? Ps?)	Au, Ag, Pb, Zn, Cu, (trace Mo)	el, S^{2-} (Te^{2-} Rosemont Hill)	Q, QPC, C, A	1,2,4,5,7
Karangahake	125	100	30	0.3	A	Pr (Qs ?)	Au, Ag, Pb, Zn, Cu	el, S^{2-} (Te^{2-} ?)	Q, QPC, C	2,4,5,7
Tui Mine	2.6	40	0.2	0.02	A	Pr	Pb, Zn, Cu (very minor Hg, Au, Bi)	S^{2-}	Q	2,3,4,11,12
Maierongomai	2.1	40	0.8	0.4 (0.6)	A	Pr	Pb, Zn, Cu, Ag, Au	S^{2-} el (Te^{2-})	Q (QPC, C)	2,4,5,11,12

Footnotes for Table 4-4.

- *¹ g Au equiv. (c.f. Brathwaite, 1981): grams of gold equivalents = the value of the Au + Ag bullion mined (in £, from Downey, 1935) divided by the value of one gram of gold. The latter is £0.135, derived from the value of one ounce of gold at the time of production (= £4.2) divided by 31.1 (1 Troy ounce = 31.1g)
- *² derived from analyses of the ore or from bullion production figures (values in brackets, see text)
- *³ A = andesite and dacite G = greywacke QD = quartz diorite
R = rhyolite
- *⁴ Ar = argillic (or clay sericite) AS = alkali silicate (biotite - albite - magnetite - quartz) Pr = propylitic Ps = potassium silicate (adularia - quartz)
Qs = phyllic or quartz-sericite S = silicification
- *⁵ el = electrum S²⁻ = sulphides Se²⁻ = selenides
Te²⁻ = tellurides
- *⁶ A = adularia Ba = barite Br = brookite C = calcite
Q = quartz QPC = quartz pseudomorphs after calcite
- *⁷ see Table 4-5

Figure 4-2: Locations of the epithermal gold and silver deposits and gold/silver ratios for the major mining centres. The main set of values were derived from bullion production figures listed in Downey (1935), whereas the values in brackets are ratios stated in the literature or calculated from recent metal production statistics, as follows: a = Ramsay & Kobe (1974), b = Fraser & Adams (1907), c = recent production records (Maratoto = Consolidated Silver, Tui Mine = Norpac), d = Bell & Fraser (1912) and Morgan (1924), and e = Henderson & Bartrum (1913).

Figure 4-3: Quartz, sphalerite, galena, chalcopyrite and pyrite cementing wall rock breccia, Chalcopyrite Lode, Petote Stream (sample 13988 reproduced life size).

Figure 4-4: Crustified vein texture in a sample from the 303m adit, Iona Region, Te Ahumata (Great Barrier Island). The vein contains mostly chalcedonic quartz but silver mineralisation occurs in bands of the lower part of the specimen. The specimen is 13cm x 14cm.

Figure 4-5: Crustified vein texture in silver mineralisation from the Camoola Vein, Maratoto. Late Stage 1 blocky calcite in the upper third of the specimen is followed by Stage 2 bands of rhodochrosite, calcite, quartz, siderite and silver mineralisation. The specimen is approximately 20cm , in the longest dimension.

Figure 4-6: Banded ore from 14 level of the Talisman Mine, Karangahake (sample 14025, reproduced life size). The dark bands are predominantly fine grained sphalerite and galena with accompanying larger grains of chalcopyrite (light grey triangular grains), whereas the white bands are quartz or calcite. Electrum is relatively abundant in polished sections.

Figure 4-7: Mineralisation with cockade structure, from May Queen, 2 level, Waiorongomai (sample 14078). Breccia fragments are surrounded by concentric bands, predominantly containing quartz, sphalerite and galena. The spaces between the oval structures are filled with quartz, pyrite and chalcopyrite. The specimen is 12cm wide by 11cm high.

Figure 4-8: Vug quartz crystals coated with late carbonates and pyrite, Silver Queen vein, Maratoto. Photo courtesy of Mr E. Coppard.

Figure 4-9: Plates of barite (up to 5mm x 5mm) coating vug quartz crystals (up to 20mm long) from the Moa Mine, Waiorongomai (sample 14070).

Gold/Silver Ratios

The gold/silver ratios shown in Fig. 4-2 and Table 4-4 were derived from two sources. One set of values was calculated by the writer from bullion (gold plus silver) production and bullion value figures listed in Downey (1935), whereas some values are also presented that are average assay values from the literature. The discrepancy between the two sets indicates that the former set are maximum values only.

Mineral Assemblages

Following Merchant's (1978) scheme, several mineral assemblages are recognised (Table 4-5). They occur as distinct episodes in the time or depth related paragenesis of the deposits and in the general order in which they are listed in Table 4-5 and described in the following sections. However, no single mineral assemblage listed occurs in all deposits and no single deposit contains all of the mineral assemblages.

1. Early Molybdenite

Molybdenite was reported from three veins by the early writers: the Sylvia, Tapu-Thames (Bossard, 1946); Ajax, Neavesville (Adams, 1915); and an unidentified vein of the Martha vein system, Waihi (Morgan, 1924). Their brief descriptions suggest that it occurred early in the vein parageneses (c.f. Merchant, 1978).

Samples of molybdenite from Neavesville and Waihi, in the Geological Survey collection, consist of quartz + molybdenite (Barker *et al*, 1980) and quartz + molybdenite + pyrite + adularia + sericite + carbonate (Brathwaite, 1980) respectively.

2. Early Pyrite

Pyrite is an early constituent in veins of most deposits and is sometimes accompanied by marcasite (e.g. Te Ahumata, Manaia and Thames). These minerals generally accompany quartz gangue but calcite also occurs in some deposits (e.g. Maratoto, Waitekauri and Waihi). This mineral assemblage is usually found cementing wall rock breccias.

3. Pyrite - Chalcopyrite Assemblage

Quartz with pyrite and chalcopyrite occurs as an early stage in veins between Tapu and Thames (e.g. Sylvia and Monowai) and in the Champion and Ruakaka veins of Tui Mine. These mineralisations also generally have associated accessory Bi minerals (Table 4-6) and gold.

The texture of the mineralisation is characterised by brecciation.

TABLE 4-5: Epithermal vein mineral assemblages.

This study

Merchant (1978)
Thames - Tapu Area

1. Early molybdenite		
2. Early pyrite		
3. Pyrite-chalcopyrite assemblage		Cu - Bi
4. Pyrite-sphalerite-galena-chalcopyrite assemblage		Pb - Zn
5. Pyrite-sphalerite-galena-chalcopyrite-electrum-silver minerals assemblage		Pb - Au
6. Sb - sulphosalt mineral assemblage		Cu - Sb
7. Pyrite-acanthite-electrum assemblage		
8. Pyrite-bonanza electrum assemblage		Gold-pyrargyrite
9. Au-Ag sulphosalt mineral assemblage		
10. Stibnite	}	stibnite-barite
11. Barite		
12. Cinnabar		

TABLE 4-6: Occurrence and mineral content of the pyrite-chalcopyrite epithermal vein mineral assemblage.

Location	Stage	Major Minerals	Minor Minerals	Reference
Tapu-Thames	Cu-Bi	Quartz, pyrite, chalcopyrite	Sphalerite, tetrahedrite, seleniferous tellurobismutite, kobellite, seleniferous tetradymite, aikinite, argentine tetrahedrite, native gold, galena, rutile, arseno- pyrite, pyrrhotite.	Merchant (1978)
Tui Mine	1	Quartz, pyrite, chalcophyrite, hematite	Bismuthinite, gold, tetradymite (wolframite? bornite?)	Weissberg & Wodzicki (1970) Robinson (1974) Ker & Wodzicki (in press) Weigel (1979)

Figure 4-10: Chalcopyrite (yellow) and pyrite (cream) cut by a later vein of quartz (dark grey) plus fine grained bismuthinite (pale blue) and native gold (brilliant yellow); Pyrite-Chalcopyrite mineral assemblage, Stage 1 Tui Mine, sample 13915. 50X.

Figure 4-11: Inclusions of native gold (brilliant yellow), bismuthinite (pale blue), pyrite (cream), tetradymite (cream, scratched) and quartz (black) in chalcopyrite (dull yellow); Pyrite-Chalcopyrite mineral assemblage, Stage 1 Tui Mine, sample 13909. 200X.

The quartz and sulphides cement wall rock breccias and are themselves brecciated and cemented by later mineral assemblages. In unbrecciated parts, euhedral pyrite grains occur cemented by quartz and anhedral chalcopyrite. Large masses of chalcopyrite occur in specimens from M Stope of the Champion Vein, Tui Mine. The chalcopyrite encloses "balls" of euhedral pyrite grains believed to be replacements of marcasite (c.f. Cochrane, 1969; Merchant, 1978).

Bismuth minerals (seleniferous tetradymite, seleniferous telluro-bismutite, kobellite and aikinite at Tapu - Thames; bismuthinite and tetradymite at Tui Mine) and gold (Figs 4-10 and 4-11) generally appear later than the main chalcopyrite - pyrite phase and are followed by more pyrite and sometimes chalcopyrite.

At Tui Mine, hematite is also an important phase and occurs at first with pyrite and chalcopyrite (Fig. 4-12) but later only with quartz (Fig. 4-13).

4. Pyrite - Sphalerite - Galena - Chalcopyrite Assemblage

Pyrite - sphalerite - galena - chalcopyrite is one of the most common forms of mineralisation presently exposed in the province. Table 4-7 lists the principal occurrences.

The gangue is usually quartz although calcite also occurs in some examples. The mineralisation typically occurs cementing wall rock breccia although it is sometimes also found in crustified veins.

The paragenesis of individual veins shows that practically any combination of the four sulphides can occur early or late although at Tui Mine an assemblage of tetrahedrite plus chalcopyrite occurs late, filling fractures in earlier mineralisation, and chalcopyrite plus pyrite occurs late in comby and vuggy quartz in some veins of the Petote Stream area, Waitekauri and Waiorongomai. In individual bands there is a tendency for sphalerite to be paired with galena and chalcopyrite with pyrite.

Textures are generally simple although brecciation and resorption of some phases sometimes makes distinction of boundary textures difficult. Nevertheless, the various minerals in individual veins usually have mutual boundary relations indicating coprecipitation. Replacement textures mainly involve replacement of pyrite by other sulphides (Figs 4-14 and 4-15).

Pyrite is often euhedral, whereas the other minerals are generally anhedral filling spaces between euhedral quartz grains, resulting in "fish-net" textures (Figs 4-16 and 4-17). Chalcopyrite is ubiquitously present as inclusions in sphalerite and may reach high proportions (Fig. 4-18). The chalcopyrite blebs are often aligned along cleavage planes and growth zones (Figs 4-19 and 4-20) and were formed by exsolution, replacement or epitaxial growth (c.f. Craig & Vaughan, 1981 p 125).

Figure 4-12: Bladed hematite (pale blue) plus chalcopyrite (yellow) and pyrite (cream) in quartz (grey); pyrite-chalcopyrite mineral assemblage, Stage 1 Tui Mine, sample 13915. Supergene goethite (slightly lighter grey than quartz) replaces the hematite. 100X.

Figure 4-13: Bladed hematite (light grey) in quartz and supergene goethite (both dark grey); pyrite-chalcopyrite mineral assemblage, Stage 1 Tui Mine, sample 13915. 50X.

TABLE 4-7: Main occurrences of the pyrite-sphalerite-galena-chalcocopyrite epithermal mineral assemblage.

Location	* ¹			* ²		* ³
	General Vein Texture	Metallic ("ore")	Vein Minerals	Gangue	Metallic/gangue mineral ratio	
Te Ahumata	banded breccia	py,mc,cp,sp,gn,thd		qtz (ca?)	low	f
Northern Colville Peninsula	breccia	sp,gn,cp,py		qtz (epidote)	high	m & c
Tokatea	breccia	sp,gn,cp,py		qtz	high	m & c
Petote Stream Area	breccia cockade	sp,gn,cp,py		qtz	high	m & c
Tapu-Thames	breccia	sp,gn,cp,py		qtz	high	m & c
Waitekauri	breccia	sp,gn,cp,py		qtz, ca, ad	low to medium	f & m
Waihi	breccia banded	sp,gn,cp,py,po		qtz, ca, ad	low to high	f & m
Tui Mine	breccia banded drusy	sp,gn,cp,py,thd		qtz	high	m & c
Waiorongomai	breccia banded cockade	sp,gn,cp,py,thd		qtz	high	m & c

*¹

See list of abbreviations

*²

Refers only to samples studied and may not be representative of whole vein

*³

c = coarse f = fine m = medium

Figure 4-14: Replacement of pyrite (pale yellow) by galena (pale bluish grey) indicated by embayments and poikilitic inclusions of galena in pyrite; sample 13959 Tokatea, Coromandel. The dark grey mineral is sphalerite (containing inclusions of yellow chalcopyrite), whereas the black mineral is quartz. 500X.

Figure 4-15: Replacement of pyrite (white) indicated by embayments of quartz (black) and sphalerite (dark grey) and inclusions of sphalerite and chalcopyrite (light grey); sample 13986, Hutt Creek (Petote Stream area). 200X.

Figure 4-16: Galena (white) intergrown with subhedral quartz (dark grey - black) in a "fish net" texture, Stage 2 Waitekauri Vein, sample 14020. 200X.

Figure 4-17: Galena-hessite composite grains (white) filling spaces between subhedral grains of quartz; Stage 2b Silver Queen vein Maratoto, sample 285/37/2. 100X.

Figure 4-18: Abundant oriented inclusions of exsolved? chalcopryite (yellow) in sphalerite (grey); Tokatea, Coromandel, sample 13960. 200X.

Figure 4-19: Abundant inclusions of chalcopryite (white) oriented in various patterns in sphalerite (grey) of sample 13978, Martha Vein, Waihi. The sphalerite grains are surrounded by quartz (dark grey) whereas inclusions of galena (white-grey, very scratched-pitted, high relief) occur in sphalerite of the left third of the photograph. 200X.

Figure 4-20: Inclusions of chalcopyrite (yellow) arranged along cleavage planes in sphalerite (grey), of sample 14072, No1 Reef, Waiorongomai. 100X.

Figure 4-21: Seams of galena (bluish white), pyrite (pale yellow), quartz (black) and minor chalcopyrite (yellow) in sphalerite (grey) of sample 13959 Tokatea Coromandel. 100X.

Figure 4-22: Poikilitic inclusions of galena (white) in sphalerite (grey) and pyrite (cream) of sample 14046 from Waihi. 100X.

More complex textures occur at Tokatea, Thames, Waihi and Waiorongomai. A sample from Tokatea (13959) contains large masses of sphalerite, with abundant inclusions of chalcopyrite, seamed by later galena, chalcopyrite, euhedral pyrite and quartz (Fig. 4-21). Galena replaces pyrite (Fig. 4-14).

Merchant (1978) described complex dendritic intergrowths of galena, quartz and sphalerite from several veins in the Tapu - Thames area (c.f. Photos 2-14 and 2-15 on p 94 of Merchant, 1978). Similar textures occur in samples from the lower levels of Waihi (Figs 4-22 and 4-23) and in a sample from Waiorongomai (Fig. 4-24). Unusual dendritic - poikilitic textures of inclusions of chalcopyrite, pyrite, galena and pyrrhotite also occur in some Waihi samples (Figs 4-25 and 4-26).

5. Pyrite - Sphalerite - Galena - Chalcopyrite - Electrum - Silver Minerals Assemblage

Mineralisation consisting of pyrite, sphalerite, galena and chalcopyrite with either or both electrum and silver minerals occurs at the locations listed in Table 4-8. The silver minerals are either acanthite (Waihi and the Camoola Vein, Maratoto), hessite (Ajax Vein, Neavesville; Silver Queen Vein, Maratoto; and Hero and Colonist Veins of Waiorongomai) or hessite in association with a variety of other silver and gold tellurides (Tapu - Thames and Thames).

Two predominant types of base metal with silver mineral assemblages occur in the Tapu - Thames (Monowai, Comstock and Sylvia mines) and Thames (Waitangi Mine) areas which Merchant (1978) classified under his Pb - Zn and Pb - Au associations. The mineralogy of each assemblage is as follows:

- (a) Precious metal mineralisation in Merchant's Pb - Zn association: quartz, sphalerite, galena, chalcopyrite, pyrite, tetrahedrite, hessite, sylvanite, stutzite (-empressite), petzite, coloradoite, altaite and gold.
- (b) Pb - Au association: quartz, galena, electrum and marcasite.

Merchant (1978) described the textures of the mineralisations as characterised by complex dendritic intergrowths between galena - quartz - sphalerite (Pb - Zn association) and galena - quartz (Pb - Au association). The tellurides of his Pb - Zn association occur intergrown with or replacing galena, and electrum of his Pb - Au association occurs as inclusions in galena or cementing pre-existing cataclastic pyrite, sphalerite or quartz.

Complex intergrowth textures between quartz, sphalerite, galena and chalcopyrite also occur in a specimen of crustified ore from 14 level of the Talisman Mine, Karangahake (Figs 4-27 and 4-28; the hand specimen is shown in Fig. 4-6). Sphalerite sometimes contains inclusions of galena, ± chalcopyrite, ± electrum arranged in poikilitic (Fig. 4-29), dendritic -

Figure 4-23: Lamellar sphalerite (light grey) in quartz (dark grey); sample 14052 from 10 level of the Martha Mine, Waihi. 100X.

Figure 4-24: Dendritic galena (white) in quartz (black) exhibiting a herringbone pattern. The dark grey mineral is sphalerite. Sample 14072 from No1 vein Waiorongomai. 100X. See also Fig. VIII-6.

Figure 4-25: Dendritic - "streaky" galena + pyrite + chalcopyrite (white) in sphalerite (grey) of sample 13978, Martha Vein, Waihi. The black mineral is quartz. 100X.

Figure 4-26: Poikilitic inclusions of galena (white), pyrrhotite (pale pink) and pyrite (pale yellow) in sphalerite (greenish grey) of sample 14040 from the Martha Mine, Waihi. Tiny inclusions of exsolved? chalcopyrite (yellow) also occur in the sphalerite. The dark grey-black mineral surrounding sphalerite is quartz and the black areas within the sphalerite are pits. X200.

TABLE 4-8: Main occurrences of the pyrite-sphalerite-galena-chalcopyrite-electrum-silver minerals
epithermal mineral assemblage.

Location	General Vein Texture	Metallic ("Ore") Minerals ¹		Gangue ¹ Minerals	Metallic/gangue ² Mineral ratio	Grain size ³
		Major	Minor			
Tapu-Thames (Sylvia and Monowai)	breccia	py, sp, gn, cp	hs, syl, stutzite, mc altaite, nagyagite, ptz, bi, el, gold	qtz	high	m & c
Neavesville (Ajax)	breccia	py	sp, cp, gn, hs (el?)	qtz, ad, brookite	low	f
Maratoto	breccia banded	py, sp, gn, cp	hs, ac, el	qtz, ca	low to medium	f
Waihi	banded	py, sp, gn, cp, ac, el	hs (Rosemont Hill Veins), thd	qtz, ca, ad	low to high	f & m
Karangahake	banded	py, sp, gn, cp	ac, el, hs	qtz, ca	medium to high	f & m
Waiorongomai	breccia banded cockade	py, sp, gn, cp	hs, el	qtz	high	m & c

¹ See list of abbreviations

² Refers only to samples studied and may not be representative of whole vein

³ c = coarse f = fine m = medium

Figure 4-27: Fine grained sphalerite (grey)-galena (white) intergrowth that makes up most of the dark bands of specimen 14025 (Fig. 4-6) from Talisman 14 level, Karangahake. In this view the galena appears to fill spaces between sphalerite grains, however in some other parts of the specimen, graphic and myrmekitic intergrowths occur. 100X.

Figure 4-28: Sphalerite (grey) - galena (white) - chalcopryite (dull yellow) - electrum (brilliant yellow) - quartz (black) intergrowth in sample 14025 from Talisman 14 level, Karangahake (c.f. Fig. 4-27). The quartz and electrum may be later than the sulphides, as in some other parts of the specimen (e.g. Fig. 4-31). 100X.

Figure 4-29: Poikilitic inclusions of galena, chalcopyrite and electrum (all white) in sphalerite (grey) of sample 14025 from Talisman 14 level, Karangahake. This texture is considered to represent a cross section of the dendritic - "streaky" texture shown in Fig. 4-30. 100X.

Figure 4-30: Dendritic - "streaky" inclusions of galena, chalcopyrite, and electrum (all white) in sphalerite (grey) of sample 14025 from Talisman 14 level, Karangahake. 100X.

"streaky" (Fig. 4-30) and myrmekitic textures. Electrum also occurs as inclusions in chalcopyrite and, at a later stage, with quartz invading the earlier sulphides (Fig. 4-31). The base metal + electrum followed by quartz + electrum sequence is repeated several times across the specimen (Fig. 4-6).

Hessite is believed to occur at Karangahake (Henderson & Bartrum, 1913; Merchant, 1978) but was not seen by the writer. It occurs with breccia texture base metal mineralisation at Neavesville (Ajax Vein), Maratoto (Silver Queen Vein) and Waiorongomai (Hero and Colonist). An almost ubiquitous association of galena and hessite was noted at Maratoto. Rare altaite was also identified in one sample from Waiorongomai (sample 14100 from the 1100' level, Colonist section) occurring with hessite as inclusions in galena.

Acanthite occurs in brecciated texture base metal mineralisation at Maratoto (Camoola Vein) and Waihi. In the former locality it occurs in both quartz and calcite gangue. Typical textures are scattered grains of acanthite, rare electrum and sulphides in the gangue mineral (Fig. 4-32). When composite grains of sulphides and electrum occur the minerals usually exhibit mutual boundary relations (Fig. 4-33).

6. Sb - Sulphosalt Mineral Assemblage

Merchant (1978) differentiated a Cu - Sb mineralisation stage in the veins between Tapu and Thames. He considered that it postdated most Pb - Zn mineralisation because it was "frequently seen as vugh infillings in earlier 'ore' or as crosscutting veinlets typically within chalcopyrite - pyrite assemblages" (Merchant, 1978 p 120). The following list of minerals was compiled from his descriptions from various occurrences: tetrahedrite, argentian tetrahedrite, enargite, chalcopyrite, chalcostibite, bournonite and robinsonite.

Robson (1979) also described Sb - sulphosalt mineralisation (his Stage 2) from a vein and float at Whangapoua. The minerals present were as follows: pyrite, miargyrite, tetrahedrite, freibergite, famatinite, sphalerite, chalcopyrite, galena and native antimony.

Erceg (1981) described an assemblage of quartz, marcasite, pyrite, famatinite, miargyrite, argentian tetrahedrite [- freibergite] and minor chalcopyrite cementing a fault breccia (which he considered to be a downward extension of the Iona Vein) at Te Ahumata. Famatinite and miargyrite have not been identified from the quartz veins in the area which contain a pyrite - sphalerite - galena - chalcopyrite assemblage (also with marcasite and tetrahedrite).

Figure 4-31: Electrum (brilliant yellow) and quartz (black) invading earlier chalcopyrite (dull yellow) and sphalerite (grey) - galena (white) intergrowth in sample 14025 from Talisman 14 level, Karangahake. 100X.

Figure 4-32: Grains of sphalerite (grey), chalcopyrite (yellow) and galena (white) scattered in calcite gangue (dark grey), sample M18186 Camoola Vein, Maratoto. The irregular margins of the sulphide grains in calcite gangue (e.g. chalcopyrite in this figure) give the appearance of a "peppered" or "splatter" texture. 100X.

Figure 4-33: Intergrowth between galena (white), chalcopyrite (yellow), sphalerite (medium grey), acanthite (pale grey, scratched) and calcite (dark grey) in sample 18186 from the Camoola Vein, Maratoto. Where contacting each other, the sulphide minerals generally have mutual boundary relations. 200X.

7. Pyrite - Acanthite - Electrum Assemblage

Pyrite, acanthite (argentite) and electrum mineralisation is reported in the early literature (e.g. Bell & Fraser, 1912; Henderson & Bartrum, 1913; Morgan, 1924) from many of the deposits and would appear to be the dominant precious metal mineralisation at Komata, Golden Cross and in the upper levels of Karangahake and Waihi. The writer was unable to obtain samples of this assemblage for study.

8. Pyrite - Bonanza Electrum Assemblage

Electrum mineralisation concentrated in extremely rich patches called bonanzas occurred at Coromandel and Thames. The bonanzas were related to structural features, generally occurring at vein intersections, and confined to near surface horizons.

The mineralogy of the two areas differs in that Merchant (1978) implied a ubiquitous association of pyrargyrite with the electrum at Thames, whereas silver minerals were apparently uncommon in the mineralisation at Coromandel (c.f. descriptions by Fraser & Adams, 1907). The minerals reported from each locality are as follows:

Coromandel (Fraser & Adams, 1907); quartz, pyrite, calcite, electrum, arsenopyrite, native arsenic, stibnite, pyrargyrite and aragonite.

Thames (Merchant, 1978); quartz, pyrite, pyrargyrite, electrum, barite, stibnite, arsenopyrite and chalcopyrite.

9. Au - Ag Sulphosalt Mineral Assemblage

Mineralisations comprising pyrite, electrum and Au - Ag sulphosalts occur at Te Ahumata, Broken Hills and in the Tapu - Thames area.

The electrum and sulphides are very fine grained and occur in chalcedonic quartz with a very low metalliferous mineral/quartz ratio. The various minerals present at each locality are as follows:

Te Ahumata (Ramsay & Kobe, 1974); quartz, pyrite, chalcopyrite, pyrargyrite, proustite, polybasite/pearceite, seleniferous agyrodite, aguilarite, naumannite and electrum. A hand specimen is shown in Fig. 4-4.

Broken Hills (Moore, 1976; 1979): quartz, barite, pyrite, cergyrite, aguilarite, naumannite/aguilarite, aguilarite/acanthite, acanthite, trechmannite, electrum, native silver and some complex Au - Ag arsenic sulphoselenides.

Norfolk Reef, Tapu - Thames (Merchant, 1978): quartz, pyrargyrite, polybasite, marcasite, chalcopyrite, pyrite, anatase, stephanite (?), miargyrite (?), galena and electrum.

Figure 4-34: Plates of barite (up to 5mm across) coating parts of a quartz crystal (40mm long) from the Welcome Vein, Waiorongomai. Sample 14099.

10. Stibnite

Stibnite occurs in late vein quartz, particularly as needles on vug quartz, at Te Ahumata, Whangapoua and Thames. Associated minerals are: pyrite, marcasite, chalcopyrite, sphalerite and arsenopyrite at Te Ahumata, pyrite at Whangapoua and barite at Thames.

11. Barite

In addition to the previously mentioned occurrences of barite with gold - silver mineralisation at Broken Hills and Thames, and stibnite mineralisation at Thames, barite also occurs as late stage coatings on vug quartz in veins between Tapu and Thames and those at Thames, Tui Mine and Waiorongomai. The barite occurs as large platy crystals (Figs 4-9 and 4-34), up to 30mm long at Tui Mine (Ansin, 1975).

12. Cinnabar

Cinnabar occurs as thin coatings on vug quartz crystals and fracture surfaces in veins at Thames (Merchant, 1978), Owharoa (Morgan, 1924), Tui Mine (Wodzicki & Weissberg, 1970) and Waiorongomai (Henderson & Bartrum, 1913).

Cinnabar deposits occur associated with a number of siliceous sinter formations around Mackaytown (Karangahake Gorge) and in the Kauaeranga Valley (east of Thames).

Oxidation and Secondary Enrichment

Introduction

The geologists of the early 1900's placed great importance on the presence of oxidation in the veins of the Hauraki Gold - Silver Province, many believing that the bonanza ores were products of secondary enrichment. The bonanza ore zone at Thames was perhaps the principal example, occurring near the surface and having a fairly level lower surface. Recently Merchant (1978) convincingly argued that this bonanza was formed by a boiling horizon in the hydrothermal system.

A poor understanding of the processes of primary mineralisation, oxidation and secondary enrichment and the typical minerals formed by each process led to confusion in the early literature over the origins of the various forms of mineralisation. Morgan (1924) in his study of the Waihi deposit considered some rich primary ore comprising pyrite, sphalerite, galena and chalcopyrite as secondary material formed by the action of descending water.

The early geologists identified "oxidised ore" by the absence of primary sulphides (e.g. pyrite, chalcopyrite, sphalerite and galena) and the presence of quartz pseudomorphs after calcite, supergene minerals such as covellite and chalcocite and oxides of iron and manganese. These occurred in some deposits down to very deep levels, for example oxidised ore was recognised from 13 level at Waihi (Bell & Fraser, 1912) and 11 level at Karangahake (Henderson & Bartrum, 1913). This oxidation was attributed to the action of descending water some considerable time after mineralisation and the depth of oxidation was believed to reflect the topography at the time of oxidation.

The minerals and features attributed to oxidation and secondary enrichment by the early writers are divided here into four separate events as follows:

(1) Hydrothermal leaching	—	Hypogene
(2) Sulphide replacement	}	Combination hypogene-supergene
(3) Solution and redeposition		
(4) Post mining mineralisation	—	Supergene

Hydrothermal Leaching

Platy or lamellar quartz, termed "quartz pseudomorphs after calcite", was a major gangue constituent in many of the mines in the province (e.g. Kuaotunu, Komata, Golden Cross, Waitekauri, Maratoto, Waihi and Karangahake) and was considered by the early geologists (e.g. Bell & Fraser, 1912; Henderson & Bartrum, 1913) to be a replacement feature of quartz after calcite.

Morgan (1924) suggested that this interpretation was incorrect and that the feature was actually a quartz plus calcite intergrowth from which the calcite had been subsequently leached out by oxidation.

Main (1971) demonstrated that Morgan's explanation was possible by dissolving out, with acid, the calcite from a block of intergrown quartz and calcite taken from the Maratoto Mine. The resulting rock exhibited the same platy quartz texture typical of the quartz pseudomorphs after calcite.

The writer basically agrees with Morgan's interpretation but considers that in many (most ?) cases the leaching was not due to supergene oxidation but rather to hypogene hydrothermal leaching caused by changes in pH or a decrease in temperature of the hydrothermal fluid (the latter effect increases the solubility of calcite in the hydrothermal fluid at $f\text{CO}_2 < 1$ molal; Holland, 1979). This is supported by several instances of vug quartz crystals occurring on the platy quartz, having been deposited

TABLE 4-9: Common secondary minerals found in the deposits of the Hauraki Gold-Silver Province and the probable primary minerals from which they were derived.

Primary mineral	Secondary Mineral					
	Oxides	Carbonates	Sulphates	Silicates	Sulphides	Native element
Au Gold-electrum						leafy gold (1) mustard gold (2)
Ag Acanthite Hessite					cerargyrite proustite pyrargyrite	wire silver scale silver } (3)
Fe Pyrite	limonite (goethite)	siderite	jarosite			
Cu Chalcocopyrite	cuprite	malachite azurite	chalcocanthite	chrysocolla		native copper (4)
Zn Sphalerite		smithsonite				
Pb Galena		cerrusite	anglesite			
Mn Rhodochrosite Manganiferous calcite	manganite pyrolusite psilomelane wad					

- Occurrences: (1) Upper levels Martha Mine, Waihi
 (2) Golden Cross, Rosemont Hill Mines of Waihi
 (3) Karangahake and Waihi
 (4) Thames and Tui Mine

there after removal of the calcite (c.f. Fig. 2 of Plate II facing page 9 of Morgan, 1924; and epimorphous quartz after calcite of Ramsay, 1971).

The hydrothermal leaching stage, which seems to be common to most veins containing abundant calcite, may in some cases be related to precious metal deposition. Although leached calcite was commonly associated with the ore in many mines the appearance of primary calcite in the veins often signified the end of economic mining (e.g. Golden Cross, Komata, Waitekauri and, to a lesser extent, the Talisman Mine at Karangahake).

Sulphide Replacement

Most of the sulphide mineralisation in the province exhibits supergene replacement to varying degrees, viz. replacement of chalcopyrite, sphalerite and galena by chalcocite, covellite and bornite. Chalcocite and covellite are the predominant products, bornite only having been recorded at a few locations (e.g. Petote Stream, Maratoto and Karangahake).

A less frequently observed replacement is that of stibnite in the Te Ahumata, Coromandel and Thames areas by kermesite (Ramsay, 1971; Fraser & Adams, 1907; and Fraser, 1910 respectively).

These replacements may have occurred during the waning hydrothermal stages or by cold ground water.

Solution and Redeposition

The prominent effects of oxidation are the solution of primary minerals and subsequent deposition of secondary oxides, carbonates, sulphates and native elements. Table 4-9 lists the common secondary minerals reported from the province by previous workers and the primary minerals from which their metallic constituents were derived. In addition the following minerals have also been cited and occur in rare quantities in the areas listed:

Arsenolite, orpiment and realgar: Tokatea Mine, Coromandel (Fraser & Adams, 1907) derived at this locality from native arsenic. Orpiment and realgar also occur at Te Ahumata (Ramsay, 1971; Erceg, 1981)

Kerargyrite: Waikoromiko Valley, Coromandel (Fraser & Adams, 1907) and Talisman Mine, Karangahake (Henderson & Bartrum, 1913).

Cervantite, diopside and melanoconite: Tapu - Thames and Thames (Fraser, 1910).

Bromargyrite and iodargyrite: Talisman Mine, Karangahake (Henderson & Bartrum, 1913).

Stilpnomelane: Waihi (Morgan, 1924).

Figure 4-35: Stalactites of limonite grown from the roof of the mine tunnel by ground water seepage since mining operations ceased. Vulcan 4A (468m) level, Waiorongomai.

Greenockite, hauleyite, tenorite, osarizawaite, linarite, beaverite, serpierite, devilline and dundasite: Tui Mine (Ansin, 1975).

Most of the solution and redeposition features were formed by weathering and circulating ground water, however a few may also have occurred during late hydrothermal stages. The solution of manganiferous calcite and rhodochrosite with subsequent deposition of pyrolusite are partly placed into this last category.

Post Mining Mineralisation

Limonite (goethite), epsomite, mirabilite, chalcantite, manganese oxides and various hydrous aluminium and iron sulphates (e.g. melanterite) were reported by Fraser & Adams (1907), Fraser (1910), Bell & Fraser (1912), Henderson & Bartrum (1913), Morgan (1924) and Ansin (1975) to form coatings on walls of abandoned sections of the mines, having precipitated from the mine waters after mining had ceased in those sections. In places limonite, chalcantite, and the hydrous aluminium and iron sulphates formed stalactites and stalagmites in the tunnels. Fig. 4-35 illustrates stalactites of limonite encountered by the writer in the Vulcan low level (4A, 468m) of Waiorongomai.

Secondary Enrichment

Although many of the mines exhibit a weathered and leached upper zone (e.g. Maratoto, c.f. Main, 1979) the degree of secondary enrichment in precious metals below this zone is probably much less than suggested by the early writers.

Leafy and mustard gold and wire and scale silver were probably formed by secondary enrichment but these are not common in the mines where they were recorded (Golden Cross, Waihi and Karangahake) and large scale secondary enrichment is negated by the fact that (as far as can be ascertained) most of the gold mined from the upper "oxidised" zones was electrum containing quantities of silver indicative of primary deposition by hydrothermal solutions (c.f. Appendix V).

Similarly, the degree of leaching implied by the early reports may also be exaggerated. For example, the oxidised near surface ore of the Martha Mine (Waihi) contained pyrite and acanthite in addition to electrum but was considered to be very leached because other sulphides were absent. The absence of chalcopyrite, sphalerite and galena was probably because they were not deposited there in the first place.

CHAPTER 5MINERAL CHEMISTRYINTRODUCTION

Analyses of minerals made with the electron probe micro analyser (EPMA) during this study are listed with a description of the analytical conditions in Appendix II and discussed in the following sections in alphabetical order. Where possible discussion is based on averages of between 2 and 25 analyses of the specific mineral in an individual sample.

EPMA analyses of minerals from the Hauraki Gold - Silver Province determined by previous workers are detailed in Table 5-1 and also discussed in the following sections where appropriate.

ACANTHITE - ARGENTITE

Acanthite and argentite are polymorphs of Ag_2S . Ag_2S is deposited in most hydrothermal deposits as argentite, but on cooling below 177°C inverts to acanthite. Therefore Ag_2S observed in samples at room temperature is acanthite and is termed so here although it is reported in the early literature on the province (e.g. Geological Survey Bulletins) as argentite.

The acanthites analysed here are seleniferous (Table 5-2), leading Main (1971) and Main *et al* (1972) to incorrectly suggest that aguilarite (Ag_4SeS) was the predominant silver mineral in the Camoola Vein of Maratoto (aguilarite was not identified by the writer).

Two analyses of the Se content of acanthite in sample 285/37/8 (M 32) were quite different (0.13 and 3.11 wt. % Se), while in sample 14043 (Wh 35) two different populations of acanthite occur, one with an average Se content of 1.00 wt. % (range of 3 analyses = 0.96 - 1.05 wt. %) and the other averaging 7.33 wt. % Se (range of 6 analyses = 6.50 - 9.73 wt. %).

Keift & Oen (1973) reported that acanthite from Salida, Indonesia contains up to 4% Se, whereas Shikazono (1978) reported acanthites with up to 10.09 wt. % Se from Japanese ore deposits.

Petruk *et al* (1974) in a study of naumannite (Ag_2Se), aguilarite and acanthite proposed that the solubility limit of Se in acanthite is approximately 4.7 wt. % Se; higher concentrations, up to 11.1 wt % were considered to be caused by an acanthite - aguilarite intergrowth. They suggested that the single phase aguilarite should contain at least 13.2 wt. % Se.

Applying this classification to the samples listed in Table 5-2, the highly seleniferous population of acanthite in sample 14043 (6.50 - 9.73 wt. % Se) represents an aguilarite - acanthite intergrowth, sample 14032

TABLE 5-1: Electron microprobe analyses of minerals of the Hauraki
Gold - Silver Province listed in previous works.

SPHALERITE

Whangapoua: Robson (1979 p121)
Coromandel: Edwards (1979 p127)
Tapu-Thames: Merchant (1978 p91 and p115)

ELECTRUM

Te Ahumata: Ramsay & Kobe (1974 p149), Erceg (1981 p51)
Broken Hills: Moore (1976 p114)
Thames: Merchant (1978 pp117 and 153)
Neavesville: Torckler (1978 p99)

TETRAHEDRITE

Whangapoua: Robson (1979 p115)
Thames: Merchant (1978 p129)

MISCELLANEOUS

Northern Great Barrier Island:

Idaite, covellite, chalcopyrite, bornite and
anomalous bornite (Weigel 1978 574-575)

Whangapoua: Pyrite, marcasite and arsenopyrite pp107-108

mlargyrite p110

freibergite p114

famatinite p117

stibnite p118

galena p123

Broken Hills: Pyrite pp110-111

native silver p117

acanthite-aquilarite, aguilarite,

aguilarite-naumannite p126

complex gold-silver arsenic

sulphoselenides pp128,132,134
and 135

Robson
(1979)

Moore
(1976)

Thames:

Aikinite and seleniferous

tetradymite p79

seleniferous tellurobismutite p81

galena and silver bismuth telluride p84

kobellite p88

hessite p98

stutzite - empressite p102

altaite p107

petzite and coloradoite p111

chalcostibite p121

bournonite p124

robinsonite p128

enargite p132

pyrargyrite and polybasite p154

unidentified minerals pp89,103,109,
127 and 165

Merchant
(1978)

TABLE 5-2: Electron microprobe analyses of acanthites. Each analysis represents an average of the number indicated. The individual analyses are listed in Appendix II.

Analyses	Maratoto Samples					Waihi Samples		Detection Limit
	285/37/7	285/37/8	M18185	M18186	14032 (GJ3)	14043 (Wh35)		
	(M14) 1	(M32) 2				Population A 6	Population B 3	
Ag	80.72	85.28	85.17	84.94	83.57	83.56	86.51	0.10
S	12.02	12.93	12.58	11.75	11.65	9.08	12.44	0.05
Se	1.94	1.62	2.63	3.87	4.67	7.33	1.00	0.13
Cu	1.93	0.18	n.a.	n.a.	n.a.	n.a.	n.a.	0.06
As	1.80	0.02	n.a.	n.a.	n.a.	n.a.	n.a.	0.08
Au	0.58	0.63	n.a.	n.a.	n.a.	n.a.	n.a.	0.20
Total	98.99	100.66	100.38	100.56	99.89	99.97	99.95	
Min. Se	1.94	0.13	2.54	3.74	4.45	6.50	0.96	
Max. Se	1.94	3.11	2.74	4.08	5.11	9.73	1.05	

n.a. = not analysed

TABLE 5-3: Electron microprobe analyses of pyrrhotites and argentian pentlandite. The pyrrhotite analyses are averages of the analyses presented in Appendix II as indicated below.

	Pyrrhotite		Argentian Pentlandite		
	Miners		Miners		
	Head	Waihi	Head		
	13965	14040	13965		
	(MH1)	(Wh29)	(MH1)	Detection Limit	
Analyses	13	7	1		
Fe	59.70	58.79	36.51	0.04	Fe
S	39.35	39.72	31.42	0.05	S
Zn	n.a.	1.34	0.07	0.05	Zn
Cu	0.15	0.01	0.70	0.06	Cu
Ni	0.06	0.00	18.26	0.04	Ni
As	0.02	0.31	0.00	0.08	As
Co	0.32	0.00	0.01	0.04	Co
Ag	0.01	n.a.	13.52	0.10	Ag
Cd	0.00	n.a.	n.a.	0.08	Cd
	<hr/>	<hr/>	<hr/>		
Total	99.61	100.17	100.49		

$X_{\text{FeS}^{\text{po}}}$ 0.94 0.92

n.a. = not analysed

(4.45 - 5.11 wt. % Se) straddles the acanthite/acanthite - aguilarite boundary (4.7 wt % Se), and the Maratoto samples (285/37/7(C6), 285/37/8, M18185 and M18186) in addition to the low Se population in sample 14043 (Wh 35) are acanthites.

The occurrence of an acanthite - aguilarite intergrowth has been reported previously from the province by Moore (1976). He noted examples of the full range of species in the acanthite - naumannite solid solution series (acanthite, acanthite - aguilarite intergrowth, aguilarite, aguilarite - naumannite intergrowth and naumannite: Petruk et al, 1974) from the Broken Hills Mine.

Shikazono (1978) related the Se content of acanthite to the aSe/aS ratio and fO_2 of the ore fluid. These factors are discussed in Chapter 11 and Appendix V.

ARGENTIAN PENTLANDITE

Argentian pentlandite (Table 5-3) occurs as tiny (up to 50 micrometres) inclusions in chalcopyrite from Miners Head (Appendix I-A). The mineral is a variety of pentlandite which contains up to 14.8 wt % silver and has the general formula $(Fe\ Ni)_{8+x} Ag_{1-x} S_8$ (Scott & Gasparrini, 1973). The Miners Head occurrence has the formula: $Fe_{5.2} Ni_{2.5} AgS_{7.8}$

Argentian pentlandite was first described by Shishkin et al (1971) from two massive copper - nickel sulphide deposits and a nickel - cobalt skarn deposit in the U.S.S.R. and subsequently by Vuorelainen et al (1972) from Outokumpu - type copper sulphide deposits and magmatic nickel - copper deposits in Finland and by Scott & Gasparrini (1973) from massive nickel - copper sulphide deposits of metamorphic origin in the Bird River area, Manitoba, Canada. In these deposits (11 in all), argentian pentlandite is generally found as inclusions in chalcopyrite. Normal pentlandite may or may not be present. Other closely associated sulphides include pyrite, pyrrhotite, sphalerite, galena and cubanite. Argentian pentlandite is the chief carrier of silver in many of the deposits.

Scott & Gasparinni (1973) suggested that because silver replaces iron and nickel only in octahedral and not tetrahedral sites of argentian pentlandite the mineral is a distinct species and not a member of an isomorphous series with normal pentlandite (as is probably the "argentian pentlandite" described from Sudbery by Mitchener [in Hawley, 1962] which contained 3.8 wt % silver).

The Miners Head argentian pentlandite occurrence is interesting in that it is the only nickeliferous mineral noted at this locality: even coexisting pyrrhotite has less than 0.1% Ni (Table 5-3).

TABLE 5-4: Electron microprobe analyses of bismuthinite and tetradymite from Tui Mine (sample 13915). The bismuthinite analysis is an average of the 9 individual analyses listed in Appendix II.

Analyses	Bismuthinite 9	Tetradymite 1	Detection Limit
Bi	77.86	60.91	0.40
S	17.74	4.71	0.05
Pb	3.67	0.00	0.03
Cu	1.15	0.07	0.06
Te	0.04	32.44	0.10
Fe	0.08	0.00	0.04
Se	0.00	0.00	0.13
Total	100.54	98.13	

BISMUTH MINERALS

Bismuthinite and tetradymite (Table 5-4) were analysed from the early stage mineralisation at Tui Mine. The bismuthinite contains an average of 3.67 wt. % Pb and 1.15 wt. % Cu, whereas these elements are present in low concentrations in the tetradymite.

Merchant (1978) analysed several bismuth minerals (aikinite, kobellite, tellurobismutite and tetradymite) from early mineralisation in the veins of the Tapu - Thames area. Kobellites from this area have Sb/Bi weight ratios between 0.32 and 1.05, 2.2 - 5.5 wt. % Ag and 0.8 - 1.8 wt. % Cu, whereas Se is a significant component in the tellurobismutite (7.0 - 8.3 wt %) and tetradymite (1.3 - 1.8 wt. %).

CHALCOPYRITE

Only a few analyses were made of chalcopyrites and they are listed in Appendix II. With the exception of the major elements and small quantities of arsenic and gold in some specimens, the concentrations of most other elements analysed were below their detection limits.

GALENA

Table 5-5 lists average analyses of galenas from 14 samples.

Maximum recorded concentrations of Ag, Sb and Fe are each 0.08 wt %. Considering the detection limits these measurements are probably not significant. The occurrence of argentian galena suggested by Fraser & Adams (1907) from several veins in the Coromandel area was therefore not confirmed.

Bi was also analysed in the galenas and although absolute values of concentration are not known because of interference problems with Pb during analysis (Appendix II), very low concentrations are indicated and are probably of a similar order to Ag, Sb and Fe.

GOLD AND ELECTRUM

The purity of gold is expressed in terms of fineness, which is the proportion of pure gold in the sample in parts per thousand. Silver is generally the most common impurity and a further parameter, true fineness, considers only the ratio of Au to Au + Ag:

$$\text{True fineness} = \frac{\text{Au}}{\text{Au} + \text{Ag}} \times 1000 \quad (5-1)$$

Gold containing 20% or more silver (true fineness of 800 or less) is termed electrum (Boyle, 1979).

Average analyses of gold and electrum are presented in Table 5-6. Most of the concentrations of S, Cu, Fe, As and Te reported in Table 5-6

TABLE 5-5: Electron microprobe analyses of galenas. Each analysis represents an average of the number indicated. The individual analyses are listed in Appendix II.

	Northern Colville Peninsula		Tokatea		Petote Stream Area		Waitekauri		Waihi		Karangahake		Tui Mine		Waiorongomai	
	13971 (DC12)	13974 (SM11)	13959 (TK1)	13985 (HC3a)	13989 (HC4 ₁)	14015 (WK6)	14040 (WH29)	14046 (WH43)	14048 (WH45)	14025 ^(b) (TI22 ₆)	14059 (Tui 17)	14060 (Tui 18)	14061 (Tui 19)	14100 (Wi98)	Detection limit	
Analyses	6	4	6	4	5	2	6	2	4	4	6	5	2	4		
Pb	86.64	86.40	86.42	86.98	86.40	86.16	86.21	85.90	86.18	86.44	86.83	87.05	86.37	86.47	0.03	
S	13.21	13.05	13.05	13.29	13.12	13.21	13.29	13.23	13.11	13.15	13.22	13.18	12.69	12.99	0.05	
Ag	0.04	0.02	0.03	0.01	0.03	0.01	0.03	0.06	0.08	0.04	0.06	0.03	0.05	0.04	0.10	
Sb	0.04	0.04	0.01	0.03	0.03	0.06	0.06	0.07	0.05	0.07	0.05	0.02	0.08	0.02	0.08	
Fe	0.00	0.01	0.05	0.00	0.01	0.00	0.04	0.08	0.00	0.02	0.01	0.07	0.00	0.00	0.04	
Total	99.93	99.52	99.56	100.31	99.59	99.44	99.63	99.34	99.42	99.72	100.17	100.35	99.69	99.52		

TABLE 5-6: Electron microprobe analyses of gold and electrum. Each analysis represents an average of the number indicated. The individual analyses are listed in Appendix II.

	Tokatea		Maratoto		Waihi		Karangahake		Tui Mine		Waiorongomai	
	13961 (TK7)	13937 (M33)	285/7/8 (M32)	14032 (GJ3)	14043 (WH35)	14046 (WH43)	14048 (WH45)	14025 ^(a) (TI22 ₂)	14025 ^(b) (TI22 ₆)	13915 (Tui 27)	13909 (Tui 30)	14092 Detection (W183) 1 limit
Analyses	7	2	5	3	8	1	7	5	1	2	8	1
Au	60.35	54.81	58.70	52.29	65.75	68.15	62.94	74.15	71.34	89.00	90.16	80.27 0.20
Ag	38.55	44.13	40.68	46.67	33.87	31.36	36.64	26.31	26.67	9.77	8.02	19.64 0.10
S	0.07	0.44	0.24	0.05	0.09	0.10	0.12	0.03	0.06	0.06	0.16	n.a. 0.05
Cu	0.01	0.01	0.02	0.01	0.01	0.00	0.12	0.00	0.00	0.01	0.12	n.a. 0.06
Fe	0.00	0.58	0.02	0.03	0.02	0.13	0.06	0.00	0.00	0.01	0.06	n.a. 0.04
As	0.18	0.00	0.09	0.50	0.09	0.00	0.15	0.12	0.00	0.00	0.00	n.a. 0.08
Te	0.04	0.01	0.06	0.10	0.06	0.00	0.02	0.02	0.05	0.08	0.01	n.a. 0.10
Total	99.20	99.98	99.81	99.65	99.89	99.74	100.05	100.63	98.12	98.93	98.53	99.91
True fineness	610	550	590	530	660	680	630	740	730	900	920	800

n.a. = not analysed

are near or below their detection limits and are therefore not significant, preventing comparison between samples.

The concentration of silver is related to physicochemical conditions during electrum or gold deposition and is discussed in Appendix V.

Zoning of silver concentration was not observed in the gold and electrum analysed here but has been reported from Te Ahumata (Ramsay & Kobe, 1974), Broken Hills (Moore, 1976) and Thames (Merchant, 1978). Electrum from the Iona Quarry at Te Ahumata is zoned with silver content decreasing from core to rim (52.4 and 15.6 wt. % Ag respectively), whereas electrum from the breccia pipe in 2 level of the Broken Hills Mine is zoned in a reverse direction with silver increasing from core to rim (25 and 64 wt. % Ag respectively). Electrum from the Norfolk Mine, Thames, is zoned from 76.7 to 50.9 wt. % Ag but Merchant (1978) failed to mention in which direction.

Zoning, particularly that resulting in silver rich rims, is generally attributed to changes in physicochemical conditions (e.g. temperature and fS_2) during electrum deposition although a silver depleted rim in electrum or gold may also be caused by selective leaching of Ag during supergene or weathering processes.

HESSITE

The hessite analyses listed in Table 5-7 contain variable quantities of arsenic (0.09 to 0.56 wt. %) although the concentration of this element appears to be much higher at Waiorongomai than Maratoto. In contrast the Maratoto hessites contain small quantities of gold (up to 0.42 wt. %) which are not present in the Waiorongomai hessites.

PYRITE

The analyses of a few pyrites are listed in Appendix II. As with chalcopyrite, with the exception of the major elements, only small quantities of arsenic and gold are present in some specimens in concentrations of significance.

Moore (1976) reported variable quantities of gold and arsenic (with maximums of 1.12 and 1.0 wt. % respectively) in pyrite from Broken Hills and Robson (1979) described pyrite - marcasite intergrowths associated with arsenopyrite in the mineralisation at Whangapoua in which the arsenic content of the pyrite and marcasite averaged 10.8 wt. %. The latter is probably a result of intergrowths with arsenopyrite.

TABLE 5-7: Electron microprobe analyses of hessites. Each analysis represents an average of the number indicated. The individual analyses are listed in Appendix II.

Analyses	Tokatea 13961 (TK7)	Maratoto 285/37/2 (M12) 285/37/6 (M13)		Waiorongomai 14092 (Wi83) 14100 (Wi98)		Detection Limits
	11	5	5	3	5	
Ag	63.03	62.71	62.51	61.24	60.87	0.10
Te	37.05	36.98	37.15	37.74	38.88	0.10
S	n.a.	0.16	0.11	0.17	0.05	0.05
Cu	n.a.	0.01	0.00	0.20	0.01	0.06
Fe	n.a.	0.01	0.01	0.01	0.00	0.04
Au	n.a.	0.42	0.39	0.06	0.00	0.10
As	n.a.	0.09	0.08	0.56	0.25	0.08
Se	n.a.	0.20	0.00	0.37	0.00	0.13
Total	100.08	100.58	100.25	100.35	100.06	

n.a. = not analysed

PYRRHOTITE

Pyrrhotite occurs naturally in hexagonal, monoclinic and "anomalous" forms. Hexagonal pyrrhotite (Fe_{1-x}S) is the only pyrrhotite structure stable above 308°C . This structure persists to lower temperatures for all but the most sulphur - rich pyrrhotite compositions. Monoclinic pyrrhotite ($\text{Fe}_{7+x}\text{S}_8$) is stable only up to 254°C but may be metastable up to 308°C , whereas anomalous pyrrhotite ($\text{Fe}_{7+x}\text{S}_8$) was described by Clark (1966) from low temperature sedimentary environments.

The pyrrhotites analysed from Miners Head and Waihi (Table 5-3) are believed to have formed at around 425°C and 325°C respectively (see Chapters 6 and 9) and were therefore deposited as hexagonal pyrrhotite although they have compositions close to the Fe_7S_8 of monoclinic pyrrhotite.

Pyrrhotite compositions are generally expressed in terms of mole fraction FeS (X_{FeS}). Average values of this parameter for the Miners Head and Waihi pyrrhotites are 0.94 and 0.92 respectively. The mole fraction of FeS in hexagonal pyrrhotite is a function of temperature and $f\text{S}_2$ (Toulmin & Barton, 1964). These factors are discussed in Appendix V where it is concluded that the Waihi pyrrhotite is iron deficient for hexagonal pyrrhotite. It may therefore have inverted to monoclinic pyrrhotite.

The minor element chemistry of the Miners Head and Waihi pyrrhotites differ in that Cu and Co are present in small quantities in the Miners Head sample, whereas As occurs in the Waihi sample. An average value of 1.34 wt. % Zn occurs in the Waihi pyrrhotite, considerably higher than the solubility limit of 0.1% ZnS (0.07 wt. % Zn) suggested by Barton & Skinner (1979). This high zinc concentration may be related to the occurrence of the pyrrhotite as inclusions in sphalerite. Similarly the copper content in the Miners Head pyrrhotite may be caused by its occurrence surrounded by chalcopyrite.

SPHALERITE

The 40 average sphalerite analyses presented in Table 5-8 have the following ranges in composition: 0.22 to 11.47 wt. % Fe, 0.09 to 0.86 wt. % Cd and 0.05 to 1.35 wt. % Mn. Little variation was observed across grains and therefore compositional zonation is considered to be minor.

The iron content of sphalerite is a function of depositional temperature and $f\text{S}_2$ and is discussed in Appendix V.

Both the concentration of Cd and Mn are quite variable, the latter exhibiting the greatest range. The Waihi sphalerites have particularly low concentrations of Cd relative to the other samples.

With the exception of sample 285/37/6 (M 13) the ratio of Cd/Mn is fairly

TABLE 5-8: (Continued)

Karangahake (Continued)					Detection Limits
Analyses	9	6	10	6	
14082 14086 14092 14100 (W153) (W158) (W183) (W198)					
S	32.51	32.52	32.19	32.70	S 0.05
Fe	0.85	1.43	0.44	0.67	Fe 0.04
Zn	65.99	65.29	66.36	65.93	Zn 0.05
Cd	0.31	0.21	0.26	0.24	Cd 0.08
Mn	0.09	0.08	0.34	0.16	Mn 0.03
Total	99.75	99.53	99.59	99.70	Total
Cd/Mn	3.4	2.6	0.8	1.5	Cd/Mn
Fe/Mn	9.4	18	1.3	4.2	Fe/Mn
Fe/Cd	2.7	6.8	1.7	2.8	Fe/Cd

TABLE 5-9: Cd/Mn ratios of sphalerites, from
the analyses listed in Table 5-8.

	Number of average analyses	average Cd/Mn ratio
Miners Head	1	5.5
Te Ahumata	1	2.5
Doctors Creek	1	0.6
Sorry Mary Stream	1	4.7
Tokatea	1	0.6
Petote Stream Area	6	2.7
Maratoto (285/37/6 excluded)	5	0.5
Waitekauri	2	0.8
Karangahake (14025 counted as 1)	2	0.4
Waihi	5	0.2
Tui Mine	5	5.7
Waiorongomai	7	2.4

consistent for sphalerites from the same area (Table 5-8) although quite variable from one area to another (Table 5-9).

Nash (1975) noted that the concentration of Mn varied sympathetically to that of Fe in sphalerites from the Mayflower Mine (Utah, U.S.A.), however comparison of the Fe contents and Fe/Mn ratios shows that such a correlation is absent here.

TETRAHEDRITE - TENNANTITE

Minerals in the isomorphous series tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) - tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$) may be classified using Td_z values where

$$z = \frac{\text{moles Sb}}{\text{moles Sb} + \text{moles As}} \times 100 \quad (5-2)$$

In this classification Td_{100} = tetrahedrite and Td_0 = tennantite

Table 5-10 lists average analyses of tetrahedrite from Tui Mine and Waiorongomai together with analyses from Whangapoua and Thames reported by Robson (1979) and Merchant (1978) respectively. Both tetrahedrite and tennantite occur in the Tui Mine mineralisation, whereas only tetrahedrite has been identified from the other locations (Table 5-10). The Tui Mine tetrahedrite (Td_{95}) and tennantite (Td_1) are different grains within the same sample. The tetrahedrites from the other localities exhibit some variation in their composition particularly at Whangapoua where a range of at least Td_{68} to Td_{100} is indicated by Robson's analyses (Table 5-10).

Zn and Fe contents of Thames, Tui Mine and Waiorongomai tetrahedrite - tennantite are similar, whereas Fe is substantially higher in Whangapoua tetrahedrite: Zn was not analysed in the latter by Robson. The Zn/Fe ratio ranges from approximately 2 to 4 and is independent of the Sb/As ratio. A similar relationship was observed by Wu & Peterson (1977) in tetrahedrites from the Casapalca vein deposit (Peru).

Where analysed, Ni, Mn and Cd are below their detection limits.

Ag is low in the Waiorongomai tetrahedrite (0.13 wt. %) and Tui Mine tennantite (0.11 wt. %) but between 0.90 and 3.94 wt. % in other samples. Wu & Peterson (1977) considered that the silver content of tetrahedrite is related to the Sb/As ratio (because Sb rich tetrahedrites can accommodate more silver in their crystal structure than Sb poor tetrahedrites) but for any given Sb/As ratio the silver content is also a function of the $a\text{Ag}^+/a\text{Cu}^+$ activity ratio in the hydrothermal fluids. The former relationship is observed between the tetrahedrite and tennantite of Tui Mine and Robson's Whangapoua tetrahedrite analyses but not over all the samples listed in Table 5-10. Apparently low Ag concentrations in the Waiorongomai and

TABLE 5-10: Electron microprobe analyses of tetrahydrites made during this study (14058, Tui Mine; 13979, Waiorongomai) and by Merchant (1978) from Thames and Robson (1979) from Whangapoua.

Analyses	Tui Mine				Waiorongomai				Thames (Merchant)				Whangapoua			
	14058				13979				1978 pl29)				(Robson 1979 pl15)			
	(Tui 15)				(Willc)				Australasian				2 Analyses of			
Td ₉₅	Td ₁				Detection				Au 28963				sample PS 31427			
	6	2	4	Limits	6	2	4	Limits	4	1			4	1		
Cu	36.25	42.79	39.31	0.06	Cu	44.9	44.5	40.4	36.19	Cu			40.4	36.19	Cu	
S	24.23	27.70	25.33	0.05	S	22.7	24.3	25.7	25.80	S			25.7	25.80	S	
Sb	29.15	0.27	21.13	0.08	Sb	19.5	19.3	21.5	26.31	Sb			21.5	26.31	Sb	
As	1.01	19.17	6.52	0.08	As	3.5	0.0	6.2	0.00	As			6.2	0.00	As	
Zn	4.87	6.77	6.22	0.05	Zn	5.2	5.6	n.a.	n.a.	Zn			n.a.	n.a.	Zn	
Fe	2.47	2.39	1.51	0.04	Fe	2.1	2.6	4.3	6.15	Fe			4.3	6.15	Fe	
Ag	2.36	0.11	0.13	0.10	Ag	2.4	0.9	1.7	3.94	Ag			1.7	3.94	Ag	
Ni	0.02	0.00	0.02	0.04												
Mn	0.00	0.00	0.00	0.03												
Cd	0.03	0.07	0.06	0.08												
Total	100.39	99.27	100.23		Total	100.3	97.2	97.9	98.39	Total			97.9	98.39	Total	
Td	95	1	67		Td	77	100	68	100	Td			68	100	Td	
Zn/Fe	2	2.8	4.1		Zn/Fe	2.5	2.1	-	-	Zn/Fe			-	-	Zn/Fe	

Garbo Mine (Thames) tetrahedrites may be related to the fluid chemistry.

True argentian tetrahedrite or freibergite occurs at Te Ahumata (Ag ranged between 13.8 and 20.7 wt. % in 7 analyses reported by Erceg, 1981) and Whangapoua (Ag ranged between 15.7 and 17.0 wt. % in 5 analyses by Robson, 1979).

GEO THERMOMETRY

Tetrahedrite - Tennantite/Enargite

- Famatinite Geothermometer

Feiss (1974) proposed a geothermometer based on phase relations within the tetrahedrite - tennantite/enargite - famatinite system (Fig. 5-1). The compositions of tetrahedrite and enargite from the Australasian mine reported by Merchant (1978), equivalent to tn 23 (average)* and en 91 (single analysis) respectively, are plotted in Fig. 5-1. Robson's (1979) tetrahedrite and famatinite analyses from the Whangapoua mineralisation are not plotted because the famatinite has a composition of en 0 and is therefore not suitable for geothermometry (c.f. Fig. 5-1).

Although experimental calibration of the system is presently absent below 390°C (Fig. 5-1), Feiss (1974) mentioned a tetrahedrite - enargite pair (tn 19 - en 96 respectively) from Julcani (Peru) for which a sulphur isotope temperature of 325°C was tentatively suggested. Comparison of the position of this pair and that of the Thames tetrahedrite - enargite in Fig. 5-1 suggests that the Thames pair was probably also deposited at a temperature around 325°C or perhaps slightly higher (330 - 340°C ?).

Minor Element Geothermometry

Bethke & Barton (1971) suggested geothermometers based on the partitioning of Cd, Mn and Se between coexisting sphalerite and galena. Because the concentrations of these elements are generally low in galena (e.g. galenas analysed by Nash [1975] and Urabe [1977] had less than 100 ppm Cd; 220 ppm Mn and 50 ppm Se) they must be analysed by some method with a higher sensitivity than EPMA (e.g. AAS).

Although such analyses were not made here, several sphalerite and galena pairs from Tui Mine were analysed using wet chemical methods by Weissberg and others (Dr. B.G. Weissberg pers. comm.) but the results (unavailable)

* Footnote: tn values are adopted in this section to describe the composition of tetrahedrites in order to conform with their usage by Feiss (1974) $tn_y = 100 - Td_z$ (5-3)

Figure 5-1: Tetrahedrite-tennantite and enargite-famatinite geothermometer (after Feiss, 1974). The 325°C point is based on a sulphur isotope temperature of a tetrahedrite-enargite pair (tn 19-en 96 respectively) from Julcani (Peru). Tetrahedrite and enargite from the Australasian Mine at Thames, analysed by Merchant, plot at 23 mole % tn - 91 mole % en and indicate a temperature of approximately 330°C.

gave conflicting temperatures. Merchant (1978) however, reported a temperature of $330 \pm 15^{\circ}\text{C}$ for manganese partitioning between sphalerite and galena from his "Lead - Zinc" association (location of samples and analytical method were not stated). Cadmium partitioning gave temperatures around 445°C which Merchant considered unrealistic.

CHAPTER 6

FLUID INCLUSION MORPHOLOGY, FILLING TEMPERATURE,

FREEZING TEMPERATURE AND SALINITY

INTRODUCTION

The origin of fluid inclusions and the theories and assumptions used in fluid inclusion research are discussed in several review papers by Roedder (1962, 1967, 1972, 1976 and 1979).

Optical examination of fluid inclusions requires the preparation of thin transparent plates of suitable minerals. In this study mainly quartz and calcite were used although a few samples of barite and sphalerite were also analysed. The preparation techniques are detailed in Appendix III.

The inclusions studied contained liquid, vapour and rarely, solid phases. Three types were recognised on the basis of the proportion of their volume occupied by the vapour phase: normal < 40% < vapour rich < 90% < vapour filled.

Primary and secondary fluid inclusions were identified by the criteria suggested by Roedder (1976). They were present in most samples analysed. Pseudosecondary inclusions were not differentiated from secondary inclusions.

Quartz was found to be the most suitable mineral for fluid inclusion studies with most samples containing primary inclusions. Calcite, although easily prepared for analysis, was generally found to contain a high proportion of secondary inclusions. Primary inclusions were rare in samples of sphalerite studied, although secondary inclusions were abundant, hence few results are presented from sphalerite samples. Barite samples were slightly better than sphalerite and their ease of preparation meant that large numbers of plates could be checked for selection of the few primary inclusions analysed.

During the course of this thesis the writer also investigated fluid inclusions in samples of quartz and calcite from some New Zealand and overseas geothermal fields, under contract to DSIR (reported in Christie, 1980). In terms of size, shape, general occurrence, filling temperature, freezing temperature and composition, the fluid inclusions in the geothermal samples were very similar to those in much of the material studied from the Hauraki Gold - Silver Province.

Figure 6-1: A zone of primary vapour filled inclusions, with negative crystal shape, in Stage 3 quartz (sample 13922) of the Silver Queen Vein, Maratoto. 63X.

Figure 6-2: A solitary primary liquid-vapour inclusion, with irregular shape, in Stage 2 quartz (sample 14064) from the Champion Vein, Tui Mine. 160X.

PRIMARY INCLUSIONS

Introduction

The primary inclusions studied range in size from sub-microscopic to 2 mm. They occupy cavities varying from perfect negative crystals (Fig. 6-1) to irregular shapes (Fig. 6-2). Some are solitary (Fig. 6-2), whereas others are aligned in groups along growth zones (Figs 6-1, 6-3 and 6-4).

The quantity and average size of primary inclusions in samples varies geographically (Table 6-1). Material from Coromandel, Waihi and Karangahake was found to be particularly difficult to use, as the preparation of large numbers of plates was required to find only a few small primary inclusions. Some samples were abandoned altogether. In contrast, practically all samples examined from Broken Hills and Neavesville (rhyolite host rock section) contained some primary inclusions and many contained "text book" specimens up to 2mm long. This phenomenon was not related to crystal size and appears not to be directly related to depth of formation. However, fluid inclusion formation is probably favoured by variations in the rate of crystal growth and the presence of suspended particles in the fluid, factors which are probably in turn related to the flow rate of the hydrothermal fluid. Some of the largest fluid inclusions (in Broken Hills and Neavesville samples) were formed under boiling conditions (discussed later) indicating that the influence of vapour bubbles and possibly turbulence may also induce fluid inclusion formation.

Vapour Rich and Vapour Filled Inclusions

The samples containing vapour-rich and vapour filled inclusions are noted in Table 6-2. Examples of vapour rich inclusions are illustrated in Figs 6-5 and 6-6, whereas vapour filled inclusions are shown in Figs 6-1, 6-7 and 6-8. These inclusions trapped quantities of vapour along with liquid indicating that the hydrothermal fluid in which the host mineral grew was boiling.

Vapour rich and vapour filled inclusions range in shape from irregular to negative crystal and some examples of elongate inclusions, similar to "cylindrical" inclusions noted by Kamilli & Ohmoto (1977), occur.

Samples containing vapour rich and/or vapour filled inclusions predominantly contain normal and vapour filled inclusion types, vapour rich types are rare and absent altogether from samples 13943 (N 39) and 14079 (Wi 41). The distinction of sample 13943 may not be justified because the

Figure 6-3: Primary liquid-vapour inclusions in "V" growth zones near the tip of a euhedral quartz crystal from the Champion Vein (Stage 2), Tui Mine. (Sample 14056). X63.

Figure 6-4: Primary liquid-vapour inclusions in "V" growth zones near the tip of a euhedral quartz crystal from the Champion Vein (Stage 2), Tui Mine. (sample 14056). 40X.

TABLE 6-1: Geographical variation of primary fluid inclusion development.

Increasing quantity and average size of primary fluid inclusion	(i)	Broken Hills and Neavesville (rhyolite host rock)
	(ii)	Miners Head, Komata and Waitekauri
	(iii)	Neavesville (andesite host rock), Maratoto, Tui Mine and Waiorongomai
	(iv)	Te Ahumata and Paritu
	(v)	Coromandel (Tokatea and Petote Stream area) Waihi and Karangahake

TABLE 6-2: A summary of the filling temperature and apparent salinity results for primary fluid inclusions (histograms are presented in Appendix I whereas the individual measurements are listed in Appendix III). Depositional temperatures were derived from the filling temperatures by adding a pressure-salinity correction to the "peak" value of the filling temperature distributions plotted as histograms (Appendix I).

SAMPLE NUMBER	V.U.W. No.	Field No.	Mineral ¹	DESCRIPTION		Stage	Associated Mineral Assemblage	FILLING TEMPERATURES			Assigned T°C	m ³	APPARENT SALINITY		NOTES		
				Location				range T°C	Peak	Correction			range eq wt % NaCl	Av.	*4	*5	*6
Miners Head	13965	MH1	q	Mine			Porphyry	365 - 402	390	30	420	26	4.5 - 14.8	10.3			S
Te Ahumata	13952	GB10	q	Sunbeam		1	2	197 - 262	(230)	< 5	240	12	0.5 - 0.9	0.7			
	13953	GB9	q	Sunbeam		1	2	214 - 265	(230)	< 5	240	6	1.1 - 1.7	1.3			
	13954	GB12	q	Barrier Reefs		2b	10	180 - 254	(220)	< 5	230						
	13971	DC12	q	Doctors Creek		2	4	262 - 346	300	15	310	1		1.9			
Northern Colville Peninsula. Kusotunu	13972	SW4	q	Sorry Mary Stream		2	4	254 - 302	280	15	290	2	1.2 - 1.7	2.1			
	14007	K3	q	Waitaia Mine		2	2	192 - 250	(250)	< 10	260						
	14008	K4	q	Waitaia Mine		2	2	184 - 249	(240)	< 10	250						
	14009	GL1	q	Golden Link Mine			?	224 - 291	260	< 10	270						
Tokatea	13955	RO1	q	Royal Oak 7 L		(7)	(7)	183 - 239	220	5	230	1		0.9			
	13956	RO7	q	Royal Oak Mine			(7)	187 - 277	(220)	5	230						
	13957	TK2	q(a)	Tokatea Big Reef			(4)	176 - 246	(230)	5	230	7	1.2 - 2.8	2.3			
	13958	BO2	q	Buffalo Mine			(4)	244 - 263	250	10	260						
Petote Stream Area	13980	AS1	q	Aitken Stream		1	4	207 - 301	(280)	10	290						
	13991	PS4	c	Chalcopryrite Lode		1	4	183 - 261	250	10	260	2	1.6 - 2.4	2.0			
	13993	PS7	c	Chalcopryrite Lode		1	4	180 - 249	210	10	220						
	13995	PS10	q	Chalcopryrite Lode		1	4	254 - 331	(280)	10	290	11	1.3 - 2.2	1.6			S
	13996	PS14a	q	Chalcopryrite Lode		1	4	216 - 293	(280)	10	290						
	13997	PS14b	q	Chalcopryrite Lode		1	4	254 - 303	280	10	290						
	14005	PS24	q	Galena Lode		1	4	244 - 271	260	10	270	2	1.6 - 3.0	2.3			
	14006	PS26	q	Petote Stream North		1	4	215 - 322	300	10	310	13	1.3 - 3.5	2.6			S
Whangapoua Broken Hills	13910	WG9	q	Waingaro Stream		4	10	190	190	0	190				V		
	13950	TR9	q	2 Level		1	(9)	200 - 274	240	0	240	11	0.6 - 1.3	0.8	V		
	13951	TR6	q	2 Level		1	(9)	203 - 293	(230)	0	230	6	0.8 - 2.2	1.3	V		6-8

SAMPLE NUMBER	DESCRIPTION		Mineral Assemblage	FILLING TEMPERATURES			Assigned T °C	n ³	APPARENT SALINITY		NOTES		
	V.U.M. No.	Field No. Mineral ¹	Location	Stage	range T °C	Peak	Correction		range eq wt % NaCl	Av.	*4	*5	*6
Neavesville	13940	M26	q	Champion adit 4		188 - 254	210	< 5					
	13941	N14	q	Ajax 2 Level		232 - 254	250	5	0.5 - 1.5	0.7			
	13942	N42	q	Ajax 1 Level		193 - 274	250	0	0.7 - 0.8	0.8	V		6-7
	13943	N39	q	Birds		221 - 224	223	0			V		
	13944	N47	q	Graces open cut		190 - 249	200	0	0.2 - 0.7	0.5	V		
	13945	N28-30	q	Graces adit		126 - 283	220	0	0.7 - 0.8	0.8	V		
	13946	N46	q	Golden Arrow		206 - 222	210	0	0.7 - 0.8	0.7	V		6-6
	13916	CNS	q	Camoola 3 L	2c	220 - 290	260	10	0.9	0.9		S	
	13917	M1q	q	Silver Queen 5 L	2d	255 - 298	260	10	0.2 - 1.1	0.7			
	"	M1c	c	" " "	2d	195 - 306	260	10	0.2 - 0.3	0.3			
Maratoto	13918	M2c	c	Camoola Vein	1	230 - 292	260	10	1.9 - 2.8	2.2			6-11
	13919	M2q	q	Camoola 3 L	3	202 - 269	230	0	0.2 - 0.9	0.6	V		
	13920	M3	q	Silver Queen 5 L	2c	230 - 323	270	10	0.2 - 1.3	0.6			
	13921	M4	q	Camoola 3 L	2a	215 - 290	250	10	0.2 - 1.3	0.8		S	
	13922	M5	q	Silver Queen 5 L	3	215 - 300	260	0	0.2 - 3.3	1.4	V	rare S 6-1, 6-9, 6-10	
	13923	M6	q	Camoola 3 L	3	230 - 292	270	10	0.2 - 1.9	1.1		S	
	13924	M8b (1)	q	Camoola 3 L	2a	275 - 295	250	10	0.3	0.3			
		(2)	q	"	"	228 - 285	250	10	0.2 - 2.0	0.6			
		(3)	q	"	"	225 - 267	290	10					
	13925	M9	q	Silver Queen	2a	258 - 320	290	0	0.5	0.5	V		
	13926	M10	q	Silver Queen 3 L	3	172 - 290	270	10	0.9	0.9		S	
	13927	M11	q	Silver Queen	2d	230 - 275	260	10	0.2	0.2		S	
	13928	M19	q	Camoola 3 L	3	239 - 315	270	10	0.2	0.2		S	
	13929	M28	c	Camoola 3 L	1	225 - 281	250	10	0.5 - 0.7	0.6			
	13930	M8a	q	Camoola 3 L	3	240 - 287	260	10	0.5 - 0.9	0.6			
	13935	M22	q	Camoola 3 L	3	224 - 291	250	0			V	rare S	

TABLE 6-2: (Continued)

TABLE 6-2; (Continued)															
SAMPLE NUMBER	DESCRIPTION		Stage	Mineral Assemblage	n ³	FILLING TEMPERATURES			Assigned T°C	n ³	APPARENT SALINITY		NOTES		
	V.U.W. No.	Field No. Mineral* ¹				Location	range T°C	Peak			Correction	range eq wt % NaCl	AV.	#4	#5
Komata	13947	Km 15q	q	Komata 8 L	(7)	33	144 - 297	(220)	0	220	3	0.8 - 3.0	1.8	V	6-5
	13947	Km 15c	q	"	(7)	38	215 - 273	250	5	260	9	1.6 - 2.8	1.9		
	13948	Km 18q	q	"	(7)	12	219 - 261	(250)	5	250	7	1.0 - 2.8	1.4		
	13948	Km 18c	c	"	(7)	38	232 - 284	260	5	270	2	0.9 - 3.0	2.0		
	13949	Km10	q	"	(7)	28	231 - 275	(250)	5	250					
Waitekauri	14010	WK1	q	Jubilee low level	3	48	236 - 290	270	10	280	1	0.8	0.8	S	
	14011	WK2	q	"	3	38	234 - 281	260	10	270	2	0.6 - 0.8	0.7		
	14012	WK3	q	"	3	47	227 - 312	260	10	270	10	0.9 - 3.2	1.7		
	14013	WK4	q	Maoriland Vein	(4)	42	171 - 286	(260)	10	270	8	0.8 - 1.6	0.9		
	14014	WK5	q	Jubilee low level	1	59	206 - 272	260	10	270	12	0.8 - 1.9	1.4	S	6-13
Waihi	13919	Wh24	q	Martha 2 Level	(7)	14	158 - 200	(190)	<5	190					
	14030	GJ1	c	Grand Junction	(7)	20	212 - 254	240	10	250	4	1.3 - 1.9	1.6		
	14031	GJ2	c	Grand Junction	(7)	14	169 - 219	(210)	10	220	1	1.6	1.6		
	14032	GJ3	c	Grand Junction	(7)	4	229 - 244	240	10	250					
	14035	Wh4	q	No.5 shaft dump	(7)	3	229	229	10	240	9	1.0 - 5.2	2.8		
	14036	Wh8	q	Martha 3 Level	(7)	1	274	274	<5	280					
	14037	Wh10	q	Martha Vein	(7)	2	199 - 204	202	<5	210		2.9	2.9		
	14042	Wh32	q(a)	Martha Mine	(7)	18	185 - 276	230	10	240	6	2.2 - 3.9			
	14044	Wh40	c	Martha 5 L	(7)	6	159 - 199	180	5	190	3	0.7 - 1.2	1.0		
	14045	Wh41	q(a)	Empire Vein 12 L	(7)	5	254 - 271	260	0	260	7	3.7 - 3.9	3.7	V	
Karangahake	14051	Wh49	q	Martha Mine	5	36	177 - 296	270	0	270				V?	
	74/7/10	Wh46	q(a)	Martha Mine	(7)	23	213 - 273	230	0	230				V?	
	14021	TL2	q	Taslisman 11 L	(7)	21	244 - 283	260	<10	270	3	2.2 - 2.4	2.3		
	14022	TL8	q	Talisman 8 L	(7)	35	224 - 257	230	<10	230	7	2.7	2.7		
	14029	MM2	q	Marmion Extended	(7)	25	195 - 289	250	<10	260					
Tui Mine	14053	Tui 3	q	Champion 5 L	2	3	271 - 285	280	10	290					
	14055	Tui 12	q	"	2	25	270 - 293	280	10	290	6	4.0 - 5.4	4.6		
	14056	Tui 13	q	"	2	58	261 - 303	290	10	300	12	0.1 - 1.1	0.7	S	6-3, 6-4

SAMPLE NUMBER	V.U.W. No.	Field No.	Mineral ¹	DESCRIPTION		Mineral Assemblage	FILLING TEMPERATURES			Assigned T°C	n ³	APPARENT SALINITY		NOTES
				Location	Stage		range T°C	Peak	Correction			range eq wt % NaCl	Av.	
Tui Mine (Cont'd)	14060	Tui 18	q	Ruakaka 3 L	2	4	283 - 295	290	10	300	13			
	14061	Tui 19	q	Champion 5 L	2	4	249 - 271	260	10	270	27			
	14062	Tui 20	q	Ruakaka 2 L	2	4	232 - 293	280	10	290	29	2.4 - 6.1	4.2	
	14063	Tui 21	s	Champion 5 L	2	4	273 - 284	280	10	290	6			
	14064	Tui 22	q	" "	2	4	255 - 308	280	10	290	87			S 6-2
	14065	Tui 23	q	" "	2	4	273 - 355	300	10	310	41			
	14067	Tui 26	b	Ruakaka	3	11	132 - 288	(230)	10	240	24			
	14068	Tui 28	q	Champion 5 L	2	4	266 - 327	280	10	290	72			S
Waiorongomai	13914	W100	q		2	5	253 - 303	270	100	280	14	0.4 - 5.5	1.5	S 6-16
	14070	W13	q	Moa Vein	2	(4)	213 - 301	270	10	270	17			V
	14070	W13	b	" "	3	11	98 - 128	110	0	110	6			V
	14074	W125	q	No.1 Vein	2	4	232 - 274	270	<10	280	39	0.7 - 2.8	2.2	
	14081	W145	q	May Queen 3 L	2	4	183 - 271	240	<10	250	40	0.9	0.9	S
	14084	W156	q	Welcome Vein	2	4	214 - 288	240	<10	250	37			
	14087	W164	q	Main Vein	2	4	236 - 283	260	<10	250	51			S 6-12
	14093	W187	q	New Find	2	(4)	234 - 274	(260)	0	260	25			S
	14094	W189	q	Welcome Vein	2	(4)	236 - 266	250	<10	260	11			
	14099	W197	b	Welcome Vein	3	11	98 - 196	110	<10	120	5	1.3 - 2.2	1.7	S

¹ Minerals: b = barite, c = calcite, q = quartz and s = sphalerite

² Associated mineral assemblage: see Table 4-5. Numbers in brackets indicate that sample was not visibly in physical contact with metalliferous minerals of the association.

³ n = number of measurements

⁴ V = vapour rich and/or vapour filled fluid inclusions present in sample

⁵ S = fibrous solid phases present in some fluid inclusions of the sample

⁶ number of figure showing photographs of fluid inclusions from the specific sample

Figure 6-5: A solitary vapour rich primary inclusion in quartz of sample 13947 from 8 level of the Komata Mine. 250X.

Figure 6-6: A vapour rich primary inclusion in quartz of sample 13946 from the Golden Arrow Opencut, Neavesville. 160X.

Figure 6-7: Vapour filled primary inclusions in quartz of sample 13942 from Ajax 1 level, Neavesville. 63X.

Figure 6-8: Vapour filled primary inclusions in quartz of sample 13950 from 2 level Broken Hills Mine. 160X.

Figure 6-9: Elongate (-cylindrical) primary fluid inclusions in quartz of sample 13922 from the Silver Queen Vein (Stage 3) Maratoto. 160X.

Figure 6-10: Elongate (-cylindrical) primary fluid inclusions in a different part of the same sample (13922) as shown in Fig. 6-9. 63X.

number of plates prepared and the number of inclusions checked were small. All the vapour filled inclusions noted in sample 14079 occur along a single plane separate from the normal type inclusions. Therefore these vapour filled inclusions may record only a single short boiling episode during the quartz deposition.

Zones of Elongate Inclusions

Zones of regularly shaped inclusions, mostly elongate, occur in large vug quartz crystals from Maratoto (samples 13919 and 13922). The elongate inclusions are orientated parallel to each other (Figs 6-9 and 6-10) and a set of crystal faces. One group occurs in a plane parallel to a crystal face (Fig. 6-11), although the elongate inclusions themselves are orientated parallel to a different set of crystal faces. Other groups occur in non-planar masses (Figs 6-9 and 6-10).

Most of the inclusions are normal types but a few vapour rich and vapour filled types also occur. The normal types have similar filling temperatures but contain liquid with a different (very low) apparent salinity to irregular shaped primary inclusions occurring outside the groups.

Solids

Many inclusions contain minute specks of a clear solid (generally spindle shaped) adhering to the vapour bubble, and therefore generally not noticed, at room temperature. On heating, these particles begin bouncing off the bubble into the liquid, increasing in frequency with increasing temperature. When the bubble disappears at the filling temperature the bouncing motion ceases and the particles adhere to the inclusion walls or float gently around in the liquid. Because they do not dissolve during filling temperature experiments these particles are probably not daughter minerals but may have been trapped, along with the liquid, during inclusion growth.

Inclusions in a few samples (Table 6-2) contain a highly birefringent fibrous mineral (Figs 6-12 and 6-13). There is a considerable variation in the particle/inclusion fluid volume ratio from one inclusion to another and in many (most?) primary inclusions of these samples the mineral is absent altogether. The mineral remains unchanged during filling temperature experiments.

During contract work on modern geothermal samples for DSIR the writer noted similar occurrences in samples from Broadlands drill holes (Figs 6-14 and 6-15). In one sample from Broadlands an inclusion of the mineral

Figure 6-11: A zone of elongate inclusions orientated parallel to a crystal face (both horizontal) and cut by a zone of secondary inclusions (vertical in photograph). The long axes of the elongate inclusions are orientated to a different crystal face from that paralleled by the overall zone. Quartz of sample 13919; Stage 3 Camoola Vein, Maratoto. 40X.

Figure 6-12: Fibrous solid (sericite?) in a primary liquid-vapour inclusion of sample 14084 (quartz) from the Welcome Vein, Waiorongomai. 630X.

Figure 6-13: Fibrous solid phase in primary liquid-vapour inclusions of sample 14014 (quartz) from Jubilee Low Level, Waitekauri. 160X.

Figure 6-14: Fibrous solid in a liquid-vapour inclusion in quartz from a depth of 680m in Broadlands drillhole 25. 250X.

Figure 6-15: Fibrous minerals in quartz (arrowed) and fluid inclusions (almost filling inclusion near left edge of photograph) in a sample from a depth of 896m in Broadlands drillhole 7. 250X.

Figure 6-16: Hexagonal solid phase in a primary liquid-vapour inclusion in quartz of sample 13914 from Colonist Smithy level, Waiorongomai. 250X.

occurs in quartz between two fluid inclusions also containing the mineral (Fig. 6-15). This occurrence suggests that solid inclusions were trapped from the hydrothermal fluid during quartz growth and in most cases acted as nuclei for trapping fluid inclusions. An included origin for the particles is consistent with the observed wide variation of particle/inclusion fluid volume ratio which would be difficult to rationalise if the particles were daughter minerals.

The appearance of the fibrous mineral is very similar to crystals of dawsonite ($\text{NaAlCO}_3[\text{OH}]_2$) described from fluid inclusions in a number of ore deposits by Coveney & Kelly (1971), who considered them to be a daughter mineral. They noted that the inclusions containing dawsonite were of low salinity (3.5 eq. wt. % NaCl) and CO_2 rich, generally containing small quantities of liquid CO_2 . Although the inclusions of samples studied here are of similar salinity (see later section), liquid CO_2 has not been identified and water and gas extraction experiments with some samples indicate low CO_2 contents of approximately 1 mole % (see next chapter). Present day geothermal waters in the Broadlands field have CO_2 concentrations of approximately 0.9 mole %.

Kamilli & Ohmoto (1977) reported the occurrence of a similar fibrous mineral in fluid inclusions from the Finlandia Vein, Central Peru. They visually identified the mineral as dawsonite but found no more than 0.5 mole % CO_2 in inclusions of the dawsonite-bearing samples. This occurrence of dawsonite and the fibrous mineral described in this study are similar. Kamilli & Ohmoto note that "the dawsonite/inclusion fluid volume ratio varies markedly in some samples. In apparently cogenetic groups of inclusions with virtually the same salinities and homogenisation temperatures, dawsonite daughters can be totally absent or completely fill the inclusion cavity".

Because of the low CO_2 concentration, variable particle/inclusion fluid volume ratio, and solid inclusion occurrence in quartz of the Broadlands sample, the fibrous particles in fluid inclusions from the Hauraki Gold-Silver Province, Broadlands geothermal field and Finlandia vein are almost certainly not dawsonite but are probably a clay mineral (e.g. sericite), included during crystal growth, which has acted as a nucleus for fluid inclusion formation.

A clear hexagonal crystal is present in a single inclusion of sample 14101 (Wi 100) from Waiorongomai (Fig. 6-16). The crystal was observed to change position between successive filling temperature measurements although no changes in size or shape occurred.

Figure 6-17: A zone of secondary fluid inclusions (most vapour filled) in barite of sample 14099 from the Welcome Vein, Waiorongomai. 160X.

Figure 6-18: A zone of secondary fluid inclusions (centre of photograph) in quartz of sample 13922, Silver Queen Vein (Stage 3), Maratoto. 40X.

SECONDARY INCLUSIONS

Inclusions occurring in curved planes, often cross-cutting zones of primary inclusions, are regarded as secondary (Figs 6-17 and 6-18). They are generally small (less than 50 micrometres) but some large secondary inclusions with an "outline" (writers term) appearance occur in clear zones of some crystals (Fig. 6-19). The latter are tabular in shape and occur together in planar zones.

Some plates of calcite were found to contain thousands of small secondary inclusions with no apparent systematic orientation. Similarly, large numbers of tiny secondary inclusions occurred near the base of vug quartz crystals giving this end of the crystals a milky appearance in hand specimen.

FILLING (HOMOGENISATION) TEMPERATURE

It is generally accepted that the most accurate method of obtaining the temperature of entrapment of fluid inclusions is by the visual observation of their filling or liquid - vapour homogenisation temperature (c.f. Roedder, 1976;1979). This parameter is measured by heating the sample in a microscope heating stage and observing the expansion of the major phase (liquid in normal type inclusions and usually vapour in vapour rich types). The temperature at which the major phase eventually fills the inclusion after disappearance of the minor phase (vapour in normal type inclusions and usually liquid in vapour rich types) is the filling or homogenisation temperature.

Filling temperatures of vapour rich inclusions are difficult to measure because of the uncertainty in establishing the point at which the last film of liquid on the inclusion walls disappears. Because of this the writer was unable to determine homogenisation temperatures in the vapour phase of any of the vapour rich fluid inclusions studied, and all filling temperatures quoted are thus of homogenisations in the liquid phase.

Results of fluid inclusion filling temperature measurements made during this study are presented as histograms in Appendix I and summarised in Table 6-2 (the individual measurements are tabulated in Appendix III, together with a description of the equipment used).

As a group, primary fluid inclusions have higher filling temperatures than secondary inclusions, although individual secondary inclusions

Figure 6-19: Secondary liquid-vapour inclusions with an "outline" appearance.
Sample 13949 (quartz) from 8 level of the Komata Mine. 160X.

Maratoto, c.f. Appendix III) have narrow secondary filling temperature ranges with modes only 10 or 20°C lower than the primary inclusions. Many secondary inclusions with filling temperatures in the primary range may be pseudosecondary inclusions.

TEMPERATURE OF ENTRAPMENT: BOILING ENVIRONMENT

Filling temperatures of inclusions trapped on the boiling curve need no correction for pressure, however the relationship between temperature of entrapment and filling temperature depends on the conditions of trapping.

Kamilli & Ohmoto (1977) suggested that minerals growing in a boiling hydrothermal fluid may trap, in separate inclusions, either random proportions of liquid and vapour (situation A) or 100% liquid in some inclusions and 100% vapour in others (situation B). (A) results in a population of inclusions with a wide range of liquid to vapour ratios, whereas (B) results in two distinct populations of inclusions, one with a high proportion of vapour and the other containing a high proportion of liquid. Filling temperature measurements on the first set of inclusions will result in an anomalously high temperature range; the lowest temperature being closest to the temperature of entrapment. Filling temperatures of all inclusions in (B) will be temperatures of entrapment (vapour rich inclusions will be homogenised in the vapour phase).

The occurrence of apparently normal type inclusions, vapour filled inclusions and a few inclusions with intermediate liquid to vapour ratios (vapour rich types) in the samples considered here, suggests that the inclusions were formed under situation (A). Kamilli & Ohmoto suggest taking the lowest filling temperature as the temperature of entrapment of these samples, however the peak of the filling temperature histogram (Appendix I) is used here for the following reasons:

1. filling temperatures were determined only from inclusions that looked like the normal type,
2. inclusions with intermediate liquid/vapour ratios (vapour rich types) are rare,
3. in all samples except 13922 (M 5) and 13947 quartz (Km 15q) the scatter of results about the mode of the histogram is not significantly greater than in filling temperature histograms compiled from samples formed from non-boiling fluids,
- and 4. in some samples using the lowest filling temperature would produce inconsistent results with samples formed under non-boiling conditions from the same area.

The wide filling temperature range recorded from sample 13922 (M 5) is anomalous whichever situation is chosen. The wide range of filling

temperatures is difficult to rationalise as a normal type inclusion distribution and is suggestive of case (A) but the lowest filling temperature is inconsistent with bracketing samples in the paragenesis.

The depositional temperatures assigned to samples formed under boiling conditions are listed in Table 6-2.

TEMPERATURE OF ENTRAPMENT: NON-BOILING ENVIRONMENT

In samples deposited under non-boiling conditions the temperature of entrapment of the inclusions is considered to be the peak ($\approx$ mode) of the filling temperature histogram (Appendix I) with the addition of corrections for pressure and salinity (see below). The spread of values about the peak is considered representative of the sample and only partially due to experimental error ($\pm 10^\circ\text{C}$). Although some thick plates were used, the thermal gradients introduced are not large enough to contribute significantly to some of the ranges of filling temperatures observed: some samples with very small filling temperature ranges were measured on thick plates, whereas others with large ranges were measured on thin plates. The wide temperature ranges may represent periodic temperature fluctuations in the hydrothermal fluid or reflect the proximity of depositional conditions to the boiling curve. Temperature changes between different growth zones could not be differentiated on the histograms.

The magnitude of the pressure correction depends on the depth of deposition and whether the load was hydrostatic or lithostatic. These aspects are discussed in Appendix I and the values estimated were used, together with the apparent salinity results (see later section) and data from Haas (1971) and Potter (1977), to derive the pressure-salinity corrections listed in Table 6-2. They have been added to the modes of the filling temperature histograms to give the temperatures of deposition also listed in Table 6-2.

DEPOSITIONAL TEMPERATURES OF SOME MINERAL ASSEMBLAGES

The temperature ranges of some of the epithermal mineral assemblages discussed in Chapter 4 are listed in Table 6-3. They were compiled by combining the assigned temperatures of deposition ($\pm 10^\circ\text{C}$) for the relevant samples listed in Table 6-2.

FREEZING TEMPERATURE

The freezing temperatures of inclusion fluids are measured in a microscope freezing stage. Because of problems of metastability, the liquid in fluid inclusions must be supercooled by generally 30°C below

TABLE 6-3: Predominant temperatures and apparent salinities during deposition of some epithermal vein mineral assemblages as indicated by the fluid inclusion data. The values are a compilation of the assigned depositional temperature and average apparent salinity values presented in Table 6-2.

Epithermal vein Mineral assemblage	Depositional Temperature (°C)		Apparent Salinity (eq. wt. % NaCl)	
	Range	Average	Range	Average
2. Early pyrite	240 - 260	250	0.6 - 2.2	1.2
4. Py-sp-gn-cp assemblage	220 - 310	280	0.7 - 4.6	2.0
5. Py-sp-gn-cp-el-Ag mineral assemblage	230 - 290	270	0.2 - 1.4	0.8
6. Py-acanthite-el assemblage	190 - 280	240	0.5 - 3.7	1.7
9. Au-Ag sulphosalt mineral assemblage	230 - 240	240		
10. Stibnite	190 - 230	210		
11. Barite	110 - 240	160		

the ice melting temperature to achieve ice nucleation. The freezing temperature is recorded as a "last point of ice melting" temperature, measured by warming the supercooled inclusion, melting the ice and recording the temperature at which the last particle of ice melts.

The methods used here, results and details of a freezing stage constructed by the Victoria University Workshop are given in Appendix III.

No evidence for the formation of liquid CO_2 , CO_2 hydrates or NaCl hydrates was noted during the freezing temperature experiments.

APPARENT SALINITY

The freezing temperature results were converted to salinity values by using the equation in Potter *et al* (1978). They are presented as histograms in Appendix I and summarised in Table 6-2 (the individual values are tabulated in Appendix III).

The salinity ranges of some of the epithermal mineral assemblages discussed in Chapter 4 are listed in Table 6-3.

Dissolved CO_2 also depresses the freezing point of solutions, and its effects are discussed in Chapter 7. No corrections for dissolved CO_2 have been made and therefore the salinity results presented here are apparent salinities only.

The histograms of primary fluid inclusion salinities presented in Appendix I give the impression of wide ranges of salinity in the original hydrothermal fluid. Although factors such as experimental error, variable quantities of CO_2 and low maximum salinity probably account for this spread in salinity values for most samples, and trapping of boiling fluid in some others, several samples have high maximum salinity and the spread in their values might reflect changes in the original mineralising fluid. Variation in some aspects of fluid composition during individual crystal growth are indicated at Broadlands by the changing oxygen isotope composition described by Blattner (1975). Salinities may also vary.

Secondary inclusions were found to generally have very low salinities compared to primary inclusions, with no measurable depression of freezing point in most samples. This eliminates the possibility of correlating secondary inclusions in samples early in the paragenetic sequence with primary inclusions later in the sequence.

CHAPTER 7

QUANTITATIVE ANALYSIS OF INCLUSION FLUIDS

INTRODUCTION

This chapter describes analyses of the dissolved salts and CO_2 present in fluid inclusions in samples of quartz and calcite from the epithermal deposits. The deuterium/hydrogen analyses of the inclusion water are described in Chapter 8.

The experimental procedure used generally follows the technique developed by Roedder *et al* (1963). The sample was crushed under vacuum to extract the water and CO_2 for quantitative and isotopic analysis. The crushed sample was removed from the vacuum line and leached with a solvent(s) to dissolve the inclusion salts. The leach was then chemically analysed and the concentrations of ions present proportioned back to an original fluid inclusion composition by using the measurement of the weight of fluid inclusion water extracted.

Two major sources of error occur in these types of analyses:

(a) contamination by solution of ions from the broken surfaces of the host mineral or from exposed minute solid inclusions in the host mineral, and (b) incomplete leaching due to adsorption of inclusion ions onto the large surface of the crushed sample.

These factors may be critical in analyses of dilute solutions yet they have received little attention in previous studies. They were investigated during this study by experimenting with different leaching methods and solutions. This led to the discovery of major contamination by solution of ions from apparently pure host minerals, a feature which has previously not been assessed.

THE CONCENTRATION OF CHLORIDE AND SOME CATIONS IN FLUID INCLUSIONS

Procedure and Results

The methods used, leach analyses and estimates of precision and accuracy are given in Appendix IV. The analyses, recalculated to apparent fluid inclusion liquid compositions, are listed in Table 7-1.

TABLE 7-1: Apparent fluid inclusion concentrations, in mg/kg (ppm), of some ions indicated by leach analyses. The concentrations in the different solutions listed for each element must be summed to give the total apparent concentration. Samples of quartz are grouped in Table 7-1A whereas samples of calcite are grouped in Table 7-1B.

Sample numbers suffixed with a, b, c and d indicate a series of samples separated according to the clarity of the crystals (a clearest), whereas the suffixes 1 and 2 indicate duplicate samples.

TABLE 7-1A Quartz samples

Solution	Tokatea Area			Petote Stream Area			Whangapona			Neavesville (A'jax)			Maratoto		
	13957 ₁ TK 2 (1)	13957 ₂ TK 2 (2)	13958 BO 2 ^a	13907 Hutt 2	13980 AS 1 ^a	13980 AS 1 ^c	13998 PS 15	14006 PS 26	13910 Wg 9	13939 N16	13941 ^a N14 ^a	13941 ^b N14 ^b	13941 ^c N14 ^c	13941 ^d N14 ^d	13919 M2 ^q
Na ⁺	A	3500	4400	3300	-	-	1300	3500	2000	-	-	580	440	500	1800
	B	1100	2400	-	-	-	470	8200	230	-	-	-	190	160	620
	C	3400	800	-	3700	6000	18	15000	64	1100	1000	-	-	-	620
K ⁺	A	-	1600	140	-	-	72	830	290	-	-	510	310	590	290
	B	-	1500	-	-	-	78	12000	130	-	-	-	310	530	180
	C	1600	430	-	180	450	32	150	29	3900	760	-	-	-	410
Ca ²⁺	A	-	150	3100	-	-	20	36000	620	-	-	85	n.d.	n.d.	4600
	B	-	7300	-	-	-	400	55000	2800	-	-	-	170	1900	9000
	C	820	n.d.	-	290	350	n.d.	110000	250	4700	1400	-	-	-	12000
Al ³⁺	A	-	460	28	-	-	46	140	n.a.	-	-	n.a.	n.d.	n.d.	n.a.
	B	-	n.d.	-	-	-	570	110	1300	-	-	-	390	470	n.a.
	C	170	3900	-	1300	1000	220	40000	260	6300	3000	-	-	-	2900
Mg ²⁺	A	-	82	34	-	-	18	460	45	-	-	16	n.d.	n.d.	410
	B	-	390	-	-	-	58	500	120	-	-	-	82	84	1200
	C	110	940	-	23	48	20	n.a.	30	320	14	-	-	-	5300
Li ⁺	A	-	450	350	-	-	160	270	170	-	-	26	25	23	35
	B	-	190	-	-	-	37	93	5	-	-	-	3	5	5
	C	120	37	-	440	320	n.d.	480	6	63	44	-	-	-	0.3
Zn ²⁺	A	-	41	n.a.	-	-	n.a.	330	n.a.	-	-	16	n.a.	n.a.	10
	B	-	28	-	-	-	n.a.	n.d.	n.a.	-	-	-	n.a.	n.a.	37
	C	n.a.	350	-	n.a.	n.a.	n.a.	890	n.a.	n.a.	n.a.	-	-	-	48
Rb ⁺	A	-	n.d.	n.a.	-	-	n.d.	n.d.	n.d.	-	-	n.a.	n.a.	n.a.	n.a.
	B	-	68	-	-	-	n.d.	20	n.d.	-	-	-	n.a.	n.a.	n.a.
	C	3.1	n.d.	-	1.2	1.4	n.d.	18	n.d.	28	n.a.	-	-	-	n.a.
Cs ⁺	A	-	n.a.	n.a.	-	-	n.d.	n.d.	n.d.	-	-	n.a.	n.a.	n.a.	n.a.
	B	-	n.a.	-	-	-	n.d.	n.d.	n.d.	-	-	-	n.a.	n.a.	n.a.
	C	3.1	n.a.	-	1.8	1.0	n.d.	29	n.d.	8.4	2.9	-	-	-	n.a.
Cl ⁻	A	-	6100	4000	-	-	1600	8900	3200	-	-	1000	1400	1600	6300
	B	-	n.d.	-	-	-	n.a.	n.d.	520	-	-	-	n.a.	n.a.	2300
	C	4600	1800	-	n.a.	n.a.	410	1300	n.d.	1100	890	-	-	-	3800

TABLE 7-1A Continued

Solution	Maratoto			Waitekauri		Waihi		Tui Mine				Wairongomui			Tokata Area		
	13928 ₁ M19 ₁	13928 ₂ M19 ₂	14013 WK4	14035 WH4	14037 ₁ WH10 ₁	14037 ₂ WH10 ₂	14054 _a Tui 6 _a	14054 _b Tui 6 _b	14056 Tui 13	14061 Tui 19 ₁	14061 ₂ Tui 19 ₂	14071 WH16	14090 WH167	14094 WH189	13958 BO ₂		
Na ⁺	{ A 920 B 220 C n.d.	{ A 1600 B 700 C 350	{ A 1100 B 300 C 600	{ A 1300 B 1500 C 45	{ A 2600 B 1600 C -	{ A 790 B 830 C -	{ A - B - C 5200	{ A - B - C 2900	{ A 2700 B 7300 C 5500	{ A 4100 B 6300 C 6800	{ A 2500 B 5000 C 4600	{ A - B - C 3500	{ A 1400 B 850 C n.d.	{ A 1000 B 1400 C 360	{ A1 3200 A2 32 A3 n.d.	Na ⁺	
K ⁺	{ A 610 B 640 C 180	{ A 630 B 650 C 280	{ A 400 B 490 C 520	{ A 560 B 200 C 18	{ A 4100 B 2500 C -	{ A 1300 B 1300 C -	{ A - B - C 1000	{ A - B - C 860	{ A 400 B 8500 C 3500	{ A 350 B 5000 C 2600	{ A 320 B 4400 C 1700	{ A - B - C 1100	{ A 270 B 47 C 190	{ A 68 B 11 C 120	{ A1 980 A2 n.d. A3 n.d.	K ⁺	
Ca ²⁺	{ A 1500 B 2600 C 5000	{ A 1500 B 1400 C 7300	{ A 950 B 1500 C 8000	{ A 56 B 2000 C 260	{ A n.d. B 3800 C -	{ A n.d. B 1200 C -	{ A - B 62000 C -	{ A - B 46000 C -	{ A 2100 B 1300 C 1400	{ A 7300 B 2300 C 7000	{ A 6400 B 2500 C 6300	{ A - B - C 910	{ A 17000 B 110000 C 7000	{ A 60 B 400 C 200	{ A1 2000 A2 n.d. A3 n.d.	Ca ²⁺	
Al ³⁺	{ A n.a. B n.a. C 1800	{ A 41 B n.d. C 1600	{ A n.d. B n.d. C 1200	{ A 28 B 190 C 23	{ A n.d. B 4400 C -	{ A n.d. B 1300 C -	{ A - B 3800 C -	{ A - B - C 3000	{ A 1700 B n.d. C 17000	{ A 990 B n.d. C 29000	{ A 884 B n.d. C 2300	{ A - B - C 1500	{ A n.d. B 510 C 100	{ A n.d. B 1200 C 300	{ A1 280 A2 n.d. A3 n.d.	Al ³⁺	
Mg ²⁺	{ A 78 B 130 C 160	{ A 20 B 350 C 1500	{ A 400 B 620 C 540	{ A 48 B 120 C 83	{ A n.d. B 660 C -	{ A n.d. B 230 C -	{ A - B 2500 C -	{ A - B 960 C -	{ A 540 B n.a. C 490	{ A 840 B 120 C 1100	{ A 680 B 110 C 400	{ A - B 89 C -	{ A 190 B 1500 C 510	{ A 14 B 14 C n.d.	{ A1 220 A2 n.d. A3 n.d.	Mg ²⁺	
Li ⁺	{ A 110 B 12 C 2	{ A 120 B 19 C 13	{ A 61 B 7 C 12	{ A 28 B 17 C 2	{ A 510 B 110 C -	{ A 160 B 23 C -	{ A - B 170 C -	{ A - B 130 C -	{ A 140 B 41 C 68	{ A 200 B 57 C 120	{ A 110 B 47 C 83	{ A - B - C 89	{ A 130 B 72 C n.a.	{ A 230 B 220 C 65	{ A1 380 A2 n.d. A3 n.d.	Li ⁺	
Zn ²⁺	{ A 16 B 9 C 87	{ A 33 B 16 C 107	{ A 21 B 14 C 36	{ A n.a. B n.a. C n.a.	{ A n.a. B n.a. C -	{ A n.a. B n.a. C -	{ A - B n.a. C -	{ A - B n.a. C -	{ A 290 B n.d. C 1900	{ A 970 B n.d. C 6000	{ A 1500 B n.a. C 7400	{ A - B n.a. C -	{ A n.a. B n.a. C n.a.	{ A n.a. B n.a. C n.a.	{ A1 n.a. A2 n.d. A3 n.d.	Zn ²⁺	
Rb ⁺	{ A n.a. B n.a. C n.a.	{ A n.a. B n.a. C n.a.	{ A n.d. B n.d. C n.d.	{ A n.d. B n.d. C n.d.	{ A n.a. B n.a. C -	{ A n.a. B n.a. C -	{ A - B 6.6 C -	{ A - B - C 5.6	{ A n.d. B 28 C 9	{ A n.d. B 12 C 5	{ A n.d. B 7 C 2	{ A - B - C 4.5	{ A n.d. B n.d. C n.d.	{ A n.a. B n.a. C n.a.	{ A1 n.a. A2 n.d. A3 n.d.	Rb ⁺	
Cs ⁺	{ A n.a. B n.a. C n.a.	{ A n.a. B n.a. C n.a.	{ A n.a. B n.a. C n.a.	{ A n.d. B n.d. C n.d.	{ A n.d. B 40 C -	{ A 7 B 11 C -	{ A - B 8.8 C -	{ A - B 9.6 C -	{ A n.d. B n.d. C 29	{ A n.d. B n.d. C 9	{ A n.d. B n.d. C 8	{ A - B 4.3 C -	{ A n.d. B n.d. C 11	{ A n.a. B n.a. C n.a.	{ A1 n.a. A2 n.d. A3 n.d.	Cs ⁺	
Cl ⁻	{ A 2600 B 1300 C 1500	{ A 2900 B 1400 C 1600	{ A 2400 B n.a. C 3600	{ A 5000 B 300 C n.d.	{ A 18000 B 1300 C -	{ A 6600 B 650 C -	{ A - B 8000 C -	{ A - B n.a. C -	{ A 4400 B 0 C 760	{ A 7400 B 1100 C 3400	{ A n.a. B n.a. C n.a.	{ A - B - C n.a.	{ A 2700 B 22 C n.d.	{ A1 2300 A2 19 A3 n.a.	{ A1 2500 A2 130 A3 100	Cl ⁻	

TABLE 7-1B: Calcite Samples

	Tokatea Area		Ngawha Geothermal Area	
	Solution	13962 RO3	NG5	
Na ⁺	{ A B	350 370	A ₁ A ₂	610 42
K ⁺	{ A B	280 98	A ₁ A ₂	120 5.8
Ca ²⁺	{ A B	n.a. n.a.	A ₁ A ₂	14000 10000
Al ³⁺	{ A B	n.d. n.d.	A ₁ A ₂	74 n.d.
Mg ²⁺	{ A B	550 1300	A ₁ A ₂	1400 740
Li ⁺	{ A B	7 9	A ₁ A ₂	13 1.7
Zn ²⁺	{ A B	19 19		
Rb ⁺	{ A B	n.d. n.d.		
Cl ⁻	{ A B	1700 49	A ₁ A ₂	1600 300

* Leach solution: A = water, B = ammonium nitrate and C = nitric acid.

- = not leached with that specific solution

n.a. = not analysed

n.d. = not detected

Experiments With Different Leaching Solutions

Previous Work

Most previous workers who extracted and analysed the salts from fluid inclusions used only water to leach their samples (c.f. Roedder, 1972; Enjoji, 1972; Casadevall & Ohmoto, 1977; Kamilli & Ohmoto, 1977; Rabone, 1977; Merchant, 1978; Weigel, 1978; and Eastoe, 1978), however Czamanske *et al* (1963) and Puchner & Holland (1966) used water followed by acid leaches (10% HNO_3 and 6N HCL respectively) in their investigations of heavy metal contents of fluid inclusions. The results of Czamanske *et al* (1963) indicate that the majority of Cu and Zn is dissolved by the acid leaches in contrast to the behaviour of Na which Puchner & Holland (1966) showed to be almost completely (> 90%) dissolved by the initial water leaches. Both studies showed that Mn is also mainly dissolved in the water leaches but to a lesser extent (70%) than Na. Puchner & Holland (1966) were unable to detect Cu and Zn in any of their leaches and were therefore unable to verify the results of Czamanske *et al* (1963) for these ions.

These results demonstrate that large ions and those with a high charge are strongly held by adsorption onto the surfaces of the crushed mineral and a strongly ionised solution is required to dissolve them.

Development of the Procedure

A single water leach was used on sample 13941b (N 14b) to test the leaching method and to establish the concentration levels of various ions in the leach for the selection of analytical methods and the preparation of appropriate standards. The leach contained measurable quantities of major ions (Table IV-3 of Appendix IV) and in approximately the proportions encountered in studies of other epithermal deposits (e.g. Enjoji, 1972; Casadevall & Ohmoto, 1977; Merchant, 1978).

Successive water leaches of samples 13958b (BO 2b), 14034 (Wh 5) and NG 5 show that the initial water leach dissolves practically all the ions dissolvable in water (the high Ca and Mg values in the second water leach of sample NG 5 are due to progressive solution of the calcite host mineral).

10% nitric acid solution was used to leach samples 13939 (N16), 13941a (N 14a), 13957₁ (Tk 2₁), 13980a (AS 1a), 13980b (AS 1b), 13980c (AS 1c), 14054a (Tui 6a), 14054b (Tui 6b) and 14071 (Wi 16) to dissolve the ions held by adsorption onto the surfaces of the crushed sample, in addition to those which would be normally dissolved by leaching with water. These leaches contained unrealistically high concentrations of Ca, Al and Mg (Table 7-1)

Figure 7-1: General concentration trends of ions leached from crushed samples of quartz by successive leaches of water, ammonium nitrate solution and nitric acid solution: A, Na^+ and Li^+ at low concentration; B, K^+ at low concentration; C, Cs^+ and Rb^+ at extremely low concentration; Mg^{2+} at low concentration but Ca^{2+} at low to high concentration; D, Zn^{2+} at low concentration but Al^{3+} at low to high concentration; E, Cl at low concentration.

to be attributed to a fluid inclusion source and indicate some contamination has occurred. Agreement of ionic ratios between "duplicate" samples (e.g. 14054₁ and 14054₂) and "clear" blanks (Appendix IV) indicate that the source of contamination is in the sample (solid inclusions or the sample itself) and not due to experimental procedural problems.

It was evident that the nitric acid solution was too strong a solvent and that an alternative was required. Therefore a further batch of samples: 13941c (N 14c), 13941d (N 14d), 13962 (RO 3), 14037₁ (Wh 10₁) and 14037₂ (Wh 10₂) were crushed and leached with water followed by 13% ammonium nitrate solution (neutral pH). This seemed to be satisfactory for the major ions but not Cs and Rb which were below their detection limits. Also these leaches did not indicate the amount of contamination present.

For a complete analysis a scheme of three successive leach solutions (water, ammonium nitrate and nitric acid) was adopted for all subsequent samples.

Leaching Patterns

The results of the multiple leach analyses (Tables IV-3 and 7-1) show that five different patterns of behaviour occur (Fig. 7-1). Na⁺ and Li⁺ (small ions with low charge) were mostly dissolved by the water leaches; the ammonium nitrate and nitric acid leaches generally dissolved progressively smaller amounts (Fig. 7-1A). K⁺ (slightly larger ion) was mainly dissolved in the ammonium nitrate leach (Fig. 7-1B), whereas practically all the Cs⁺ and Rb⁺ remained until the nitric acid leach (Fig. 7-1C). Ca²⁺ and Mg²⁺ also followed the pattern shown in Fig. 7-1C but at high concentrations indicating progressive solution of a contaminating source. Al³⁺ and Zn²⁺ followed another pattern, shown in Fig. 7-1D, whereas Cl⁻ followed that shown in Fig. 7-1E. Al³⁺ and Zn²⁺ in the water and nitric acid leaches are mainly from contamination.

Identification of Contaminants

Quartz Analyses

In order to determine the source of contamination in the leaches of crushed quartz crystals several samples of quartz were analysed by wet chemical and EPMA methods.

Uncrushed chips were selected from the leached samples, powdered, acid digested and the resulting solutions analysed by atomic absorption and flame emission methods at Chemistry Division, DSIR. The results are presented in Table 7-2. Several trace elements, principally Ca, Al and Li,

TABLE 7-2: The concentrations of some trace elements in the samples of quartz used for fluid inclusion analyses. The analyses were made by staff at Chemistry Division, D.S.I.R., using atomic absorption and flame emission methods on solutions formed by acid digestion of the samples.

Sample Number		Location		Concentration in mg/kg (ppm)					
V.U.W. No.	Field No.			Na	K	Ca	Al	Mg	Li
13957	TK2	Tokatea	Tokatea Big Reef	53	91	55	1620	13.3	150
13958	BO2	"	Buffalo Mine	127	52	59	2610	6.7	395
13907	Hutt 2	Petote	Stream Area, Hutt Creek	79	22	51	1713	5.3	254
13980	AS1	" " "	Aitken Stream	34	3	11	1660	2.5	221
13998	PS15	" " "	Petote Stream	71	18	59	1379	6.9	177
14006	PS26	" " "	Petote Stream	32	67	370	1440	8.2	136
13910	Wg9	Whangapoua,	Waingaro Stream	99	32	29	1759	6.8	224
13912	N40	Neavesville	Ajax 2 L	12	8	17	85	3.4	12
13938	N44	"	Ajax 1 L	15	8	18	121	3.2	24
13941	N14	"	Ajax 2 L	26	435	25	633	6.9	27
13919	M2 _a	Maratoto	Camoola 3 L	12	19	48	160	9.0	11
13926	M10	"	Silver Queen 3 L	84	16	279	1430	2.9	151
13928	M19	"	Camoola 3 L	25	30	27	1150	4.1	179
13948	Km18	Komata,	8 Level	12	8	17	124	3.4	17
14013	WK4	Waitekauri,	Maoriland Vein	19	22	46	252	8.2	22
14034	Wh5	Waihi No 5 Shaft	Mullock heap	72	69	58	1153	4.4	189
14035	Wh4	" " "	" "	37	19	35	38	2.8	6
14037	Wh10	"	Martha 3 L	66	62	100	496	7.6	57
14054	Tui 6	Tui Mine	Champion 5 L	21	34	40	621	3.9	49
14056	Tui 13	" "	" "	180	128	120	2160	19.2	209
14059	Tui 19	" "	" "	238	135	167	3040	36.4	277
14071	Wi16	Waiorongomai	Canadian Ck float	43	74	62	901	11.1	95
14090	Wi67	"	Main Vein	12	12	20	110	5.1	12
14091	Wi80	"	" "	29	16	25	523	6.5	89
14094	Wi89	"	Welcome "	75	15	19	2372	3.3	396
14098	Wi94	"	Inverness "	70	20	34	1889	4.0	384

are present in considerable quantities.

Samples 13951 (TR 6), 13973 (SM 7), 13980 (AS 1) and 14102 (N 40) were analysed by EPMA (Table 7-3). The 3 micrometre diameter spots analysed were found to contain widely varying quantities of Al (0 to 3300 ppm). The EPMA is not able to analyse Li and the other trace elements, if present, were below their detection limits. Samples 13951 (TR 6), 13973 (SM 7) and 13980 (AS 1) contain Al distributed throughout the quartz, whereas Al was not detected in EPMA analyses of sample 14102 (N 40). The average concentration of aluminium in sample 13980 (AS 1) determined by 23 EPMA analyses is similar to the concentration determined by wet chemical analysis (1920 ppm and 1660 ppm respectively).

These results suggest that in some samples (e.g. 13980) Al may be held in the lattice structure of quartz or distributed throughout the quartz in microinclusions, whereas in other samples (e.g. 14102) it occurs in small solid mineral inclusions.

Solid Inclusions in Quartz

Following the discovery of unexpectedly high levels of some ions in the quartz, thin sections were made of uncrushed crystals from some of the samples analysed (only a few samples contained sufficient material for sectioning). Sample 14102 (N 40) was found to contain small inclusions of sericite (confirmed by EPMA analysis), whereas three small grains of feldspar ? were present in a thin section of sample 13980 (AS 1). Morgan (1924) reported that sericite was a common constituent of quartz in the Waihi mine and Merchant (1978) suggested that it may be a contaminating source of his fluid inclusion analyses of quartz samples from the Tapu - Thames and Thames areas.

Polished plates of quartz (prepared for fluid inclusion filling temperature and freezing temperature experiments) from the same samples as used in the crushing and leaching experiments are visibly free of possible contaminants, however plates of some other samples; 13951 (Tr 6), 13973 (SM 7) and 14012 (WK 3), contain solid inclusions. In sample 13973 (SM 7) inclusions of calcite (confirmed by EPMA analysis) are aligned along a "V" growth zone near the apex of the crystal (Figs 7-2 and 7-3), whereas similar inclusions occur along a healed fracture in sample 13951 (Fig. 7-4). Fibres of an unidentified mineral (probably sericite) occur in sample 14012 (Fig 7-5). In all examples, mineral inclusions were observed in only one plate of the dozen or so prepared for each sample.

The occurrence of a fibrous mineral, probably sericite, in primary fluid

TABLE 7-3: Concentration of aluminium (mg/kg or ppm) in quartz determined by electron microprobe analyses (3 micrometer diameter beam).

Sample Number	13912 (N40)	13951 (TR6)	13973 (SM7)	13980 (AS1)
Analysis Number				
1	n.d.	n.d.	880	1070
2	n.d.	(140)	1040	1980
3	n.d.	n.d.	1130	1110
4	n.d.	n.d.	n.d.	1280
5	n.d.	n.d.	1040	1020
6	n.d.	1060	2390	1880
7	n.d.	(70)	930	(200)
8	n.d.	n.d.	2370	500
9	n.d.	3000	560	(160)
10		3030	870	420
11		590	2970	420
12		1780	2440	2430
13		2120	430	(110)
14		n.d.	3200	930
15		n.d.	3310	970
16		n.d.	1560	350
17		n.d.	3160	
18			3570	
19			2410	
20			2970	
21			2520	
22			2680	
33			1730	
Mean	-	690	1920	930
Standard deviation	-	1094	1068	694
Largest value	-	3030	3310	2430

n.d. = not detected detection limit $\approx$ 350 ppm

Figure 7-2: Inclusions of calcite along a "V" growth zone near the apex of a quartz crystal from Sorry Mary Stream, Northern Colville Peninsula (sample 13973). 63X.

Figure 7-3: Inclusions of calcite along a "V" growth zone in quartz of sample 13973. Similar view to Fig. 7-2 but at higher magnification and different plane of focus. 160X.

Figure 7-4: Inclusions of an unidentified mineral in a planar zone (healed fracture?) in a quartz crystal from 2 level of the Broken Hills Mine (sample 13951). 63X.

Figure 7-5: Inclusions of an unidentified fibrous mineral (sericite?) in quartz from the Jubilee Low Level mullock heap, Waitekauri (sample 14012). 63X.

inclusions of many samples was noted in the previous chapter (c.f. Figs 6-12 and 6-13). This mineral was identified within fluid inclusions of four of the analysed quartz samples: 13926 (M 10), 13928 (M19), 14006 (PS 26) and 14056 (Tui 13).

In view of the above documented occurrences of solids in the quartz crystals and fluid inclusions it is probably not unreasonable to assume that small quantities of any mineral, stable under the physicochemical conditions prevailing at the time, could be included in the growing quartz crystal. Therefore one or perhaps several of the common gangue and wall rock alteration minerals; albite, adularia, sericite, chlorite, calcite, epidote, kaolinite and zeolite may be present as inclusions in the quartz.

Evidence From Previous Work on Trace Element Compositions of Quartz

(a) Introduction

Previous studies on trace elements in quartz indicate that apart from their occurrence as mineral inclusions, small quantities of Al^{3+} and some alkali cations substitute for Si^{4+} in the lattice structure and large quantities of various trace elements may occur as microinclusions of polycrystalline precipitates.

(b) Substitution of Al^{3+} for Si^{4+}

Deer, Howie & Zussman (1963) reported several studies indicating that Al^{3+} , balanced with Na^+ and Li^+ , substitutes for Si^{4+} in the quartz lattice. Frank-Kamenetsky & Kamentsev (1968) considered that Al^{3+} isomorphously substitutes for Si^{4+} but that the charge balancing alkali cations are inserted into the voids of the quartz structure. Stavrov *et al* (1978) concluded from their analyses of quartz samples from igneous and hydrothermal vein environments that Li^+ is the major alkali metal charge compensator for Al^{3+} in Si^{4+} substitution.

Al^{3+} substitution for Si^{4+} forms the basis of the aluminium in quartz geothermometer of Denen *et al* (1970). However, the aluminium geothermometer was empirically based on samples with very low concentrations of aluminium, for example from 200 to 300°C, the range of temperatures of deposition of the quartz samples analysed here, the geothermometer predicts corresponding aluminium concentrations between 50 and 80 ppm. Several recent studies have questioned the validity of the aluminium in quartz geothermometer because like this study many of the samples they analysed contained

Table 7-4: Concentration of CaCO_3 in quartz samples assuming that all the calcium (and magnesium) detected in the quartz analyses (Table 7-2) is present as inclusions of calcite.

Sample Number V.U.W. No. Field No.	Apparent wt. % CaCO_3 in quartz
13957 TK2	0.014
13958 BO2	0.015
13907 Hutt 2	0.013
13980 AS1	0.003
13998 PS15	0.015
14006 PS26	0.093
13910 Wg9	0.007
13912 N40	0.004
13938 N44	0.005
13941 N14	0.006
13919 M2 _q	0.012
13926 M10	0.070
13928 M19	0.007
13948 Kml8	0.004
14013 WK4	0.011
14034 Wh5	0.015
14035 Wh4	0.009
14037 Wh10	0.025
14054 Tui 6	0.010
14056 Tui 13	0.030
14059 Tui 19	0.042
14071 Wil6	0.015
14090 Wi67	0.005
14091 Wi80	0.006
14094 Wi89	0.005
14098 Wi94	0.009

relatively high concentrations of aluminium. For example, Browne & Wodzicki (1977) found up to 170 ppm Al in hydrothermal quartz from Broadlands, and Schotford (1975) reported analyses up to 549 ppm Al in samples of quartz from pegmatite and hydrothermal veins. Stavrov *et al* (1978) considered that the quantity of Al^{3+} substitution for Si^{4+} in quartz was primarily a function of the availability of Li^+ (i.e. the concentration of Li^+ in the hydrothermal fluid) and not temperature. The upper concentration limit of Al^{3+} that may substitute for Si^{4+} in quartz is therefore not defined by the aluminium in quartz geothermometer and is unknown.

(c) Microinclusions of Polycrystalline Precipitates

Chernov & Khadzhi (1968) identified 0.04 micrometre diameter inclusions in quartz formed by the segregation of Na^+ , whereas Flicstein & Schieber (1974) reported 2 to 30 micrometre diameter inclusions, containing Al, Mg, Fe and Na, from both natural and synthetic quartz. The quartz analysed by Flicstein & Schieber contained a total of 2300 ppm Al and 400 ppm Mg, attributed to the microinclusions which in the natural quartz contained up to 15.28 wt % Al, 14.42 wt. % Mg and 9.74 wt. % Fe.

Discussion

The trace element compositions of the quartz samples listed in Table 7-2 are attributed to mineral inclusions, substitution of Si^{4+} in the quartz lattice by Al^{3+} and alkali metals, and also possibly their occurrence in polycrystalline microinclusions.

Ca and Mg are considered to occur mainly as inclusions of calcite (Table 7-4), whereas (some) Na, K and Al occur as inclusions of sericite and feldspar. The best example of the latter is sample 13941 (N 14) which has high concentrations of K but low concentrations of Al, Li and Na relative to the other samples. The Al/K atomic ratio is approximately 2, indicative of the presence of inclusions of sericite which were identified in thin section.

Most of the other samples contain relatively high concentrations of Al, Li and Na but low values of K precluding a simple balance with minerals such as sericite or feldspar (Fig. 7-6). Fig. 7-7A demonstrates that there is a correlation between the concentrations of Al and Li suggesting substitution by these elements for Si^{4+} in the quartz lattice, however the Al:Li atomic ratio is too high (1.99:1) for a correct charge balance (i.e. 1:1). Addition of Na (Fig. 7-7B) or Na + K (Fig. 7-7C) to the

Figure 7-6: Weight ratio plots of quartz trace elements and some possible contaminating minerals, the latter calculated from analyses (some averaged) in the literature (mainly Deer *et al.*, 1966). 1 = adularia, 2 = albite, 3 = chlorite, 4 = chlorite clay, 5 = epidote, 6 = inter-layered illite - montmorillonite (sericite), 7 = lepidolite, 8 and 9 = different muscovites, 10 = paragonite, 11 = wairakite, and 12 = zinwaldite. Apart from sample 13941 (arrowed) the quartz trace element compositions do not balance simply between possible mineral contaminants. The trace elements of sample 13941 may be accounted for by the presence of sericite and calcite.

Figure 7-7: Graphs illustrating the correlation between the concentrations (in units of ppm/atomic weight) of Al and some alkali metals in the quartz trace element compositions. The plotted linear regression lines indicate ratios of A, $Al_{1.99}:Li_1$ (correlation coefficient = 0.911); B, $Al_{1.78}:[Li+Na]_1$ (correlation coefficient = 0.937), and C, $Al_{1.72}:[Li+Na+K]_1$, (correlation coefficient = 0.949).

TABLE 7-5:

Composition of deep waters (in ppm) from some modern geothermal fields. The values are from analyses of well waters sampled at the surface (with consequent steam separation) but recalculated to represent the original composition of the fluid in the reservoir. Uncorrected analyses of some geothermal waters are given in Ellis & Mahon (1977), Ellis (1979) and Weissberg et al. (1979).

	T°C	pH	Na	K	Ca	Mg	Li	Rb	Cs	Cl	SiO ₂ * ¹	SO ₄ * ²	H ₂ S* ³	CO ₂ * ⁴	Na/K	Source
Broadlands	2	261	6.2	713	152	1.5	0.001	7.9	1.5	1.2	1,183	547	5.4	100	2,000	5
Broadlands	13	255	6.3	690	140	1.6	-				1,160	523	4	65	4,700	5
Wairakei	24	250	6.6	880	150	8.4	-				1,570	475	20	16	432	6
Salton Sea	1 IID	320	4.7	50,400	17,500	28,000	54	215	137	16	155,000	400	5.4	16	>150	3
Hveragerdi	6 - 7	195	8.3	190	20	0.4	-				170	222	66	2.7	95	10
Reykjanes	8	270	5.0	10,170	1,450	1,570	1.0				19,600	612	30	32	1,440	7
El Tatio	7	254	5.9	3,340	580	146	0.1				5,960	516	20	7.5	810	6
Matsao	E205	245	2.9	4,030	665	1,090	95				9,800	470	260	63	1,800	6

Source 1 = Seward (1979)

2 = Analyses listed in Table 13-6 of Ellis (1979), recalculated to ppm

alkali metal fraction improves the charge ratio but insufficiently for a correct balance (1.78:1 and 1.72:1 respectively).

Dr R.L. Goguel (pers. comm.) analysed sample 13980 (AS 1) by infrared spectroscopy and found that the Li^+ is accompanied by H^+ indicating that the lattice substitution is Al^{3+} balanced with $\text{Li}^+ + \text{H}^+$. Goguel (pers. comm.) considers that because of their small size the Li^+ and H^+ are able to fit into the quartz lattice structure with Al^{3+} , whereas Na^+ and K^+ are too large and are therefore probably not significantly involved in the substitution. Instead these latter ions probably occur in inclusions of minerals or as microinclusions of polycrystalline precipitates like those observed by Flicstein & Schieber (1974).

Estimation of Inclusion Composition

Introduction

Because of the contamination problems it is evident that each leach analysis must be assessed individually to see if contamination has occurred and to what degree. The factors discussed in the following sections were used in this assessment.

Chemistry of Modern Geothermal Fluids

A general chemical composition for the inclusion fluids may be predicted by comparison with modern geothermal waters. Table 7-5 lists some analyses of modern geothermal waters. The analysis of Broadland's water is particularly relevant to this study because these waters have passed through and equilibrated with similar rock types to those of the Hauraki Gold - Silver Province and they are actively precipitating base metals at depth and precious metals near the surface (c.f. Weissberg *et al*, 1979).

Several geothermometers and thermodynamic relationships based on the chemistry of geothermal waters have been proposed by workers in this field and some of these have been used in previous fluid inclusion crushing and leaching studies to assess the validity of their analyses.

The Na/K geothermometer has been applied successfully to many modern geothermal waters (Ellis & Mahon, 1977) indicating that the exchange reaction;

describing the interaction of the water with wall rock mineralogy, is a controlling factor on the water chemistry.

However, waters in some overseas geothermal fields contain much higher concentrations of calcium than the New Zealand waters and their compositions were considered by Fournier & Truesdell (1973) to be controlled by another reaction:

Fournier & Truesdale (1973) proposed an empirical Na-K-Ca geothermometer to take account of this reaction. These waters with higher calcium concentrations generally have low Na/K ratios (compared with those expected from the Na/K geothermometer) and are typically of high overall salinity. In extreme examples, such as the Salton Sea, California, calcium may become a major component (Table 7-5).

Recently, Giggenbach (1981) proposed that the dominant reaction determining the chemistry of waters in geothermal systems of the New Zealand type was the conversion of primary plagioclase by CO_2 to form calcite and clays:

Taking into account the different hydrothermal alteration zones and the various chemical processes acting within them (c.f. Meyer & Hemley, 1967; Rose & Burt, 1979) the different views cited above may be reconciled by considering that the reaction described by equation (7-1) predominates in the potassic zone and in some propylitic alteration zones in which adularia is present, whereas in other propylitic zones the reaction described by equation (7-3) predominates. The involvement of calcium in the plagioclase reactions [e.g. equation (7-2)] is not considered important here because the plagioclase feldspars present in rocks of the Hauraki Gold - Silver Province are not very calcic.

Therefore although the Na/K geothermometer may provide a guide to the water chemistry expected in fluid inclusions of the samples analysed here, it is not universally applicable and exceptional Na/K ratios may occur.

In summary, if the fluids in inclusions have formed by the same processes as modern geothermal waters with low CO_2 content, low salinity inclusions should have Na/K ratios in accordance with the Na/K geothermometer and Ca should be only a minor constituent. More saline inclusions may have Ca as a major constituent with concomitant low Na/K ratios and failure of the Na/K geothermometer. The concentrations of Na, K and Ca however would be expected to give sensible temperatures using the Na-K-Ca geothermometer. Inclusions formed from waters with high CO_2 content may have Na/K ratios quite different from those expected by comparison with the Na/K geothermometer yet have low concentrations of Ca.

Other cations, namely Li, Mg, Cs and Rb, occur in very low concentrations in in all cases.

Charge Balance

Uncontaminated analyses should have an approximate charge balance of the major ions:

$$\frac{\text{ppm Na}^+}{\text{at.wt. Na}} + \frac{\text{ppm K}^+}{\text{at.wt. K}} = \frac{\text{ppm Cl}^-}{\text{at.wt. Cl}} \quad (7-4)$$

An exact balance is unlikely because of the inaccuracies in the method and also because an excess positive charge may be balanced by SO_4^{2-} and HCO_3^- , whereas an excess negative charge may be balanced by Ca^{2+} etc. These factors could account for an error of up to $\pm 100\%$ in equation (7-4).

Leaching Patterns of Individual Ions

General leaching trends for the different ions in the multiple leach analyses have been described earlier (c.f. Fig. 7-1). Analyses free of contamination should show a progressive decrease in concentration from one leach to the next, except in the case of large ions and those with large charge which might be expected to "hang on" until one of the stronger solvents is used.

The general patterns of Na, K, Rb, Cs and Cl are thought to be the behaviour of these ions in contamination free analyses, whereas the patterns of Ca, Al and Mg are thought to indicate contamination. Deviation of Na, K and Cl from the general trends to one of progressive increasing concentration through the successive leaches is considered to indicate contamination.

Comparison of Ionic Ratios Between Quartz and Leach Analyses

Comparison of ratios such as Li/Al and Mg/Ca of the quartz and fluid inclusion leach analyses may be used to indicate if contamination has occurred. This method was not rigorously applied in the case of Na and K because of the uncertainty of their location in the quartz. For example, if they are held as a result of substitution in the quartz lattice or as late segregations in polycrystalline microinclusions it is conceivable that they may have been incorporated in the same ratios as in the parent hydrothermal fluid.

TABLE 7-6: Selected partial chemical analyses of fluid inclusions. Concentrations are in mg/kg or ppm except mNaCl (moles/kg).

	Tokatea (Coromandel)	Petote Stream Area (Coromandel)	Whanga- poua	Neavesville (Ajax)	Maratoto	Tui Mine	Waiorongomai								
13957	13958 _a	13962	13907	13980	13998	13910	13938	13941	13919	13926	14054	14071	14090	14091	14098
(TK2)	(BO2 _a)	(RO3)	(Hutt	(AS1)	(PS15)	(Wg 9)	(N44)	(N14)	(M2 _q)	(M10)	(Tui6)	(Wi16)	(Wi67)	(Wi80)	(Wi94)
			2)												

Na	3400	7600	720	3300	4900	1800	2300	740	3000	2700	5200	3500	2300	4* 5.7*		Na
K	1600	2700	380	140	320	180	450	630	850	550	1000	1100	500	2.6*		K
Mg												89				Mg
Li			16					31	40		170	89				Li
Rb												4.5				Rb
Cs												4.3				Cs
Cl	4600	8300	1600	4000	3900	2000	3700	1220	12,000	11,000	8000		2700			Cl
mNaCl	0.16	0.32	0.05	0.13	0.16	0.07	0.11	0.04	0.09	0.07	0.24		0.09			mNaCl

* Na/K ratio only

Prediction of Na, K and Ca Contamination by Quartz Trace Element Ratios

By assuming that the concentrations of Al, Mg and Li of the leaches are from contamination, their ppm values may be multiplied by the appropriate ratios (e.g. Na/Al, Na/Li, K/Al and Ca/Mg) of the quartz analyses to predict levels of accompanying Na, K and Ca contamination.

Particles of the fibrous mineral, noted from fluid inclusions in polished plates prepared for filling temperature and freezing temperature work, may not contribute significantly to the trace element compositions of the quartz but could be strong contaminants in the leaches. Assuming these particles are sericite, K contamination in the leaches from this source can be predicted by substituting the Al values of the leaches in an average analysis of sericite.

Conclusions

The indications and degree of contamination of the various leaches are discussed in Appendix IV and the partial fluid inclusion analyses which are considered essentially free of contamination are listed in Table 7-6.

This investigation has demonstrated that contamination from the host mineral is a major problem in crushing and leaching experiments of low salinity fluid inclusions. Single or multiple water leaches have relatively high Ca, Mg, Li and Zn concentrations although charge balance with chloride is possible in many cases. Leaching with solutions of ammonium nitrate and nitric acid proves that the bulk of these concentrations are from contamination by the host mineral. A test for this contamination in water leaches may be the concentration of aluminium.

THE CONCENTRATION OF CO₂ IN FLUID INCLUSIONS

Measurement

The concentration of CO₂ in fluid inclusions was determined for 16 samples by measuring the pressure of CO₂ in the vacuum line during crushing and water extraction experiments described in Appendix IV. The results are listed in Table 7-7.

An estimate of the precision of the CO₂ concentration measurements may be gained from the duplicate analyses of samples 13928 (M 19), 14037 (Wh 10) and 14061 (Tui 19). Analyses of sample sets split according to their clarity (13941, 13958 and 13980; Appendix IV) may not be used for this purpose because any differences between the individuals in each set may be caused by different proportions of primary and secondary fluid inclusions if the concentration of CO₂ in each generation is different.

TABLE 7-7: Concentration of CO₂ (mole %) measured from fluid inclusions, with an indication of precision error ($\pm$ mole % CO₂) calculated from the duplicate analyses of samples 13928(M19), 14037(Wh10) and 14061(Tui 19).

Sample Number V.U.W.No. Field No.	Location	Measured water yield (mg)	Measured mole % CO ₂	$\pm$ precision error (mole % CO ₂)
13957 TK2 ₂	Tokatea Tokatea Big Reef	9	0.4	0.6
13958 BO2 _a	" Buffalo Mine	7	0.5	0.8
BO2 _b	" " "	12	1.1	0.4
13962 RO3	" Royal Oak Mine 7 L	13	1.9	0.4
13907 Hutt 2	Petote Stream area; Hutt Creek	8	1.4	0.7
13980 AS1 _a	" " " Aitken Stream	22	0.7	0.1
AS1 _c	" " " " "	30	1.1	0.1
13998 PS15	" " " Petote Stream	6	0.7	0.8
13910 Wg9	Whangapoua, Waingaro Stream	8	2.0	0.7
13931 N16	Neavesville Ajax 2 L	29	0.4	0.1
13941 N14 _b	" " "	55	0.2	0.1
" N14 _c	" " "	28	0.2	0.1
13919 M2 _q	Maratoto Camoola 3 L	7	0.2	0.8
13926 M10	" Silver Queen 3 L	11	0.8	0.5
13928 M19 ₁	" Camoola 3 L	27	0.2	0.1
" M19 ₂	" " "	15	0.4	0.2
14035 Wh4	Waihi No.5 Shaft mullock heap	6	2.0	0.8
14037 Wh10 ₂	" " " " "	4	1.8	1.0
" Wh10 ₁	" " " " "	2	4.1	1.1
14051 Tui 13	Tui Mine Champion 5 L	18	0.8	0.1
14061 Tui 19 ₁	" " " "	12	1.4	0.4
" Tui 19 ₂	" " " "	20	0.7	0.1
14094 Wi89	Waiorongomai, Welcome Vein	9	1.0	0.6

The duplicate analyses exhibit a trend of increasing apparent CO_2 concentration with decreasing water yield which becomes more marked in samples with low water yield (i.e. ΔCO_2 concentration increases down the series: 13928, 14061 and 14037). This relationship was used to construct the graph of precision error (mole % CO_2) versus water yield illustrated in the inset of Fig. 7-8. The precision errors for the individual analyses, derived from this curve, are listed in Table 7-7 and shown as error bars in the plot of CO_2 concentration versus water yield (Fig. 7-8).

Maximum Limits of CO_2 Concentration Determined
From Phase Relations in the System $\text{H}_2\text{O} - \text{CO}_2$

Introduction

Maximum limits of CO_2 concentration can be estimated by considering the phase relations in the system $\text{H}_2\text{O} - \text{CO}_2$ at low temperature (Fig. 7-9) in terms of (a) the absence of liquid CO_2 and (b) the absence of clathration during freezing temperature experiments.

Absence of Liquid CO_2

Liquid CO_2 was not observed in any fluid inclusions studied by the writer and only one instance of its occurrence in the Hauraki Gold - Silver Province has been reported previously: Merchant (1978) described inclusions in quartz from the Garbo Mine (Karaka Creek, Thames) containing, by volume, 50 - 60% water vapour, liquid water [20 - 35% ?] and 15 - 20% liquid CO_2 and homogenising in the vapour phase at around 330°C .

A minimum pressure of 65 bars is necessary for liquid CO_2 formation in fluid inclusions at 25°C (Fig. 7-9). Extrapolation of the solubility data of Wiebe & Gaddy (1940), Malinin & Savelyeva (1972) and Malinin & Kurovskaya (1975) indicates that approximately 2.5 mole % CO_2 (1.4 moles CO_2 per kg of solution) may be dissolved in an 0.2 molal NaCl solution (average NaCl equivalent concentration for the solutions considered here) under 65 bars pressure. The Ostwald distribution coefficient at 25°C is about 0.8 (c.f. Fig. 3 of Ellis & Goldring, 1963) indicating that approximately 80% of the CO_2 in the fluid inclusion is dissolved in the liquid phase, whereas 20% occurs in the vapour phase. Therefore a total CO_2 concentration in excess of approximately 3 mole % is required to form liquid CO_2 in a fluid inclusion.

Figure 7-8: Plot of measured CO₂ concentration versus the yield of water obtained (proportional to volume of inclusions sampled) from fluid inclusions in samples of quartz and calcite crushed under vacuum. The error bars were calculated from the precision error curve (see error graph, inset) estimated empirically from the duplicate analyses of sample 13941, 13958 and 13980. Inclusions with CO₂ concentrations greater than 1.5 mole % should exhibit CO₂ clathration effects during freezing temperature experiments, whereas inclusions with CO₂ concentrations greater than 3 mole % should contain liquid CO₂ (see text). Neither of these properties were observed, suggesting that CO₂ concentration measurements to the right of the clathration line (> 1.5 mole % CO₂) are probably in error.

Figure 7-9: Phase diagram for the system H₂O - CO₂. (From Collins, 1979).

TABLE 7-8: Concentrations of CO₂ assigned to the fluid inclusions (Section A of Table) on the basis of measurement and phase relations. The freezing point depressions (Section B of the Table) that should result from these CO₂ concentrations is generally much greater than that measured during fluid inclusion freezing temperature experiments (Section C of Table).

A			B		C		
Sample Number	CO ₂ concentration	Depression of freezing point due to mCO ₂ (°C)	Observed	Fluid inclusion freezing temperatures °C	Of the sample listed plus other samples from the same area	Of sample listed average maximum	
V.U.W. No.	Field No.	Assigned mole % CO ₂	Assigned molality		average	maximum	
TOKATEA							
13957	TK2	0.4	0.2	-0.4	-1.4	-1.7	
13958	BO2	0.8	0.5	-0.9			
13962	RO3	1.5	0.8	-1.5			
PETOTE STREAM AREA							
13907	Hutt 2	1.4	1.4	-1.5			
13980	AS1	0.9	0.5	-0.9			
13998	PS15	0.7	0.4	-0.7	-0.9	-1.3	
WHANGAPOUA							
13910	Wg9	1.5	0.8	-1.5			
NEAVESVILLE							
13939-13941	N16-N14	0.3	0.2	-0.4	-0.4	-0.6	
MARATOTO							
13919	M2q	0.2	0.1	-0.2	-0.3	-0.5	
13926	M10	0.8	0.4	-0.7	-0.5	-0.5	
13928	M19	0.3	0.2	-0.4	-1.6	-1.6	
WAIHI							
14035	Wh4	1.5	0.8	-1.5			
14037	Wh10	1.5	0.8	-1.5			
TUI MINE							
14051	Tui 13	0.8	0.4	-0.7	-0.4	-0.6	
14061	Tui 19	1.0	0.6	-1.1			
WAIORONGOMAI							
14094	Wi89	1.0	0.6	-1.1			
						-0.9	
						-3.4	

Absence of Clathration

The clathrate compound $\text{CO}_2 \cdot 5.75 \text{ H}_2\text{O}$ was not observed to form in fluid inclusions during freezing temperature experiments made by the writer and was not reported by Merchant (1978) or Erceg (1981), the only other studies in which freezing temperatures of fluid inclusions were determined in samples from the Hauraki Gold - Silver Province. However, because the fluid inclusions in some samples are small and poorly visible, it is possible that clathration may have occurred without being observed. Therefore the apparent absence of clathration in samples from the Hauraki Gold - Silver Province, although of significance in most samples, may not be applied as a universal indicator of maximum CO_2 content in all samples for which fluid inclusion freezing temperature information has been presented (Appendix III).

The CO_2 - hydrate occurs in fluid inclusions at 0°C under pressures greater than 13 bars (Fig. 7-9). The Henry's Law constant at 0°C for dilute NaCl solutions is 790 (Mr J.W. Hedenquist, pers. comm.; c.f. Fig. 2 of Ellis & Goldring, 1963) and therefore by substitution of these values in the Henry's Law equation (c.f. Appendix V) the indicated mole fraction of CO_2 under these conditions is 0.016. Rounding off this figure suggests that concentrations of CO_2 in excess of 1.5 mole % are required for clathration.

Discussion

The limits of CO_2 concentration calculated for clathration and liquid CO_2 are plotted in Fig. 7-8 and indicate that the measurements of fluid inclusion CO_2 concentration between 1.5 and 3 mole % CO_2 (13962 at 1.9, 13910 at 2.0, 14035 at 2.0 and 14037₁ at 1.8) are suspect and the one above 3.0 (14037₂ at 4.1) is probably in error. The first series of samples have precision error bars extending into the clathrate free field of Fig. 7-8 (below 1.5 mole % CO_2) and therefore may represent concentrations of or slightly less than 1.5 mole % CO_2 .

Assigned Values of CO_2 Concentration

Table 7-8 lists the values of CO_2 concentration assigned to the samples after consideration of the various factors discussed above.

Fluid Inclusion Salinity (Freezing Temperature) Corrections

The salinity values determined from freezing temperature measurements of fluid inclusions (c.f. Appendix III) are apparent salinities because, in addition to the dissolved salts (e.g. NaCl and KCl), dissolved CO_2

depresses the freezing point of water by 1.86°C for every mole of CO_2 per kg of solution.

The depression of freezing point effect of the CO_2 concentrations determined in the previous section are listed in Table 7-8 together with the available fluid inclusion freezing temperature information. The latter is listed in two forms: one series of results (average and maximum freezing temperature) for the specific sample listed and another set including results for all samples from the parent deposit. The latter are included because in some samples insufficient freezing data are available to give a representative result.

In many cases the corrections for dissolved CO_2 are equal to or exceed the measured freezing temperatures, indicating that either (or both) the measured CO_2 concentrations are overestimates or the measured freezing temperatures underestimate the concentration of solutes.

Given the inaccuracies of the CO_2 and freezing temperature measurements and the few data available, routine application of CO_2 concentration corrections to the apparent salinity data presented in this thesis are impossible and therefore no corrections are made. However, the CO_2 measurements are important in demonstrating that CO_2 is quantitatively an important solute and may be the major solute in some dilute solutions (e.g. with apparent salinities < 2 eq. wt. % NaCl).

Other Implications of CO_2 Concentrations

The high concentration of CO_2 relative to other solutes in some samples may explain the widely variable freezing temperature results of individual samples. These may result from variations in CO_2 content from one inclusion to another implying widely varying CO_2 concentrations (by an order of magnitude) during crystal growth.

Apparent salinities of most secondary inclusions measured (even those with filling temperatures similar to those of primary fluid inclusions) were too low to measure, indicating that the hydrothermal fluids were not only very dilute in terms of salts but also contained only very minor concentrations of CO_2 .

CHAPTER 8

HYDROGEN ISOTOPES

INTRODUCTION

The systematics of deuterium/hydrogen (D/H) ratios and their use as indicators of water origin in the geological environment were reviewed by Taylor (1974, 1979). D/H ratios are reported as δD per mil values which are parts per thousand (‰) deviation from Standard Mean Ocean Water (SMOW). δD of SMOW is 0. Positive δD values indicate enrichment in the heavy isotope (D) relative to the standard, whereas negative δD values indicate enrichment in the light isotope (H).

Ocean, connate (formation water), metamorphic and magmatic waters are believed to be characterised by certain values of δD , whereas δD of meteoric water varies widely and systematically with latitude and altitude. However, at any particular location the mean δD value of the meteoric water is constant in time provided latitude, altitude and climate remain constant.

METHOD OF ANALYSIS

The method for the extraction of water from the fluid inclusions is described in Appendix IV. Hydrogen was separated by passing the water over hot zinc in a vacuum line and isotopically analysed in a mass spectrometer. Maximum experimental error on the isotopic measurement is considered to be ± 1 per mil.

TEST SAMPLE

The δD of fluid inclusion water in a sample of calcite cuttings from approximately 1000m in drill hole 5 of the Ngawha geothermal field, Northland, was measured at -32 per mil.

The total discharge δD compositions of water from Ngawha drill holes 4 and 9 are -35 per mil and -34 per mil respectively, however the deep fluid composition is suggested to be closer to -26 per mil (Browne *et al*, 1981 p 119).

Considering the difference in age between the inclusions and well water (not known), the measured variations in well water δD values (c.f. Browne *et al*, 1981) and the uncertainty of the deep fluid composition, the general agreement (a maximum difference of 6 per mil) between the fluid inclusion measurement and modern well water indicates that the method used here can be accurate.

TABLE 8-1: δD values of water extracted from fluid inclusions in samples from some epithermal deposits. All samples are quartz except sample 13962 (Royal Oak Mine, Tokatea) which is calcite. The large negative value (-75 per mil) for sample 14013 (Waitekauri) is attributed to contamination by air admitted through a crack formed in the sample tube during crushing.

Sample Number		I.N.S. No. R5486/-	Location		Depo- sition- al Stage	Weight of crushed water (g)	Yield of water (mg)	δD_{SMOW}
V.U.W. No.	Field No.		General	Specific				
13957	TI 2 ₁	5	Tokatea	Tokatea Big Reef		58	23	-34
"	TK 2 ₂	25	"	" " "		*N/R	9	-28
13958	B02a	21	"	Buffalo Mine mullock heap		43	7	-32
"	B02b	24	"	" "		43	12	-36
13962	R03	27	"	Royal Oak Mine 7L		*N/R	13	-33
13907	Hutt 2	31	Petote Stm	Area. Hutt Creek	2	33	8	-49
13980	AS1 a	9	"	Aitken Stream	2	66	22	-39
"	b	8	"	" "	2	63	30	-46
"	c	10	"	" "	2	45	8	-31
13998?	PS15	33	"	Petote Stream Chalcopyrite lode	2	23	6	-37
14006	PS26	20	"	Petote Stm, "north"	2	29	6	-27
13910	Wg 9	32	Whangapoua	Waingaro Stream	4	21	8	-48
13939	N16	6	Neavesville	Ajax 2L		42	29	-36
13941	N14a	3	"	" "		52	20	-29
"	N14c	1	"	" "		45	55	-38
"	N14d	17	"	" "		49	28	-38
"	N14e	16	"	" "		42	31	-36
13919	M2q	12	Maratoto	Camoola Vein 3L south stope	3	28	7	-11
13926	M10	13	"	Silver Queen Vein 3L	3	29	11	-49
13928	M19 ₁	15	"	Camoola Vein 3L	3	55	27	-41
"	M19 ₂	14	"	" " "	3	39	15	-44
14013	WK4	11	Waitekauri	Maoriland Vein		36	10	-75
14035	Wh4	29	Waihi	No.5 shaft mullock heap		44	6	-45
14037	Wh10 ₁	19	"	Martha Vein		49	2	+ 5
"	Wh10 ₂	18	"	" "		50	4	+ 5
14053	Tui6 a	7	Tui Mine	Champion Vein	3	54	12	-27
"	Tui6 b	4	"	" "	3	*N/R	21	-35
14056	Tui13	26	"	Champion Vein 5L Raise 17	2	62	18	-34
14061	Tui19 ₁	22	"	Champion Vein 5L DD cross cut	2	36	12	-35
"	Tui19 ₂	23	"	" " "	2	39	20	-35
14071	Wi16	2	Waiorongomai	Canadian Creek, float	2	59	47	-37
14090	Wi67	30	"	Diamond Gulley	2	35	3	-23
14094	Wi89	28	"	Welcome Vein, northern adit	2	53	9	-37

* Not Recorded

RESULTS

Table 8-1 lists the δD analyses of water from fluid inclusions in samples of quartz and calcite from a few of the epithermal deposits.

Most values lie in a -23 to -50 per mil range. The very light (-75 per mil) value for sample 14013 (WK 4) is due to air contamination admitted through a crack in the sample tube, developed during crushing.

A graph of δD versus water weight (Fig. 8-1) shows that very small samples have more positive δD values than larger ones and that duplicate analyses show a trend toward positive values with decreasing sample size. These trends are probably caused by fractionation of the sample in the vacuum line during vacuum distillation stages or contamination by "foreign" water in the line or on surfaces of the sample (e.g. atmospheric vapour producing light values). The fractionation and contamination are insignificant with large samples but drastically effect the δD of some samples below 10 mg. Similar problems were encountered by Taylor et al (1979).

An absolute water weight limit for reliable analyses is difficult to assign. For example, 6 mg of sample 14035 (Wh 4b) seems to give a sensible δD value, whereas the same weight for sample 13919 (M 2q) does not.

Several quartz samples were split into two or more samples, used for crushing runs, according to their clarity (Appendix IV). The 13980 series (3 samples) and 13941 series (5 samples) do not show any systematic change in δD down the series; Xa, Xb, Xc and Xd due to an increasing proportion of secondary inclusions. If the δD of primary and secondary inclusion waters is different this factor is completely overshadowed by the sample weight problem discussed above.

Representative analyses selected after appraisal of the samples, in terms of the factors mentioned above, are presented in Table 8-2. The selected δD values range from -33 to -49 per mil with an average around -40 per mil.

These results differ from those determined from Tui Mine samples by Robinson (1974). He reported δD values of -70 per mil and -24 per mil for Stage 2 galena and Stage 3 quartz primary fluid inclusions respectively. The -70 per mil value may indicate the presence of magmatic water as postulated by Robinson (1974) or leakage during crushing (c.f. sample 14013, Table 8-1). The -24 per mil value, about 10 per mil heavier than the general value for late Stage 2 - Stage 3 Tui Mine fluid measured here, may have suffered similar problems of contamination as many of the samples analysed in this study.

Figure 8-1: Plot of δD values measured from fluid inclusion waters, extracted by crushing samples of quartz and calcite under vacuum, versus the weight of water sampled. Dots represent measurements of different samples, whereas samples in which more than one measurement were made (either of duplicate or quality series; see text) are shown by specific symbols. Different measurements of the same sample generally exhibit a trend of decreasing δD with decreasing water weight, probably due to fractionation during sample separation (as noted in the figure) or contamination by isotopic exchange with adsorbed water already present in the vacuum line. Therefore the high δD values, and the very low δD value resulting from leakage, are rejected leaving a range of -33 to -49 per mil which is believed to represent the original waters.

ORIGIN OF THE WATERS

Introduction

The naturally occurring types of waters that are considered to be involved in the ore forming processes are; ocean, meteoric, geothermal, formation (connate), magmatic and metamorphic (Taylor, 1974, 1979; Sheppard, 1977).

Because volcanism in the Coromandel Peninsula and Great Barrier Island was subaerial, ocean water is not considered to be an important component of the mineralisations. The absence of metamorphic rocks (greywacke is not considered a metamorphic rock for the purposes of this discussion) in the area indicates that metamorphic water was also not involved. Most geothermal waters have been shown to be composed of heated recycled meteoric waters (Ellis & Mahon, 1977; Taylor, 1979) and therefore these two classes are considered together.

The range of possible types of water involved in the mineralisations considered here is therefore narrowed to meteoric - geothermal, formation and magmatic waters. These are considered separately below.

Meteoric and Geothermal Waters

Robinson (1974) reported a δD value of -30.5 per mil for Te Aroha thermal waters and an average composition of -30.1 ± 1.0 per mil (range: -28.9 to -31.3) for Te Aroha meteoric waters. Thermal spring waters on Great Barrier Island, however have heavier values: -19.1 to -21.8 per mil (Dr M.K. Stewart pers. comm.).

Assuming that the fluid inclusion waters measured here were originally meteoric water, the trend of lighter values (up to a maximum of 20 per mil) than present meteoric water may be attributed to changes in climate, altitude and latitude.

A reduction in mean annual temperature of 1°C would cause meteoric waters to be depleted in deuterium by approximately 5.6 per mil (c.f. Stewart & Taylor, 1981) and therefore a maximum decrease in temperature of approximately 3.5°C would be required to explain the entire range of fluid inclusion values without involvement of any other process. A reduction of around 2°C is probably more realistic for periods of cooler climate during the late Tertiary.

δD of meteoric water varies by approximately -1.8 per mil for every 100m increase in altitude (c.f. Stewart & Taylor, 1981) and therefore this effect may be secondary but additional to climatic changes for the very heavy δD fluid inclusion values, but could possibly be invoked as the

TABLE 8-2: Selected δD values for fluid inclusion waters from the epithermal deposits

General Location	Sample Number V.U.W. No.	Field No.	Water Weight mg	δD SMOW per mil	Average δD per mil
Tokatea	13957	TK 2 ₁	23	-34	} -34
	13958	BO 3 _b	12	-36	
	13962	RO 3	13	-33	
Petote Stream	13907	Hutt 2	8	-49	} -44
	13980	AS 1 _b	30	-46	
	13998	PS 15	6	-37	
Whangapoua	13910	Wg 9	8	-48	-48
Neavesville	13941	N 14 _c	55	-38	-38
Maratoto	13926	M 10	11	-49	} -46
	13928	M 19 average	27, 15	-42	
Waihi	14035	Wh4	6	-45	-45
Tui Mine	14053	Tui 6 _b	21	-35	} -35
	14056	Tui13	18	-34	
	14061	Tui19 average	12, 20	-35	
Waiorongomai	14071	Wi 16	47	-37	} -37
	14094	Wi 89	9	-37	

primary process for the lighter values.

Variation of meteoric water δD values with changes in latitude are quite marked (e.g. Kaitaia: -14 per mil and Invercargill: -48 per mil; Stewart & Taylor, 1981). The effect of the change in latitude of the North Island with sea floor spreading since the time of mineralisation (probably up to 10 m.y. B.P.) is difficult to assess but may have contributed slightly to the difference between the δD values of the fluid inclusion waters and those of present day meteoric water. There is no trend in the δD values of Table 8-2 with changing latitude from north (Tokatea, Petote Stream and Whangapoua) to south (Tui Mine and Waiorongomai), probably because of the small difference in latitude and also because of possible differences in age of mineralisation.

Magmatic Water

Primary Magmatic Water

The range of δD values for primary magmatic water is considered to be -50 to -85 per mil, with values typically around -70 per mil (Taylor, 1979). The fluid inclusion waters measured here are outside this range and are therefore not primary magmatic waters.

Modified Magmatic Water

Some heavy δD values have been reported for magmatic water from fumarolic condensates, for example: White Island, -5.8 to -27.5 per mil (Stewart & Hulston, 1976); Iceland, -44 to -61 per mil (Aranson & Sigurgeisson, 1968); Satsuma - Iwojima, Japan, -17 to -27 per mil (Matsuo *et al*, 1974) and Showashinzan, Japan, -32 per mil (Mizutani, 1978).

Several explanations have been suggested to explain these occurrences of apparently isotopically heavy magmatic waters, mainly the mixing of the magmatic water with sea water, surface water or formational water. For example, the latter was used by Mizutani (1978) to explain the Showashinzan δD values. However, Stewart & Hulston (1976) seem to have abandoned the involvement of primary magmatic water altogether at White Island by suggesting that the δD values at this location resulted from vapour separation, near the surface, from a boiling mixture of surface water and sea water which had infiltrated the volcano. Some other occurrences of heavy magmatic water remain unsolved and indicate that magmatic water, probably due to some secondary process, may have δD values heavier than -50 per mil.

Waters of Magmas Derived by Mixing of Primary Magma with Sedimentary Rocks

The hypothesis that the andesite and rhyolite magmas, responsible for the volcanic rocks of the Coromandel Peninsula and Great Barrier Island, were not primary but were formed by mixing with, or anatexis of, Mesozoic sedimentary rocks suggests that the δD of such magma may be very different from primary magma. Varying proportions of primary magma and sedimentary rock would produce intermediate values. The possible range of δD values for magmas derived by these processes is unknown.

Formation (Connate) Water

The only non-volcanic rock type of any significance in the Coromandel Peninsula and on Great Barrier Island is the Mesozoic sedimentary rocks. These probably contain water mainly held in hydrous minerals although a little interstitial water may be present. The latter is probably ocean water ($\delta D = 0$ per mil). It is unlikely that these rocks could supply much water to the mineralising system without metamorphism and evolution of water from the hydrous minerals.

Mixed Meteoric - Magmatic Waters

The entire range of measured values of fluid inclusion waters could be formed by a mixture, in various proportions, of primary magmatic water, with a δD lighter than -50 per mil, and meteoric water, with a δD value around -30 per mil (present day value).

CONCLUSIONS

δD values of fluid inclusion waters, representing intermediate and late stages in epithermal mineralisations of the Coromandel Peninsula, form a comparatively tight cluster (± 9 per mil) around -40 per mil and are concluded to represent waters of predominantly meteoric origin with possibly a small magmatic component in the earlier stage fluids.

The average 10 per mil depletion in deuterium compared with present day meteoric water is considered to result from precipitation of the waters during a cooler climate and at higher altitudes and latitudes (in order of importance) than present.

CHAPTER 9

SULPHUR ISOTOPESMEASUREMENT

Sulphide minerals were concentrated by heavy liquid (methylene iodide) separations of the 0.5 - 0.125mm size fraction of aggregates obtained by crushing the sample in a piston crusher or picked from the sample with a vibratool. Individual sulphide minerals were hand picked (with a wet fine paint brush) from these concentrates under a stereo microscope and fibre optic light source (Schott cold light source KL 150B).

Barite, the only sulphate mineral analysed, occurred as plates growing on earlier quartz (Figs 4-9 and 4-34) and was easily separated by breaking the plates off the quartz with a pair of pliers.

The ratios of the sulphur isotopes ^{34}S and ^{32}S of the sulphide and sulphate minerals were analysed by the methods outlined in Robinson (1974). The results, listed in Table 9-1, are given as $\delta^{34}\text{S}$ per mil values which are parts per thousand deviation of the $^{34}\text{S}/^{32}\text{S}$ ratio of the mineral relative to that of the Canon Diablo Troilite standard (CDT). The standard by definition is 0 per mil. Samples having a higher proportion of the heavy isotope (^{34}S) than the standard have positive $\delta^{34}\text{S}$ values and are said to be heavier than the standard or enriched in ^{34}S . Conversely, samples which have a higher proportion of the light isotope (^{32}S) compared with the standard have negative $\delta^{34}\text{S}$ values and are said to be lighter than the standard or depleted in ^{34}S .

GEO THERMOMETRY

The $\delta^{34}\text{S}$ of sulphide and sulphate minerals precipitating from solution is dependant on a number of variables including temperature, pH and $\delta^{34}\text{S}$ of the total sulphur in solution (Ohmoto, 1972). For a given set of these conditions, $^{34}\text{S}/^{32}\text{S}$ fractionation occurs between different minerals precipitating together and has been shown to be in the order: sulphate > pyrite > sphalerite > chalcopyrite > galena (c.f. Fig. 10.3 of Ohmoto & Rye, 1979). Therefore the fractionation between a pair of these minerals can be used to calculate their depositional temperature by comparison with experimentally calibrated fractionation curves (c.f. Figs 46 and 47 of Friedman & O'Neil, 1977), provided the minerals in question grew under the same conditions.

The reliability of the various pairs as geothermometers is in part a

TABLE 9-1: $\delta^{34}\text{S}$ values of sulphide and sulphate minerals and depositional temperatures calculated from isotopic fractionation between sulphide mineral pairs.

Sample Number V.U.W. No. Field No.	Location	Stage	I.N.S. No.	*1	*2	$\delta^{34}\text{S}$ ‰ (CDT)	sp - gn $\Delta^{34}\text{S}$	t°C	py - cp $\Delta^{34}\text{S}$	t°C	Other $\Delta^{34}\text{S}$	t°C
MINERS HEAD												
Mine												
13965	MH1a		R5168-157		py	+ 1.1						
			R5168-158		cp	+ 1.0			0.1	∞		
13965	MH1b		R5168-159		py	+ 1.8						
			R5168-160		cp	+ 1.3			0.4	∞		
TE AHUMATA												
13908	GB5	Za	R9401-2		py	+ 0.7						
13953	GB9	1	R9401-3		py	+ 1.3						
			R9401-4		cp	+ 0.7						
13954	GB12	2b	R5168-156		sb	+ 0.6						
13963	GB2	2b	R5168-155		sb	+ 0.4						
13964	GB6	2b	R5168-154		sb	- 0.2						
13969	GB4	2a	R9401-1		py	+ 0.4						
NORTHERN COLVILLE PENINSULA												
13974	SM11a	2	R5168-47		cp	+ 2.4						
			R5168-49		sp	+ 2.6						
			R5168-48		gn	+ 0.9	1.7	370				
	SM11b	2	R5168-104		py	+ 3.7			0.7	530		
			R5168-105		cp	+ 3.0						
			R5168-106		sp	+ 3.1						
			R5168-107		gn	+ 1.2	1.9	340				
13975	SM12a	2	R5168-67		py	+ 3.3						
			R5168-66		cp	+ 2.9			0.4	800		
	SM12b	2	R5168-43		py	+ 3.4						
			R5168-44		cp	+ 1.4			2.0	200		
			R5168-45		sp	+ 2.5						
			R5168-46		gn	+ 0.4	2.0	320				
13971	DC12c	1	R5168-108		cp	+ 2.8						
			R5168-109		sp	+ 2.6						
			R5168-110		gn	+ 0.8	1.8	350				
13971	DC12d ₁	1	R5168-137		cp	+ 2.8						
			R5168-139		gn	+ 0.6						
	DC12d ₂	1	R5168-68		py	+ 4.1						
			R5168-69		cp	+ 2.8			1.3	320		
			R5168-71		sp	+ 1.8						
			R5168-70		gn	+ 0.5						
13968	Tg1		R9401-11		py	+ 2.7	1.3	450			py-gn _{3.6}	280
Tangiaro Stream												
KUAOTUNU												
13977	Wt4	2	R9401-27		py	+ 0.6						
14004	Wt15	2	R9401-28		py	+ 1.0						
14028	Wt18	2	R9401-29		py	+ 0.6						

TABLE 9-1: Continued

Sample Number V.U.W. No. Field No.	Location	Stage	*1 I.N.S. No.	*2 Mineral	$\delta^{34}\text{S}$ ‰ (ODT)	sp - gn $\Delta^{34}\text{S}$	py - cp $\Delta^{34}\text{S}$	Other $\Delta^{34}\text{S}$
14000	Petote Stream, Calena Lode	1	R5168-30	py	+ 3.4			
14001		1	R5168-29 R5168-76 R5168-75	sp py sp	+ 2.5 + 3.7 + 2.2			py-sp 0.9 300
13911	WHANGAPOUA Waingaro Stream	4	R5168-34 R5168-55	sb py	+ 1.5 - 2.1			
13904 13905	NEAVESVILLE Graces Adit Graces Adit		R9401-8 R9401-7	py py	- 0.3 - 0.4			
285/37/6	MARATOTO Silver Queen Vein	2c	R5168-41 R5168-37	cp sp	+ 1.4 + 1.0			sp-cp 0.4 330
13906	KOMATA 8 L		R9401-6	py	+ 2.8			
14010	WAITEKAURI Jubilee Low Level	2a 2a	R5168-23 R5168-61 R5168-60 R5168-25 R5168-20 R5168-20 R9401-20 R9401-21/22 R9401-23 R5168-38 R5168-27 R9401-24 R9401-25 R9401-26 R5168-40 R5168-39 R5168-51 R5168-31 R5168-2 R5168-15 R5168-19	gn py cp sp gn py sp gn cp sp cp sp(l) sp(d) py cp cp sp(l) sp(d) sp gn	+ 0.8 + 2.5 + 2.2 + 2.1 + 0.3 + 2.1 + 1.7 + 0.1 + 2.0 + 3.8 + 3.0 + 2.5 + 2.7 + 2.2 + 1.9 + 3.1 + 3.2 + 2.7 + 3.8 + 1.5	0.3 900 1.8 350 1.6 390		
14016		2a						
14017	Jubilee 2 L	2a						
14018	Jubilee Low Level	2a					0.3 900	
14020		2a				2.3 280		
14039	WAIHI Martha Mine		R5168-24 R5168-5	sp gn	+ 0.9 - 1.0	1.9 340		

TABLE 9-1: Continued

Sample Number V.U.W. No. Field No.	Location	Stage	I.S.N. No. *1	Mineral *2	$\delta^{34}\text{S}_{\text{SO}}$ (CDT)	sp - gn $\Delta^{34}\text{S}$ t°C	py - cp $\Delta^{34}\text{S}$ t°C	Other $\Delta^{34}\text{S}$ t°C	
14041	Wh30 Martha Mine		R5168-43 R5168-42 R5168-30 R5168-1 R9401-13 R9401-14 R9401-15 R9401-16 R9401-17	py cp sp gn sp gn py cp sp	+ 2.1 + 1.6 + 1.2 - 0.8 + 2.0 + 0.3 + 2.8 + 3.5 + 1.8		0.5 680		
14051	Wh49a Martha Mine					2.0 320			
Wh49b						1.7 370	reversed		
14023	TL17 KARANGAHAKE Talisman Mine		R5168-54 R5168-8 R5168-3	cp sp gn	+ 3.0 + 2.9 + 0.7	2.2 290			
14066	Tui 25 TUI MINE Champion Vein 5 L	1	R5168-151 R5168-150 R5168-152	py cp ba	+ 2.5 + 1.7 +18.8		0.8 470		
14067	Tui 26 Ruakaka Vein	3							
14070	W13 WAIORONGOMAI Moa Vein	3	R5396-3 R5168-13 R5168-16	ba sp gn	+18.8 + 1.5 - 0.7				
14073	W122a No.1 Reef (Waterfall)	1	R5168-50 R5168-10 R5168-14 R5168-33 R5168-12 R5168-84 R5168-85 R5168-86 R5168-87 R5168-95 R5168-94 R5168-93	cp sp sp sp gn py cp sp gn cp sp gn	+ 1.7 + 0.3 + 0.8 + 1.0 - 1.4 + 1.4 - 0.1 - 0.4 - 2.2 + 0.6 0.0 - 1.6 + 3.0 + 0.2 - 2.0 + 1.8 + 2.5 + 1.5	2.2 290			
14075	W122b " "	1							
W127	" "	1							
14076	W133a Colonist Smithy Level	1				2.3 280			
W133b	Colonist Smithy Level	1				1.8 350	1.5 280		
W135	Colonist Smithy Level	1				1.6 390			
14077	W139a 1 May Queen 2 L	1	R5168-90 R5168-91 R5168-72 R5168-73 R5168-74 R5168-63 R5168-62 R5168-65 R5168-64	sp gn py cp sp py cp py cp	+ 3.0 + 0.2 + 1.8 + 2.5 + 1.5 + 1.5 + 1.5 + 1.3 + 1.2	2.2 290	0.7 520		
14078	W139a 2 " "	1					0.0 ∞		
W139a 3	" "	1					0.1 ∞		

TABLE 9-1; Continued

Sample Number V.U.W. No. Field No.	Location	Stage	*1 I.S.N. No.	*2 Mineral	$\delta^{34}\text{S}$ ‰ (CDT)	sp - gn $\Delta^{34}\text{S}$, t°C	py - cp $\Delta^{34}\text{S}$, t°C	Others $\Delta^{34}\text{S}$, t°C
14078	May Queen 2 L	1	R5168-79 R5168-80 R5168-81	py cp sp	+1.4 +1.2 +1.2		0.2	> 900
14080	May Queen 2 L	1	R5168-25 R5168-26 R5168-27 R5168-28	py cp sp gn	+1.3 +1.1 +0.9 -0.9		0.2	∞
14082	Bonanza Vein	1	R5168-40 R5168-41 R5168-42 R5168-77 R5168-78	py cp sp py sp	+0.8 +0.8 -0.2 +1.2 +1.4	1.8	0.4	350 800
14083	" "	1	R5168-88 R5168-89 R5168-82 R5168-83	py sp sp sp	+0.8 +1.3 +0.9 +0.9			
14085	Welcome Vein, Southern Adit	1	R5168-44 R5168-45 R5168-29 R5168-22	py cp sp gn	+2.2 +1.5 -1.0 +1.3	2.5	0.2	> 900
14086	" " " "	1	R5168-52 R5168-53 R5168-9 R5168-11	py cp sp sp	+0.7 +0.4 +0.3 -2.0		0.5	680
14088	Main Vein (Waterfall)	1	R5168-17 R5168-96 R5168-97	gn sp gn	-2.0 -2.0 +18.9	2.4		270
14089	" " " "	1	R5168-153 R5168-102 R5168-103	ba sp gn	+0.4 -1.4 -0.3	1.8		350
14092	Colonist Smithy Level	1	R9401-19	py		1.8		350
14099	W183b	1						
14100	Welcome Vein Hero 1100' Level	3 1						
W170	Vulcan 2 L	2						

*1 Institute of Nuclear Sciences (D.S.I.R.) sample number

*2 ba = barite cp = chalcopyrite gn = galena py = pyrite sb = stibnite sp = sphalerite
 sp(1) = light coloured sphalerite and sp(d) = dark coloured sphalerite.

function of the magnitude of their fractionation. Therefore the reliability should be in the order: pyrite-galena > sphalerite-galena > pyrite-chalcopryrite > pyrite-sphalerite > sphalerite-chalcopryrite (sulphate is omitted as it is rarely found in an equilibrium assemblage with the common sulphides). However, previous studies have found that pyrite, although seemingly in textural equilibrium with other sulphides, may not be in isotopic equilibrium, as shown by the failure to comply with the fractionation trend pyrite > sphalerite > chalcopryrite > galena. Therefore sphalerite-galena pairs appear to be the most reliable.

The $\Delta^{34}\text{S}$ ($\delta^{34}\text{S}_x - \delta^{34}\text{S}_y$) between cogenetic pairs of sphalerite-galena, pyrite-chalcopryrite, pyrite-sphalerite and sphalerite-chalcopryrite and their derived temperatures, using published fractionation curves, are given in Table 9-1. $\Delta^{34}\text{S}$ and calculated temperatures for all sphalerite-galena and pyrite-chalcopryrite pairs are presented, whereas this information is given for pyrite-galena, pyrite-sphalerite and sphalerite-chalcopryrite pairs only if sensible temperatures are obtained and sphalerite or galena is absent from the sample, precluding the use of sphalerite-galena pairs. The fractionation curves of Kajiwarra & Krouse (1971) are used for pyrite-galena, pyrite-chalcopryrite, pyrite-sphalerite and sphalerite-chalcopryrite pairs, whereas for sphalerite-galena pairs the curve of Czamanske & Rye (1974) is used, because of its demonstrated agreement with fluid inclusion filling temperatures in a number of ore deposits (Rye, 1974).

The maximum experimental error of ± 0.2 per mil on each mineral gives rise to an experimental error of ± 0.4 per mil on the $\Delta^{34}\text{S}$ of a mineral pair. The error on calculated temperatures is different for the different mineral pairs due to their different fractionations, for example at 300°C : $+40$ for pyrite-galena, $+65$ for sphalerite-galena, $+110$ for pyrite-chalcopryrite, $+200$ for pyrite-sphalerite and $+\infty$ for sphalerite-chalcopryrite, and increases with increasing temperature. For simplicity the error range on all calculated temperatures in this thesis are considered to be $\pm 40^\circ\text{C}$ for pyrite-galena, $\pm 60^\circ\text{C}$ for sphalerite-galena, $\pm 100^\circ\text{C}$ for pyrite-chalcopryrite, $\pm 150^\circ\text{C}$ for pyrite-sphalerite and $\pm 200^\circ\text{C}$ for sphalerite-chalcopryrite pairs.

The sphalerite-galena pairs give internally consistent temperatures which are also generally comparable to the fluid inclusion filling temperatures from quartz of the same depositional stage. However, pyrite-chalcopryrite pairs generally give higher temperatures than seemingly cogenetic sphalerite-galena pairs in some deposits and unreasonably high temperatures in others (c.f. Table 9-1) raising some doubt on the reliability

of the pyrite-chalcopyrite pairs altogether. Because galena and sphalerite are absent from some mineralisation stages, and in some deposits absent altogether, a solution to the pyrite-chalcopyrite problem is important.

The fractionation between pyrite and chalcopyrite for the expected temperature range, e.g. 1.4 per mil at 300°C, is larger than the estimated maximum experimental errors, which in this case would reduce the 1.4 per mil fractionation to 1.0 per mil. Therefore the absence of significant fractionation (>0.6 per mil, equivalent to $<600^{\circ}\text{C}$) between a pyrite-chalcopyrite pair is considered real and indicates that the mineral pair are not cogenetic. Two explanations are possible. Either the chalcopyrite was deposited after the pyrite under different chemical or temperature conditions or the chalcopyrite is formed partly by replacement of the pyrite without complete isotopic re-equilibration of the sulphur.

The determination of pyrite and chalcopyrite paragenesis by examination of their texture in polished ore mounts is generally not possible because the use of their grain boundary relationships and the criteria of idiomorphism has been shown to be unreliable (Stanton, 1972), with pyrite tending to form euhedral boundaries against other minerals even if precipitating later than the adjacent minerals. Isotopic evidence is therefore important.

Averaging pyrite-chalcopyrite values is no guarantee of achieving better accuracy because if the pyrite and chalcopyrite are out of equilibrium, due to either replacement of pyrite by chalcopyrite or different periods of deposition, all samples should be equally effected.

Consider, for example, the early pyrite, chalcopyrite and hematite mineralisation at Tui Mine. Robinson (1974) determined five $\Delta^{34}\text{S}$ py-cp values for samples from the Champion and Ruakaka Lodes, ranging from 0.6 to 1.2 per mil and averaging 1.0 per mil, the latter indicating a depositional temperature of $400 \pm 80^{\circ}\text{C}$. With the addition of sample 14066 ($\Delta^{34}\text{S}$ py-cp = 0.8 per mil) from this study the average value of six pyrite-chalcopyrite pairs is 0.9 per mil indicating a temperature of 430°C .

It could be argued that the occurrence of a range of Δ py-cp values indicates that the samples are not equally effected by the problem. If equilibrium was approached at some time, for example by a short period of overlapping pyrite and chalcopyrite deposition, the most representative analysis of the series will probably be the one with the largest Δ py-cp value (and therefore the lowest depositional temperature). In the case of the early Tui Mine mineralisation this would be 1.1 per mil, indicating a temperature of 370°C .

Therefore it seems that there is no unambiguous solution to the pyrite-

TABLE 9-2: A. Depositional temperatures calculated for some deposits from the isotopic fractionation of sulphur between co-genetic pairs of sulphide minerals (mainly sphalerite and galena).
 B. Isotopic composition of sulphur species in solution at the assigned temperatures (based on a combination of sulphur isotope and fluid inclusion data), calculated from the $\delta^{34}\text{S}$ values of the sulphide and sulphate minerals using fractionation factors from Ohmoto & Rye (1979).

	Stage	A		B		
		Temperatures from sulphur isotope data	Assigned Temperature ($^{\circ}\text{C}$)	Fluid Composition		
				$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (per mil)	$\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ (per mil)	$\delta^{34}\text{S}_{\text{SO}_2}$ (per mil)
Miners Head			425	+1		+10
Te Ahumata	1		250	}	{	+26
	2 _a		220			+28
	2 _b		240			+27
Northern Colville Peninsula (Sorry Mary Stm + Doctors Creek)		350	325	+3	+23	
Kuaotunu	2-3		250	-1	+24	
Tokatea	low levels		280	+2	+25	
Petote Stream	1	340	300	+2	+24	
Whangapoua	2		280	}	{	+20
	4		200			+27
Tapu Thames	"Cu-Bi"		400	+2* ¹		+12
	"Pb-Zn"	350* ¹	280	+2* ¹	+25* ²	
Thames	gold-pyrargyrite		230	+2* ³	+29	
	barite			-7	+19* ⁴	
Neavesville	Bluffs section		220	-2	+25	
Maratoto	2	300	280	+2	+25	
Waitekauri	2	340	280	+3	+26	
Waihi	low levels	340	325	+2	+23	
Karangahake	low levels	290	300	+3	+25	
Tui Mine	1	400* ⁵	400	+2* ⁶		+12
	2	320	300	+3* ⁶	+25	
	3 (barite)		200	-12	+18* ⁷	
Waiorongomai	1	320	325	+1	+22	
	3 (barite)		150	-16	+19* ⁸	

*¹ See Table I-L-2, data from Dr B.W. Robinson (pers. comm.)

*² Agrees with Robinson's (see Table I-L-2) +24.7 per mil value measured in barite from Monowai 3L

*³ See Table I-M-1, data from Dr B.W. Robinson (pers. comm.)

*⁴ Average $\delta^{34}\text{S}$ barite measured by Robinson (see Table I-M-1); used to calculate $\delta^{34}\text{S}_{\text{H}_2\text{S}}$

*⁵ Robinson (1974)

*⁶ Averaged from data reported by Robinson (1974)

*⁷ Averaged from $\delta^{34}\text{S}$ barite values reported by Robinson (1974) and sample 14067 listed in Table 9-1; used to calculate $\delta^{34}\text{S}_{\text{H}_2\text{S}}$

*⁸ Average $\delta^{34}\text{S}$ barite of samples 14070 and 14099 (see Table 9-1); used to calculate $\delta^{34}\text{S}_{\text{H}_2\text{S}}$

chalcopyrite problem. The accuracy of temperatures determined by pyrite-chalcopyrite fractionations can only be established by comparison with temperatures obtained by other methods or, if these are not available, by consideration of the paragenesis in comparison with similar mineral assemblages in other deposits where depositional temperature is known.

In the case of the early Tui Mine mineralisation an estimate of a realistic temperature can be made by considering the temperatures of later galena, sphalerite, pyrite and chalcopyrite mineralisation. Robinson (1974) reported average $\Delta\text{sl-gn}$ values of 2.3 per mil for the Champion Lode and 1.6 per mil for the Ruakaka Lode indicating temperatures of 280°C and 380°C respectively. The latter is probably too high because at least one $\Delta\text{sl-gn}$ value (1.2 per mil for samples 58-60, Table 5 of Robinson, 1974) gives an unrealistic temperature estimate of approximately 480°C indicating that the galena and sphalerite are not cogenetic. Re-averaging the other samples gives a $\Delta\text{sl-gn}$ value of 1.8 per mil and a temperature of 350°C for Ruakaka Stage 2 mineralisation. Stage 1 mineralisation was probably deposited at higher temperatures than Stage 2 mineralisation and therefore temperatures between 370 and 430°C would be possible. Robinson's original value of 400°C is used for thermochemical calculations in Appendix V and modelling of the mineralisation in Appendix I-U.

I consider therefore that temperatures of mineral deposition derived from $\Delta\text{py-cp}$ values are unreliable when unsupported by other evidence and at best may only represent maximum temperature values.

In conclusion, the temperatures assigned to the various deposits on the evidence of the fractionations of sulphur isotopes between coexisting mineral pairs are listed in Table 9-2. The temperatures presented represent three of the epithermal mineral assemblages (c.f. Chapter 4) as follows:

Pyrite - chalcopyrite assemblage: Tui Mine samples discussed previously. Average temperature assumed to be 400°C

Pyrite - sphalerite - galena - chalcopyrite assemblage: temperatures range between 255°C and 400°C but average around 300°C

Pyrite - sphalerite - galena - chalcopyrite - electrum - silver minerals assemblage: Maratoto samples giving three temperatures; 275°C , 290°C and 330°C .

FLUID CHEMISTRY

Sulphur Species in Solution

The dominant sulphur species present in hydrothermal fluids at high temperature ($\geq 400^\circ\text{C}$) are H_2S and SO_2 , whereas below $400 - 350^\circ\text{C}$ the reduced species may be represented by HS^- (in addition to H_2S), and oxidised species by sulphate (e.g. HSO_4^- and SO_4^{2-}). The exact temperature at which the concentration of SO_2 equals the concentration of total sulphate is dependant on the $f\text{H}_2\text{O}$, $\sum\text{S}$, $f\text{O}_2$, pH and salinity of the fluid (Ohmoto & Rye, 1979).

Ohmoto & Rye (1979) classified the aqueous sulphur species that could become quantitatively significant in hydrothermal fluids at temperatures below about 350°C into three groups: (1) H_2S , (2) HS^- and (3) sulphates (SO_4^{2-} , HSO_4^- , KSO_4^- , NaSO_4^- and CaSO_4). These authors considered that isotopic fractionation between H_2S and HS^- is much smaller than estimated by Sakai (1968) and that for practical purposes it can be assumed to be 0. Isotopic fractionations between the various sulphate species are also small (Ohmoto, 1972) and when compared with the large sulphate - sulphide fractionation can similarly be ignored. Therefore the isotopic compositions of the two sulphide species and the isotopic composition of the various sulphate species can be approximated by considering only a single species from each class. H_2S is chosen to represent the sulphide fraction, whereas SO_4^{2-} is used to represent the sulphates. This is because in most previous sulphur isotope studies of fossil and modern hydrothermal solutions these particular species have been considered to be the dominant representatives of their respective classes. Also, the isotopic fractionation between H_2S and SO_4^{2-} has been the subject of greater study than any other sulphate - sulphide pair and is therefore probably the best known.

$\delta^{34}\text{S}$ of Sulphur Species in Solution

When minerals are precipitated from a hydrothermal fluid, sulphide mineral sulphur fractionates against the aqueous sulphide species, whereas sulphate mineral sulphur fractionates against the aqueous sulphate species. Therefore the $\delta^{34}\text{S}$ values of the various sulphur species in solution (here represented by H_2S and SO_4^{2-}) can be calculated using the relevant fractionation factors (c.f. Fig. 10.3 of Ohmoto & Rye, 1979) if the temperature is known and isotopic equilibrium conditions are assumed.

Within the temperature range of interest here ($> 200^\circ\text{C}$) $\delta^{34}\text{S}_{\text{sp}}$ and $\delta^{34}\text{S}_{\text{cp}}$ are close to $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and therefore averaged analyses of either or

both of these minerals (depending on whether one or both are present) were used to approximate most of the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values presented in Table 9-2. Where sphalerite and chalcopyrite analyses were unavailable, $\delta^{34}\text{S}_{\text{py}}$ values were used taking into consideration the small fractionation between pyrite and H_2S . For sulphate the isotopic analyses of barite were used directly to approximate the parent SO_4^{2-} in solution, however most of the $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ values of Table 9-2 were derived using the fractionation between SO_4^{2-} and H_2S at the assigned temperature.

$\delta^{34}\text{S}$ of the Total Sulphur in Solution

$\delta^{34}\text{S}$ of the total sulphur in solution ($\delta^{34}\text{S}_{\Sigma\text{S}}$) is the sum of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$. This parameter is not only dependant on the individual values of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ but also on the relative concentrations of sulphide and sulphate (c.f. Fig. 5 of Rye & Ohmoto, 1974).

$\delta^{34}\text{S}_{\Sigma\text{S}}$ in hydrothermal solutions can be deduced by considering the $\delta^{34}\text{S}$ values of the sulphide and sulphate minerals and the mineral stability relations on $f\text{O}_2$ versus pH diagrams. Some mineral assemblages limit the possible values of $\delta^{34}\text{S}_{\Sigma\text{S}}$ to a small range.

Stage 1 mineralisation at Tui Mine consists of quartz, pyrite, chalcopyrite and hematite with minor gold, bismuthinite and tetradymite. Fractionation of $\delta^{34}\text{S}$ between coprecipitated pyrite and chalcopyrite was used by Robinson (1974) to indicate a depositional temperature around 400°C . Robinson's (1974) $f\text{O}_2$ versus pH diagram for this mineralisation is reproduced in Fig. I-U-9 of Appendix I. The hydrothermal fluid in equilibrium with the observed mineral assemblage must plot near the pyrite + chalcopyrite/hematite boundary and therefore probably had a $\text{H}_2\text{S} : \text{SO}_4^{2-}$ ratio greater than 1 (1:2 ?). The average $\delta^{34}\text{S}$ value for Stage 1 chalcopyrite analysed by Robinson is 2.5 per mil indicating a $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ of approximately 2.5 per mil. At 400°C $\Delta_{\text{H}_2\text{S}-\text{SO}_4^{2-}}$ is approximately 16 per mil and therefore $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ would be 18.5 per mil. If the ratio of $\text{H}_2\text{S}:\text{SO}_4^{2-}$

in the fluid is 1:2, $\delta^{34}\text{S}_{\text{S}} \approx 13$ per mil. Given the inaccuracies of the temperature measurement, construction of the $f\text{O}_2$ versus pH diagram (at 350°C as opposed to isotopic data at 400°C), the value of $\Delta_{\text{H}_2\text{S}-\text{SO}_4^{2-}}$ and the possibility that equilibrium may not have been completely achieved, only boundary limits of say +10.5 per mil ($\text{H}_2\text{S} : \text{SO}_4^{2-} = 1:1$) and +16.0 per mil ($\text{H}_2\text{S} : \text{SO}_4^{2-} = 1:5$) can be confidently assigned to $\delta^{34}\text{S}_{\text{S}}$. However, Robinson (1974) used the $\delta^{34}\text{S}$ value of +16 per mil for late stage barite to fix the value of $\delta^{34}\text{S}_{\text{S}}$ by assuming that this barite was deposited by a fluid containing sulphur almost exclusively as SO_4^{2-} in which case $\delta^{34}\text{S}_{\text{S}} \approx \delta^{34}\text{S}_{\text{SO}_4^{2-}} \approx +16$ per mil.

Similarly, late stage barite from Thames (Kuranui Mine $\delta^{34}\text{S} = +19.1$ per mil, Moanataiari 3 level $\delta^{34}\text{S} = +17.2$ per mil, and Halycon Mine $\delta^{34}\text{S} = +19.7$ per mil, Table I-M-1; data from Dr B.W. Robinson, pers. comm.) and Waiorongomai ($\delta^{34}\text{S} = +18.8$ per mil) indicates precipitation from a sulphate dominated fluid with $\delta^{34}\text{S}_{\text{S}}$ around +16 per mil.

An alternative explanation for these barites and those of Tui Mine could be precipitation from a sulphide dominated fluid with a low value of $\delta^{34}\text{S}_{\text{S}}$. However, $\Delta_{\text{H}_2\text{S}-\text{SO}_4^{2-}}$ at the temperature of barite precipitation (probably 200°C or less) is approximately +30 per mil (or greater with decreasing temperature), necessitating a $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ more negative than -10 per mil with a similar value for $\delta^{34}\text{S}_{\text{S}}$, a situation not compatible with the $\delta^{34}\text{S}$ values for earlier sulphides (between -1 and +4 per mil). Therefore these barites could not have been precipitated in isotopic equilibrium with fluids having a $\delta^{34}\text{S}_{\text{S}}$ around 0 per mil under any combination of H_2S and SO_4^{2-} .

In contrast, barite from the Tapu - Thames area (Monowai 3 level, $\delta^{34}\text{S} = +24.7$ per mil, Dr B.W. Robinson, pers. comm.) was precipitated from a fluid with $\delta^{34}\text{S}_{\text{S}}$ around 0 per mil and dissolved sulphur predominantly in reduced form because Merchant (1978 p 239) recorded fluid inclusion filling temperatures for this occurrence between 282 and 330°C ($\Delta_{\text{H}_2\text{S}-\text{SO}_4^{2-}}$

is approximately 22 per mil at 300°C).

Late mineralisation was also used to determine $\delta^{34}\text{S}_{\text{S}}$ at the Maratoto Mine by Robinson & Christie (1980). They recorded $\delta^{34}\text{S}$ values for main stage sulphides (pyrite, chalcopyrite, sphalerite and acanthite) averaging 2.1 per mil, whereas two analyses of late stage pyrite gave $\delta^{34}\text{S}$ values of +16.0 and +16.9 per mil. Sulphate minerals have not been reported in any stage of the mineralisation. A $\delta^{34}\text{S}_{\text{S}}$ of +16 per mil was concluded by assuming that main stage mineralisation was formed from a fluid with an $\text{H}_2\text{S} : \text{SO}_4^{2-}$ ratio of approximately 1:1 but that this ratio changed with time so that during late stage pyrite precipitation the fluid sulphur species was almost entirely H_2S and $\delta^{34}\text{S}_{\text{S}} \approx \delta^{34}\text{S}_{\text{H}_2\text{S}} \approx \delta^{34}\text{S}_{\text{py}}$.

The presence of pyrrhotite in assemblages of sulphide minerals, with $\delta^{34}\text{S}$ values around +1 per mil, at Miners Head (depositional temperature approximately 425°C) and in the low levels of the Waihi Mine (depositional temperature approximately 325°C) necessitates a similar interpretation to that for the late Maratoto fluid. Precipitation of pyrrhotite (with pyrite) at the temperatures considered here occurs from fluids in which sulphide predominates over sulphate, or SO_2 in the case of Miners Head (Figs I-A-7 and I-S-9 of Appendix I). Therefore $\delta^{34}\text{S}_{\text{S}}$ of the hydrothermal fluid is not substantially different from $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and hence $\delta^{34}\text{S}$ of the sulphides. Allowing for the fact that pyrrhotite is a minor phase relative to other sulphides occurring at Miners Head and is very rare in the low levels of the Waihi Mine, $\delta^{34}\text{S}_{\text{S}}$ at these localities was probably between +1 and +8 per mil. A value of +5 is selected as being representative.

Minerals that limit the possible isotopic composition of the parent hydrothermal fluids are absent from most other deposits for which $\delta^{34}\text{S}$ values of the sulphides are known. Their mineral assemblages and sulphide sulphur isotope data are compatible with $\delta^{34}\text{S}_{\text{S}}$ values between approximately 0 and +18 per mil by considering different mixes of sulphate to sulphide concentrations in the hydrothermal fluid. Low values of $\delta^{34}\text{S}_{\text{S}}$

TABLE 9-3: $\delta^{34}\text{S}$ values of the total sulphur in solution ($\delta^{34}\text{S}_{\Sigma\text{S}}$) during formation of some of the deposits and the probable source of sulphur. $\delta^{34}\text{S}_{\Sigma\text{S}}$ values were derived from the dissolved sulphide/dissolved sulphate ratios of the hydrothermal fluids, estimated on the $f\text{O}_2$ versus pH diagrams (Appendix 1), and the individual values of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ (Table 9-2).

	$\delta^{34}\text{S}_{\Sigma\text{S}}$	Source of Sulphur
Miners Head	+ 1	Magmatic
Te Ahumata	+ 1	Magmatic
Northern Colville Peninsula (Sorry Mary Stm + Doctors Creek)	+ 3	Magmatic
Kuaotunu	0	Magmatic
Tokatea	+ 2	Magmatic
Whangapoua	0	Magmatic
Tapu Thames (Cu-Bi and Pb-Zn)	+ 2	Magmatic
Thames (gold pyrrargyrite)	+ 16	Sedimentary
Neavesville	+ 16	Sedimentary
Maratoto	+ 16	Sedimentary
Waitekauri	+ 4	Magmatic
Waihi	+ 5	Magmatic
Karangahake	+ 5	Magmatic
Tui Mine	+ 16	Sedimentary
Waiorongomai	+ 16	Sedimentary

(e.g. +5 per mil) are consistent with high sulphide to sulphate concentrations, whereas high values of $\delta^{34}\text{S}_{\text{S}}$ (e.g. +16 per mil) are consistent with sulphate equal to or in excess of sulphide.

In conclusion, values of $\delta^{34}\text{S}_{\text{S}}$ which have been determined for some of the mineralisations of the Hauraki Gold - Silver Province, by the methods outlined above, are listed in Table 9-3.

SOURCE OF SULPHUR

Introduction

Two possible sources of sulphur for the mineralisations of the Hauraki Gold - Silver Province have been discussed previously in the literature: sedimentary and magmatic.

Sedimentary Sulphur

Robinson (1974) and Robinson & Christie (1980) postulated that the sulphur in sulphide and sulphate minerals at Tui Mine and Maratoto originated as Jurassic sea water sulphate deposited with sediments now forming the greywacke basement of the Coromandel Peninsula and Great Barrier Island. Sea water sulphate during the Jurassic is believed to have had an average $\delta^{34}\text{S}$ value of +17 per mil (Claypool *et al.*, 1972) and therefore could readily account for the $\delta^{34}\text{S}_{\text{S}}$ value of +16 per mil postulated for the hydrothermal fluids.

Similarly, Kusakabe (1974) considered that his assigned value of +15.1 per mil for $\delta^{34}\text{S}_{\text{S}}$ of Wairakei geothermal waters indicated a Mesozoic greywacke source for the sulphur.

Robinson & Christie (1980) proposed that the mechanisms involved were the solution of sulphate from the greywacke suite rocks by the hydrothermal fluid and gradual reduction to sulphide, by Fe^{2+} in the mafic minerals of the volcanic wall rocks or by magmatic hydrogen, during transport. The $\delta^{34}\text{S}$ values of the sulphide and sulphate species in solution gradually become heavier as the proportion of sulphide to sulphate increases, provided isotopic equilibrium conditions prevail (complete exchange between sulphide and sulphate).

Roser (in prep.) suggested that sulphur is present in greywacke as sulphate; in connate water, and sulphide of both volcanic and sedimentary origin. $\delta^{34}\text{S}$ values between -5.6 and -4.0 per mil were determined from six samples of pyrite in Wellington argillites by Roser (in prep.), whereas Mr. F. Reid (pers. Comm.) determined values of +13.5 and +13.9 for pyrites

TABLE 9-4: $\delta^{34}\text{S}$ values of pyrite in greywacke suite rocks of the Kawerau area. Data courtesy of Mr F. Reid

A. Pyrite in fresh greywacke from surface exposures in the Kawerau area

Sample Number		$\delta^{34}\text{S}_{\text{CDT}}$ Pyrite
<u>V.U.W. No.</u>	<u>Field No.</u>	<u>(per mil)</u>
15960	HQ2	+13.5
16024	OS2	+13.9

B. Pyrite in hydrothermally altered greywacke from drill core

Sample Number		Drill hole	Depth	$\delta^{34}\text{S}_{\text{CDT}}$ Pyrite
<u>V.U.W. No.</u>	<u>I.N.S. No.</u>	<u>No.</u>	<u>m</u>	<u>(per mil)</u>
15980	R5865/01	KA25	1164	+5.9
15981	R5865/03	KA25	1195	+6.0
15984	R5865/07	KA25	1398-1399	+5.5
15995	R5865/04	KA23	1036	+4.5
15996	R5865/08	KA23	1067	+5.0
15999	R5865/02	KA23	995	+3.9
16001	R5865/05	KA22	1156-1157	+6.2
-	R5865/06	KA24	1210	+6.1
-	R5865/09	KA24	1234	+5.6

in unaltered greywacke (Reid's samples HQ 2 and OS 2 respectively, Table 9-4) from Kawerau. In contrast, Reid determined that hydrothermally altered greywacke of the Kawerau geothermal area contained pyrite with $\delta^{34}\text{S}$ values between +3.9 and +6.2 per mil (Table 9-4).

Giggenbach (1977) analysed the isotopes of sulphur in unaltered greywacke from areas bordering the Taupo Volcanic Zone. He separated sulphide and sulphate fractions chemically and concluded that average $\delta^{34}\text{S}$ values of both fractions were between +6 and +7 per mil, with ranges of -7.3 to +15.7 per mil for sulphide and -7.8 to +17.8 per mil for sulphate.

Giggenbach's (1977) maximum value for sulphate is similar to the +17 per mil value suggested by Robinson (1974) for sea water sulphate incorporated into the sediments, however the range of values measured by Giggenbach (down to -7.8 per mil) suggests that some secondary process has variably depleted the sedimentary sulphate of ^{34}S . This may be due to one, or a combination, of the following: diagenesis, metamorphism, hydrothermal alteration, ground water leaching, surface weathering or surface bacterial action. If some of these latter processes have been active in depleting ^{34}S , Giggenbach's light $\delta^{34}\text{S}$ sulphate values may not be representative of greywacke at depth (e.g. 1-3 km). The average value in these deep rocks is probably heavier than the +7 per mil value suggested by Giggenbach and may be as much as the +17 per mil value suggested by Robinson (1974), Kusakabe (1974) and Robinson & Christie (1980), however exact definition is not possible with the information available at present.

The $\delta^{34}\text{S}$ of total sulphur in greywacke depends on the individual $\delta^{34}\text{S}$ values of sulphate, sulphide and other sulphur sources and their proportions. Therefore values from about +17 per mil to some lighter value are possible.

Magmatic Sulphur

Measured $\delta^{34}\text{S}$ values of igneous rocks average close to the meteoritic value of 0 per mil and therefore primary (mantle) magma is considered to have a $\delta^{34}\text{S}$ value of 0 per mil (Ohmoto & Rye, 1979).

Although no measurements have been made on the volcanic and intrusive rocks of the Coromandel and Whitianga Groups they are considered to have $\delta^{34}\text{S}$ values heavier than the meteoritic value due to the contribution of crustal material in their formation. Based on measurements of the sulphur isotopes in greywacke, and the values reported in the literature for geothermal waters at Wairakei and Ketetahi, and fumarolic discharges from White Island, Giggenbach (1977) derived the following series of $\delta^{34}\text{S}$ values for the rocks of the Taupo Volcanic Zone: basalt, 0 per mil; andesite,

+2 to +4 per mil (in accord with the White Island measurements of +3 to +3.5 per mil); rhyolite, +4 to +5 per mil and greywacke, +6 to +7 per mil.

Similar values of +2 to +4 per mil for andesites are postulated here for the Coromandel Group andesites and dacites but the rhyolites of the Whitianga Group are probably heavier than Giggenbach's range for Taupo rhyolites, especially if the value for Manaia Hill Group greywacke is around +17 per mil (see previous section).

Discussion

$\delta^{34}\text{S}_{\text{S}}$ of andesitic magma is believed to be around +4 per mil, whereas $\delta^{34}\text{S}_{\text{S}}$ of greywacke suite rocks could be as high as +17 per mil. $\delta^{34}\text{S}_{\text{S}}$ of rhyolitic magma is probably intermediate. Therefore if a sulphur source with a $\delta^{34}\text{S}$ value of around +4 per mil is indicated for a specific deposit, a magmatic origin is concluded. In contrast, if a value of around +16 per mil is indicated the sulphur probably originated from the sedimentary rocks. Values between +4 and +16 per mil may indicate either a rhyolite magma or sedimentary source of sulphur.

Suggested sources of sulphur for some of the deposits of the Hauraki Gold - Silver Province are listed in Table 9-3.

CONCLUSIONS

Both magmatic and sedimentary sulphur are considered to have contributed to the mineralisations of the Hauraki Gold - Silver Province although their respective roles differ between individual deposits.

CHAPTER 10PHYSICOCHEMISTRY AND MODEL OF
PORPHYRY COPPER MINERALISATIONPHYSICOCHEMISTRYIntroduction

The geochemical environments of mineralisation for the individual porphyry copper deposits of the Hauraki Gold - Silver Province are estimated in Appendix I using data calculated in Appendix V. This section collates and summarises that information into a comparative description of all of the deposits.

Geochemical Environment

Porphyry copper deposits of the Hauraki Gold - Silver Province (the Needles, Miners Head, Paritu, Manaia and Tapu - Thames) are believed to have formed at temperatures above 400°C from solutions in equilibrium with biotite or sericite (propylitic or quartz - sericite alteration). Secondary orthoclase has been identified only at Paritu where it occurs rarely, possibly associated with the formation of tourmaline veinlets.

The mineral assemblages at the various locations are: (1) Needles: bornite and chalcopyrite; (2) Miners Head: chalcopyrite, pyrite, sphalerite, pyrrhotite, argentian pentlandite and galena; (3) Paritu Coastal Section: pyrite, chalcopyrite, molybdenite, pyrrhotite, arsenopyrite and wolframite; (4) Paritu Drill Holes (biotite quartz diorite phase): pyrite, chalcopyrite and magnetite; (5) Manaia: pyrite, chalcopyrite, magnetite; and (6) Tapu - Thames: pyrite, chalcopyrite and a sequence of pyrrhotite, magnetite and hematite. In addition tourmaline occurs at Paritu (Coastal Section) and Manaia.

Fluid inclusion evidence is available only for the Miners Head deposit which formed at approximately 425°C from non-boiling fluids with a salinity of approximately 10 eq. wt. % NaCl.

The mineralisations are modelled on an fO_2 versus temperature diagram (Fig. 10-1) at a temperature of 425°C. Sulphur was present in the fluid predominantly as H_2S . The absence of bornite from most deposits and presence of pyrrhotite (a mineral rarely recorded from porphyry copper deposits) in some, suggests low sulphur fugacities. The low oxygen fugacities indicated by the absence of magnetite from assemblages of the Paritu Coastal Section and some stages of other deposits (B in Fig. 10-1)

Figure 10-1: Oxygen fugacity versus temperature diagram (based on Fig.4 of Burnham & Ohmoto, 1980) relating the f_{O_2} - t fields of the Hauraki Gold-Silver Province porphyry mineralisation (all modelled at $425^{\circ}C$) to the stability fields of pertinent iron-bearing mineral assemblages (at approximately 1 kbar), aqueous sulphur species (at $pH=4$) and overseas porphyry copper deposits (stippled area). The Needles bornite + chalcopyrite, and the Paritu and Manaia magnetite + pyrite + chalcopyrite mineralisations are represented by field 1, whereas field 2 is the Miners Head and Paritu Coastal Section pyrrhotite + pyrite + chalcopyrite mineralisations. The arrow represents the changing physicochemical conditions indicated by the iron-bearing mineral sequence: pyrrhotite followed by magnetite followed by hematite, identified from the Tainui (Tapu-Thames) porphyry deposits by Merchant (1978). Fluids containing sulphur predominantly in reduced form are indicated for the Hauraki Province mineralisations, however fluids with predominantly oxidised sulphur species (more typical of economic porphyry copper deposits c.f. Burnham & Ohmoto, 1980) may have been present at the Needles, Paritu (Oongohi Stream), Manaia and Tainui if the deposits were formed at much higher temperatures (e.g. $600^{\circ}C$).

implies low total sulphur for these mineralisations (c.f. Burnham & Ohmoto, 1980).

These features may account for the indicated poor development of copper and molybdenum mineralisation in the deposits.

MODEL FOR PORPHYRY COPPER MINERALISATION

Introduction

Several genetic features of overseas porphyry copper deposits and models for their formation are briefly described below before a model is presented for the deposits in the Hauraki Gold - Silver Province. For discussions of the geology, mineralisation and classification of porphyry copper deposits the reader is referred to the original references cited below and the reviews by Lowell & Guilbert (1970), Rose (1970), Guilbert & Lowell (1974), Hollister (1978) and Titley & Beane (1981).

Genetic Features of Porphyry Copper Deposits

Although individual porphyry copper deposits differ in specific details such as alteration and ore mineral assemblages, Gustafson & Hunt (1975) considered that these differences are only "variations on a theme" and that similar processes and evolutionary trends are common to all porphyry copper deposits.

Several features commonly found in overseas porphyry copper deposits, that are important to the consideration of their genesis, are:

1. their association with porphyritic calc-alkaline or alkaline rocks,
 2. their relative shallow emplacement (generally in the subvolcanic environment),
 3. the general occurrence of concentric patterns of hydrothermal alteration and mineralisation,
- and 4. the usual presence of breccia features such as "crackle" breccias, breccia dikes and breccia pipes.

In addition, stable isotope evidence suggests that waters associated with potassic zone alteration and mineralisation were magmatic, whereas those associated with alteration and mineralisation in the phyllic zone (and therefore probably also the argillic and propylitic zones) were meteoric or formational waters (c.f. Taylor, 1974, 1979; Sheppard, 1977).

Fluid inclusions also record the existence of two separate fluids, one a highly saline fluid at high temperature (700 - 500°C), boiling in

Figure 10-2: Models previously proposed (see text) for porphyry mineralisation:

- A. Mineralisation and hydrothermal alteration are formed by a magmatic fluid moving out from a crystallising pluton.
- B. Proximal high temperature mineralisation and high grade hydrothermal alteration are formed by a magmatic aqueous vapour phase violently released from a pluton during crackle breccia formation. Relatively distal, lower temperature mineralisation and lower grade hydrothermal alteration are formed by incursion of, and mixing of the magmatic fluid with, ground water convection cells.
- C. Mineralisation and hydrothermal alteration are formed by ground water convection through a subsolidus pluton. A vapour dominated steam phase is generated locally above the pluton.

some deposits, and the other a cooler ($400 - 200^{\circ}\text{C}$) non-boiling fluid of moderate salinity (Nash, 1976).

Models Proposed by Previous Writers

Fig. 10-2 illustrates three models that have been proposed to explain the formation of porphyry copper deposits:

(a) The first model is a simple orthomagmatic model (e.g. Rose, 1970) in which a magmatic fluid moves out from the intrusion forming the different alteration and mineralisation zones in response to falling temperature.

(b) The evidence from stable isotopes and fluid inclusions outlined in the previous section has prompted several authors (e.g. Burnham, 1967, 1979; Holland, 1972; Whitney, 1975; Henley & McNabb, 1978; and Burnham & Ohmoto, 1980) to propose the involvement of a magmatic aqueous vapour phase generated by retrograde boiling (c.f. Burnham, 1979) during the early stages of hydrothermal alteration and mineralisation. In some models (e.g. Henley & McNabb, 1978; Burnham, 1979; Burnham & Ohmoto, 1980) circulating ground water (meteoric or formation water) becomes the predominant alteration and mineralising agent during the intermediate and late stages.

(c) Cathles (1977) proposed a model in which mineralisation and hydrothermal alteration is formed by ground water convection through a subsolidus pluton. He considered that a vapour dominated steam zone would be generated above some plutons and would account for the boiling recorded by fluid inclusions. The magmatic water input in this system is presumably small compared to models (a) and (b).

Factors Determining the Style of Alteration and Mineralisation

The predominant factors which determine the style of alteration and mineralisation in porphyry copper deposits, and which of the three models described previously operates, are:

- (1) water content of the magma,
 - (2) potassium content of the magma,
 - (3) depth of emplacement of the intrusion,
- and (4) tensile strength of the country rocks.

(1) Water Content of the Magma

A minimum content of water is required in the magma to generate a magmatic aqueous phase for mineralisation, however too much water will cause the magma to crystallise in the plutonic environment (Burnham, 1979; Burnham & Ohmoto, 1980; Gustafson, 1979). Between these two extremes the

relative water content determines the quantity of mineralising fluid available and, together with some other factors (e.g. the depth of mineralisation and tensile strength of the country rocks), the degree of retrograde boiling and brecciation of the country rock (generally the upper solidified parts of the pluton). Some intrusives may contain sufficient water to generate several cycles of retrograde boiling, brecciation and mineralisation.

(2) Potassium Content of the Magma

The potassium content of the magma influences the compositions of both the crystallising rock (increasing potassium content down the series; quartz diorite, granodiorite and quartz monzonite) and the partitioning magmatic aqueous phase (e.g. Na/K and KCl/HCl ratios). These factors are important in determining the pattern of hydrothermal alteration produced (i.e. whether abundant K-feldspar alteration occurs in the potassic zone). High potassium and low potassium type deposits are represented by the 'Lowell & Guilbert model' and the 'diorite model' respectively (the reader is referred to Hollister, 1978, for a review of these models).

The porphyry copper deposits of the Hauraki Gold - Silver Province may be classified as diorite type deposits because they are associated with quartz diorite and granodiorite intrusives and secondary orthoclase is either absent or not well developed in their "potassic zones" (c.f. the alkali silicate alteration of Tapu - Thames; Merchant, 1978). The predominant type of alteration associated with copper mineralisation in these deposits is quartz - sericite (phyllic).

(3) Depth of Emplacement of the Intrusion

The effects on porphyry copper deposit morphology resulting from different depths of magma emplacement were discussed by Sutherland - Brown (1976) and Nielsen (1976). Deposits formed in the plutonic environment contain mineralisation generally confined to veins and have poorly defined hydrothermal alteration zones. In contrast, hypabyssal and volcanic porphyry copper deposits contain both disseminated and vein mineralisation and the hydrothermal alteration zones are generally well developed.

These properties probably result from differences in rock permeability and the ability of retrograde boiling to produce extensive fracture systems in shallow environments, allowing for more extensive circulation of hydrothermal fluid (both magmatic and meteoric - formation waters) and

hydrothermal alteration.

In the depth related classification scheme of Nielsen (1976) the deposits at the Needles, Miners Head, Paritu and Manaia are hypabyssal types, whereas the Tapu - Thames deposits are volcanic. Breccia dikes (hydrothermal and igneous) occur associated with most of the deposits and the deposits at the Needles and Miners Head are themselves mineralised breccia dikes. Quartz vein stockworks, although identified from the Paritu, Manaia and Tapu - Thames deposits, are not extensive, indicating that either crackle breccias were not well developed for one of several reasons (e.g. low water content of the magma) or that the main vein stockwork zones are below the levels of exposure or depths drilled.

(4) Tensile Strength of the Country Rocks

Burnham & Ohmoto (1980) and Sillitoe (1980) discussed the effects of fracture and failure of the overlying country rocks during retrograde boiling of subvolcanic intrusives. This parameter is interdependent with depth.

Limited fracturing may produce the crackle breccias believed to be associated with stockwork vein formation, whereas large fractures may allow the formation of hydrothermal breccia, igneous breccia or porphyry dikes and pipes. In the extreme case, complete failure of the rock may result in caldera formation and explosive volcanism with dispersion of the metals.

Merchant (1978) identified several circular geomorphic features in the andesites of the Tapu - Thames area and suggested that they were eroded calderas. Some are coincident with the centres of porphyry mineralisation (e.g. a 2 km diameter feature surrounds the Ohio Creek deposit) and offer another possible explanation for the presently indicated poor development of subvolcanic porphyry copper mineralisation (c.f. Sillitoe, 1980).

Model for the Hauraki Gold - Silver Province Porphyry Copper Deposits

The model illustrated in Fig. 10-3 and described below is based mainly on Sillitoe (1973; 1980), Burnham (1979) and Burnham & Ohmoto (1980) and emphasises the development of the patterns of hydrothermal alteration and mineralisation in the porphyry copper deposits of the Hauraki Gold - Silver Province. It is divided into two major environments: magmatic and hydrothermal.

Figure 10-3: Model for porphyry copper formation in the Hauraki Gold-Silver Province. Following emplacement of a pluton (A), the concentration of volatiles near the roof causes the development of a cupola zone intruded into the hypabyssal environment (B). Ground water convection cells form (C), causing widespread hydrothermal alteration in the country rocks. Venting of the cupola to the surface produces subaerial volcanism. Cessation of volcanism and retrograde boiling, accompanying crystallisation of the magma, forms a magmatic aqueous vapour phase which accumulates near the top of the cupola (D). Eventually the fluid pressure exceeds the confining pressure and hydraulic fracturing of the confining rocks occurs (E). The magmatic fluid is violently expelled through the newly created channels to form stockworks, veins, breccia dikes or igneous dikes. Mineral deposition may result from the effects of mixing of the magmatic fluid with ground water.

Major findings

(equivalent to the H_2O - saturated solidus of the magma i.e. the temperature, for a given total pressure, below which hydrous silicate melt is not thermodynamically stable) NaCl and KCl make up approximately 90% of the total chlorides and the NaCl/KCl and $\text{H}_2\text{S}/\text{SO}_2$ ratios typically ≈ 1 .

Hydrothermal Environment

After leaving the crystallising magma the magmatic hydrothermal vapour phase reacted with the solidified parts of the intrusion and the country rocks causing hydrothermal alteration and mineral deposition.

In some deposits the NaCl/KCl ratio of the fluid was sufficiently low to cause potassium metasomatism ("potassic" alteration) and the formation of secondary quartz and biotite (Miners Head and Tapu - Thames) or orthoclase (Paritu Coastal Section), whereas in others with relatively high NaCl/KCl and low KCl/HCl ratios, hydrogen metasomatism was the major form of high temperature alteration, forming secondary quartz and sericite (equivalent to phyllic alteration).

In the former deposits, potassium metasomatism caused depletion of potassium in the fluid and, together with the release of Na^+ by the wall rocks, resulted in an increase in the NaCl/KCl ratio of the fluid. Therefore a stage of hydrogen metasomatism was also initiated in these deposits. Dissociation of HCl and other acids with decreasing temperature was probably also an important factor in causing hydrogen metasomatism.

At some stage in these sequences the magmatic hydrothermal fluid encountered and mixed with deeply circulating meteoric water. In most porphyry copper deposits this is considered to occur in the phyllic alteration zone and is an important mechanism of mineral deposition.

The meteoric water caused hydrolysis of the magmatic SO_2 to H_2S and H_2SO_4 via the reaction:

Burnham & Ohmoto (1980) suggested that SO_2 may also react with ferrous iron bearing minerals in the wall rocks via:

The resultant increase in H_2S activity caused metal sulphide (particularly pyrite) deposition and production of HCl as follows:

The magmatic fluids of the Hauraki Gold - Silver Province had relatively high $\text{H}_2\text{S}/\text{SO}_2$ ratios (c.f. Fig. 10-1), especially in the case of the Paritu Coastal Section, and therefore the SO_2 hydrolysis effect would be limited and probably accounted for only minor metal sulphide deposition. Dilution

and a decrease in temperature during mixing of the magmatic fluid with meteoric water were probably the main deposition mechanisms.

In the deposits with the lowest H_2S/SO_2 ratios in their magmatic fluids (Manaia and Tapu - Thames), the SO_2 hydrolyses and subsequent acid producing reactions were sufficient to shift the fluid/mineral equilibria from sericite to kaolinite (or pyrophyllite) and produce an argillic alteration zone consisting of kaolinite, sericite, quartz and pyrite. This argillic alteration tended to neutralise the pH of the fluid, increasing the KCl/HCl ratio.

With the increasing KCl/HCl ratio, caused by quartz - sericite (phyllic) or argillic alteration, together with decreasing temperature, reactions involving CO_2 and calcium metasomatism became important and minerals such as chlorite, calcite and epidote were produced, forming propylitic alteration zones. However, some of these zones probably existed before porphyry copper mineralisation, due to the pre-existing hot meteoric water convective system formed at an early stage of intrusive activity. In these cases the quartz - sericite and argillic alteration zones probably overprinted large volumes of propylitically altered rock.

CHAPTER 11PHYSICOCHEMISTRY AND MODEL OFEPITHERMAL VEIN MINERALISATIONINTRODUCTION

This chapter investigates the physicochemistry of the depositional environments of the various types of epithermal mineralisation found in the Hauraki Gold - Silver Province in order to identify the characteristic processes that form the individual mineral assemblages. A model for the deposition of a hypothetical deposit, containing the various mineral assemblages, is presented.

However, before commencing this discussion it is necessary to briefly review the current knowledge on the transport of metals and non-metals in hydrothermal solutions and the processes that cause mineral deposition.

REVIEW OF MINERAL TRANSPORT AND DEPOSITION
IN THE HYDROTHERMAL ENVIRONMENTTransport of Metals in Hydrothermal Solutions

The experimental and thermodynamic evidence on the solubility of metals in hydrothermal solutions, reviewed by Barnes (1979), indicates that metals are transported in hydrothermal solutions as chloride and sulphide complexes, although other ligands (e.g. hydroxide) may be important under certain chemical conditions.

Present evidence suggests that cadmium, copper, iron, lead, silver and zinc are transported predominantly as chloride complexes, whereas antimony and mercury are transported predominantly as sulphide complexes (c.f. Barnes, 1979).

Gold is transported as both chloride and sulphide complexes, their relative importance being dependant on the temperature and oxidation state of the fluid. Gold chloride complexes appear to be dominant in high temperature and relatively oxidising solutions, whereas gold thio complexes are dominant at temperatures below approximately 300°C and under relatively reducing conditions.

Thermodynamic and mineral structural evidence, together with the evidence indicated by the natural occurrence of silver minerals in ore deposits and geothermal areas, suggests that in addition to chloride complexes, sulphide complexes are also important transporters of silver. Barnes (1979) suggested that at lower temperatures sulphide complexes

are more important, as for gold, but that above 300°C chloride complexes become dominant. The separation between regions of dominance of chloride and sulphide complexes is complex and depends on conditions of ΣS , ΣCl , pH, T and fO_2 .

Deposition of Metals from Hydrothermal Solutions

Introduction

The deposition of metals from hydrothermal solutions occurs at a point where the transporting complexes become unstable. Barnes (1979) discussed representative reactions for metal sulphide deposition from chloride and sulphide complexes. His reactions and the most important factors that make them proceed (listed in order of effectiveness) were as follows:

(a) Chloride complexed metals

Proceeds with $+\Delta m_{S^{2-}}$, $-O_2$, $+\Delta pH$, dilution, $-\Delta T$, $-\Delta P_t$

(b) Sulphide complexed metals

Proceeds with $-\Delta m_{S^{2-}}$, $+O_2$, $-\Delta pH$, dilution, $-\Delta T$, $-\Delta P_t$

$\Delta m_{S^{2-}}$

A change in the concentration of sulphide [e.g. H_2S for equation (11-1) and $HS^- + H_2S$ for equation (11-2)] has the opposite effect on the solubility of the two types of complexes.

The concentration of H_2S in solution may increase (causing deposition of metals from chloride complexes) by sulphate reduction; reaction from organic compounds or mixing with sulphide solutions, whereas it may decrease (causing deposition of metals from sulphide complexes) because of boiling and consequent separation into the vapour phase.

O_2

Oxidising conditions may cause deposition of metals from sulphide complexes, whereas reducing conditions favour deposition from chloride complexes.

Barnes (1979) considered that oxidation was the most effective chemical process to cause instability of the sulphide complexes because it decreases both total sulphide concentration and pH. However, the limiting

factor is the quantity of oxidant locally available.

Oxidation may occur because of interactions of the solution with wall rock minerals, for example the conversion of magnetite to pyrite in the wall rocks, or by mixing with oxygenated waters.

Reduction in terms of the concentration of sulphide has been dealt with under the Δm_S^2 - heading above.

pH

Changes in pH have opposite effects on the stability of chloride and sulphide complexes. Increased pH, caused by either reaction with carbonates or feldspars, or boiling off acidic gases, causes deposition of metals from chloride complexes, whereas a decrease in pH may change the sulphide activity product ($a_{HS^-} \cdot a_{H_2S}$) by the reaction:

causing deposition of metals from sulphide complexes.

Barnes (1979) also noted that because the complex $Me(HS)_3^-$ reaches maximum concentration where $pH = pK_{H_2S}$ any pH below this value causes deposition.

Dilution

Dilution (e.g. by mixing with circulating meteoric water) causes deposition of metals from both chloride and sulphide complexes because of the decreased chloride and sulphide concentration.

$-\Delta T$

A decrease in temperature causes decreasing solubility of both types of complex but a large change in temperature is required to precipitate a significant quantity of sulphide.

$-\Delta P_t$

A decrease in pressure without initiation of boiling is considered to have only a minor effect in promoting sulphide deposition from solution. The effects of boiling have already been discussed.

Metal Zoning

Barnes (1975; 1979) considered that the generalised zoning sequence: molybdenite-arsenopyrite-pyrrhotite-pentlandite-stannite-chalcopyrite-sphalerite-tetrahedrite-galena-acanthite-gold tellurides-stibnite-cinnabar, typical of most hydrothermal deposits and similar to that observed here,

correlates with increasing solubility of the metal complexes. Switching between adjacent minerals in the sequence (e.g. chalcopyrite-sphalerite) happens where the relative concentrations of the metals in the deposit are locally reversed.

Transport and Deposition of Non-metals

Quartz

Silica is present in hydrothermal solutions generally as species with the formula $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The solubility of the silica polymorphs is dependent on temperature and pressure but virtually independent of ionic strength and pH in the acid to slightly alkaline range (Holland, 1979). The primary mechanism for quartz deposition in ore deposits is considered to be a decrease in temperature (Holland, 1979).

Calcite

The solubility of calcite in hydrothermal solutions can be expressed as follows:

Calcite solubility increases with decreasing temperature and increasing CO_2 pressure (but decreases with increasing CO_2 pressure at constant total pressure when $m\text{CO}_2 > 1$ mole/kg). Decreasing temperature alone will therefore not precipitate calcite from solution. Holland (1979) considered that calcite was deposited in most ore deposits as a result of boiling [causing a decrease in $m\text{CO}_2$ and a shift of the equilibria to the left in equation (11-4)] and changes in pH due to wall rock reactions.

Barite

The solubility of barite increases with increasing temperature, pressure and ionic strength (c.f. Holland, 1979). The simplest depositional mechanism is one of decreasing temperature.

GEOCHEMICAL ENVIRONMENTS OF THE EPITHERMAL VEIN

MINERAL ASSEMBLAGES AND CAUSES OF MINERAL DEPOSITION

Introduction

The geochemical environments of mineralisation in some individual epithermal deposits are investigated in Appendix I using the data calculated in Appendix V. The conclusions derived from these different

deposits provide sufficient information to collectively discuss the physicochemistry of the depositional environments and mechanisms for several of the vein mineral assemblages discussed in Chapter 4.

Pyrite - Chalcopyrite Assemblage

Geochemical Environment

Early vein mineralisations of Tapu - Thames and Tui Mine were deposited at high temperature (around 400°C) by fluids of near neutral pH (in equilibrium with sericite in the wall rocks).

Boiling occurred during the Tapu - Thames mineralisation but no evidence for or against boiling of the early Tui Mine fluid is available.

Although Merchant (1978) cited an individual occurrence of pyrrhotite in mineralisation of his Cu-Bi mineral association in the Tapu - Thames area, pyrite - chalcopyrite assemblages seem to have generally been deposited in the veins of Tapu - Thames and Tui Mine at high fS_2 and fO_2 (Figs 11-1 and 11-2). These parameters were higher at Tui Mine than in the Tapu - Thames veins as indicated by the occurrence of hematite (high fO_2) and possibly bornite (high fS_2) in the former.

Sulphur was present predominantly as H_2S in the Tapu - Thames fluids but SO_2 or SO_4^{2-} were also important constituents in the Tui Mine fluid (Fig. 11-2). The concentration of total sulphur in solution was around 0.05m.

Mineral Deposition

Mineral deposition from chloride complexed metals in solution probably occurred because of an increase in pH of the fluid due to reactions with the wall rocks (e.g. sericitisation of the feldspars) and in the case of the Tapu - Thames deposits because of boiling and loss of the acidic gases such as CO_2 . Dilution and reduction are also suggested as possible mechanisms in later sections.

Pyrite - Sphalerite - Galena - Chalcopyrite $\pm$ Electrum $\pm$ Silver Mineral, and Sb - Sulphosalt Mineral Assemblages

Introduction

The pyrite - sphalerite - galena - chalcopyrite, pyrite - sphalerite - galena - chalcopyrite - electrum - silver mineral, and Sb - sulphosalt mineral assemblages are considered together in this section. The mineral-

Figure 11-1: f_{S_2} versus f_{O_2} diagram (400°C) for the pyrite-chalcopyrite mineral assemblage in veins at Tapu-Thames and Tui Mine. The details of construction of the diagram are given in Appendix V.

The field for the early Tapu-Thames mineralisation is defined by rare pyrrhotite (early) and more common pyrite-chalcopyrite-sphalerite. The iron content of sphalerites from the latter assemblage indicates log f_{S_2} values between -4.4 and -4.6 at 400°C.

The field for the early Tui Mine mineralisation is defined by common pyrite-chalcopyrite, less common pyrite-hematite and hematite, the mole fraction of silver in native gold (indicating log f_{S_2} values between -3.9 and -4.6) and also possible very rare bornite.

These fields indicate that the pyrite-chalcopyrite mineral assemblage is generally deposited at relatively high sulphur and oxygen fugacities.

Figure 11-2: fO_2 versus temperature diagram (based on Fig.4 of Burnham & Ohmoto, 1980) relating the fO_2 - t fields of the Tapu-Thames and Tui Mine pyrite-chalcopyrite mineral assemblages to the stability fields of pertinent iron-bearing mineral assemblages (at approximately 1 kbar) and aqueous sulphur species (at pH=4). The early Tapu-Thames mineralisation was deposited from a fluid containing dissolved sulphur predominantly in reduced form, whereas the concentration of aqueous oxidised sulphur species may have been equal to, or exceeded, the concentration of aqueous reduced sulphur species during deposition of the early Tui Mine mineralisation.

TABLE 11 - 1: Geochemical parameters for some representatives of the pyrite - sphalerite - galena - chalcopyrite [†] electrum [†] silver mineral, and Sb - sulphosalt mineral assemblages, derived from the data presented in Appendix I.

	t°C	pH	pH diagnostic alteration-vein minerals	Predominant S species in solution
Te Ahumate Stage 1	240	6	sericite - adularia	sulphide
Paritu	325	5.6	sericite - adularia	sulphide
Tokatea Base metal	280	4.5 - 6.5	sericite (adularia?)	sulphide
Petote Stream Stage 1	300	5.6	sericite	sulphide
Whangapoua Stage 2	280	4.5 - 5.5	sericite	sulphide
Tapu - Thames Pb-Zn	280	4.9	sericite	sulphide
Neavesville Ajax	250	6.2	sericite - adularia	sulphide - sulphate
Maratoto Stage 2	280	5.5 - 6.5	sericite - adularia	sulphide - sulphate
Waitekauri Stage 2	280	5.6 - 6.2	sericite - adularia	sulphide
Waihi low levels	325	5.0 - 5.7	sericite - adularia	sulphide
Waihi intermediate levels	280	4.5 - 6.6	sericite and sericite - adularia	sulphide
Karangahake low levels	300	5.1 - 5.6	sericite - adularia	sulphide
Tui Mine Stage 2	300	6.0 - 6.3	sericite - adularia	sulphide - sulphate
Waiorongomai Stage 1	325	5.3 - 5.6	sericite	sulphide - sulphate

isations consist predominantly of pyrite, sphalerite, galena and chalcopyrite in quartz and calcite gangue but acanthite, hessite, electrum and various Sb - As sulphosalts occur in some deposits.

Geochemical Environment

Table 11-1 lists some of the aspects of the mineralisations considered in this section.

Temperatures of mineral deposition are considered to be generally in the region of 270 to 340°C but mineralisations at lower temperatures occurred at Neavesville (250°C) and Te Ahumata (240°C). No conclusive evidence of boiling was noted from any of the deposits although widely spread fluid inclusion filling temperature histograms (e.g. Maratoto) may indicate proximity to the boiling curve.

The hydrothermal fluids were in equilibrium with sericite and in many cases adularia in the wall rocks and veins, indicating near neutral pH conditions.

Sulphur fugacities during mineralisations of this stage for the different areas are very similar (allowing for the difference in temperature) with bornite absent from all deposits and pyrrhotite present only in two samples from Waihi.

The concentration of total sulphur in solution varies with temperature of mineralisation but is similar for deposits formed at similar temperatures.

In most deposits sulphur was present in solution predominantly in reduced form although in others the ratio of dissolved sulphate to dissolved sulphide is quite variable (Fig. 11-3) and, in the case of the Camoola Vein of Maratoto, may have exceeded 1. The occurrence of selenium in some sulphides (e.g. acanthite) is considered to indicate oxidising conditions in some veins at Maratoto and Waihi.

The occurrence of telluride minerals in some deposits is related to the concentration of total tellurium in solution (Fig. 11-4) and $f\text{Te}_2$ (Fig. 11-5) which were particularly high in the veins of Tapu - Thames and Thames (hessite, stutzite, sylvanite, altaite, tellurobismutite, petzite, coloradoite and nagyagite) and Waiorongomai (hessite and altaite).

Mineral Deposition

Although the causes of mineral deposition vary between deposits of this group, two mechanisms are considered prevalent: changes in fluid pH (due to reactions of the fluid with the wall rocks) and the $\text{SO}_4^{2-}/[\text{H}_2\text{S} + \text{HS}^-]$ ratio (oxidation - reduction generally caused by mixing with different fluids).

Figure 11-3: fO_2 versus pH diagram for the pyrite-sphalerite-galena-chalcocopyrite + electrum + silver minerals, and the Sb-sulphosalt mineral assemblages. The diagram was constructed for a temperature of 300°C and a concentration of total sulphur in solution of $0.01m$, by the methods outlined in Appendix V. The position of the kaolinite/sericite boundary, sericite/K-feldspar boundary and stability fields for the various deposits have been extrapolated from several diagrams at different temperatures (Appendix 1).

Field 1 = Neavesville (Ajax), Maratoto (Stage 2), Tui Mine (Stage 2) and Waiorongomai (Stage 1).

Field 2 = Te Ahumata (Stage 1), Northern Colville Peninsula (Sorry Mary Stream and Doctors Creek), Waitekauri (Stage 2) and Waihi (intermediate levels).

Field 3 = Tokatea (base metal), Petote Stream area (Stage 1) and Tapu-Thames (Pb-Zn).

Field 4 = Whangapoua (Stage 2).

Field 5 = Waihi (Low levels).

Most representatives of these assemblages are formed from solutions at near neutral pH and containing dissolved sulphur predominantly in reduced form.

Figure 11-4: fO_2 versus concentration of total tellurium in solution diagram (based on Fig.10-4 of Ahmad, 1979) illustrating the stability fields of some telluride bearing pyrite-sphalerite-galena-chalcopyrite $\pm$ electrum $\pm$ silver mineral assemblages at $t = 250^\circ\text{C}$, $m \Sigma S = 0.01m$, $\text{pH} = 5.5$ and $I = 1$. Increasing concentrations of total tellurium in solution are indicated down the following series:

- (a) hessite (stippled): Tokatea, Tapu-Thames, Thames, Neavesville (Ajax), Maratoto (mainly the Silver Queen vein), Waihi (Rosemont Hill veins only) Karangahake and Waiorongomai.
- (b) coloradoite (crosses): Thames.
- (c) altaite (diagonal lines): Tapu-Thames, Thames, and Waiorongomai (one occurrence).
- (d) calaverite and native tellurium (not designated): Tapu-Thames (one occurrence reported by Ramdohr, 1980).

Some error is apparent in the phase relations shown because the occurrence of altaite with electrum, but not calaverite, in the Hauraki Gold-Silver Province is believed to occur at higher oxygen fugacity than shown on the diagram (even taking into account the extrapolation between the depositional temperature and modelled temperature). Therefore the electrum/calaverite boundary may be at higher values of $\log m \Sigma \text{Te}$ than those for the gold/calaverite boundary, at any given value of $\log fO_2$.

Figure 11-5: $f\text{Te}_2$ versus $f\text{S}_2$ diagram for some telluride mineral-bearing pyrite-sphalerite-galena-chalcopyrite $\pm$ electrum $\pm$ silver minerals assemblages. The diagram was constructed for a temperature of 300°C by the methods outlined in Appendix V. Increasing $f\text{Te}_2$ is indicated for the progression of mineral assemblages: hessite (stippled), coloradoite (crosses), altauite (diagonal lines), calaverite and native-tellurium, present in some of the Hauraki mineralisations (see list in caption of Fig. 11-4). Higher values of $f\text{S}_2$ are indicated for the altauite occurrences (see Fig. 11-4) than shown in the diagram, as indicated by the arrow and therefore the electrum/calaverite boundary is considered to be at a higher value of $f\text{Te}_2$ than the gold/calaverite boundary shown (e.g. $\log f\text{Te}_2 = -7$).

The variable concentration of dissolved CO_2 , indicated by fluid inclusion studies, probably had a marked effect on fluid - wall rock equilibria, calcite deposition, calcite solution and pH, however insufficient data are available to investigate these effects in detail.

Pyrite - Acanthite - Electrum Assemblage

Geochemical Environment

Although pyrite - acanthite - electrum mineralisation is reported in the early literature from many of the deposits and would appear to be the dominant precious metal mineralisation at Komata, Golden Cross and in the upper levels of Waihi and Karangahake, the writer was unable to obtain samples of this assemblage. Quartz veins exposed in the upper levels of Waihi and 8 and 12 levels of the Talisman Mine (Karangahake), and quartz plus calcite veins exposed in 8 level Komata, contain no visible mineralisation (except for pyrite) even though assays indicate the presence of gold and silver (generally low grade).

Fluid inclusions in quartz and calcite of these veins indicate depositional temperatures around $200 - 230^\circ\text{C}$ and these temperatures are considered to approximate those of pyrite - acanthite - electrum mineralisation.

The fluid was in equilibrium with sericite and possibly also adularia in the wall rocks indicating a near neutral pH. Kaolinite is reported from the veins and wall rocks of some deposits but it is considered to represent a later stage of alteration.

The occurrence of boiling was noted in some material from Komata and Waihi but its relationship to the mineralisation is unknown.

Mineral Deposition

Pyrite - acanthite - electrum mineralisation probably occurred due to a number of different factors operating at different locations. Boiling may have been important at Komata and possibly for some of the Waihi mineralisation. Decreases in fluid pH were probably also important at Waihi. Mixing of the hydrothermal fluid with near surface meteoric water is another possible mechanism and may have been important at Karangahake.

Ore deposition appears to have been often associated with zones of leached calcite (gold tenor was reported to fall on intersection of primary calcite) suggesting that, if the two are associated, conditions causing hydrothermal leaching (decreasing pH, decreasing temperature, and increasing $f\text{CO}_2$) were conducive to the deposition of electrum and acanthite.

Pyrite - Electrum Assemblage

Introduction

Pyrite - electrum mineralisation at the Bluffs section of Neavesville was not differentiated from the pyrite - acanthite - electrum assemblage in Chapter 4, because of its very limited occurrence. However, a separate description is included here because of the good geochemical control on the environment of deposition.

Geochemical Environment

Fluid inclusions indicate that the pyrite - electrum assemblage was deposited at approximately 220°C from boiling fluids with log $f\text{CO}_2$ around 1.2. A near neutral to slightly alkaline pH is indicated by the presence of adularia in the wall rocks. $f\text{S}_2$ values, calculated from the composition of electrum analysed by Torckler (1978), help define the dissolved sulphate/dissolved sulphide ratio to a value of approximately 1 for a concentration of total sulphur in solution of 0.01m (c.f. Fig I-N-9 of Appendix I).

Mineral Deposition

The principal mechanism of electrum deposition appears to be boiling in a relatively oxidising environment.

Pyrite - Bonanza Electrum Assemblage

Geochemical Environment

Pyrite - bonanza electrum mineralisation occurred in quartz veins at Coromandel (Kauri Block and Kapanga Mines) and Thames.

Merchant (1978) concluded that the Thames bonanzas were formed at approximately 230°C from boiling fluids. Kaolinite and sericite were present in the veins and wall rocks indicating that the fluids were acidic.

A similar environment is envisaged for the Coromandel bonanzas although no fluid inclusion evidence is available to substantiate this hypothesis.

Mineralogical evidence indicates a predominantly reducing environment during both Coromandel and Thames mineralisations, with sulphur present in solution predominantly as H_2S . However, the presence of barite and enargite in some of the Thames mineralisation may indicate the local occurrence of oxidising conditions, possibly a downward incursion of the acid sulphate water environment present in the overlying alunited rhyolite rocks.

The concentration of total sulphur in solution is considered to have been about 0.001m.

Values of $\log f\text{CO}_2$ as high as 1.5 or possibly 2 are possible without the formation of graphite in the Thames bonanzas but this parameter must have been lower than 0.5 at Coromandel.

Mineral Deposition

If the boiling environment hypothesis is correct, boiling would have been the predominant mechanism causing mineral deposition. Boiling off of H_2S from the fluid would cause instability of gold and silver sulphide complexes in solution and the acidic environment indicated for the Thames mineralisation would also help promote deposition.

Au - Ag Sulphosalt Mineral Assemblage

Geochemical Environment

Epithermal pyrite, Au - Ag sulphosalt and electrum mineralisation occurs in quartz veins at Te Ahumata, Broken Hills and Thames.

Filling temperatures of fluid inclusions in quartz from this assemblage indicate water temperatures around 220°C at Te Ahumata (Erceg, 1981) and 230°C at Broken Hills (this study). The Broken Hills fluid was boiling.

Sericite and kaolinite occur in the wall rocks, although adularia has also been identified at Te Ahumata and Broken Hills. The kaolinite is interpreted as a late stage overprint on earlier sericite plus K-feldspar assemblages and therefore the pH of the early fluids was probably near neutral.

The occurrence of seleniferous and selenide minerals in this assemblage suggests a relatively high dissolved sulphate/dissolved sulphide ratio in the hydrothermal fluid (c.f. Appendix V). Some assemblages at Broken Hills also contain barite, indicating that this ratio may have exceeded 1.

The concentration of total sulphur in solution was approximately 0.001m.

Mineral Deposition

Mineralisation occurred as a result of instability of the metal sulphide complexes in solution caused by mixing of the hydrothermal fluid with dilute cool near surface waters (causing dilution, a decrease in temperature, and oxidation of the hydrothermal fluid) and, in the case of Broken Hills, boiling.

Stibnite

Geochemical Environment

The stibnite mineralisation at Whangapoua (Waingaro Stream) was deposited at temperatures of approximately 200°C or less from boiling fluids, whereas similar mineralisation occurred at Te Ahumata from non-boiling fluids at temperatures around 240°C. Information on conditions of stibnite mineralisation at Thames is not available.

Fluids depositing stibnite were acidic (in equilibrium with kaolinite and sericite in the veins and wall rocks) and characterised by relatively low oxygen and carbon dioxide fugacities, and high concentrations of total sulphur. Sulphur in solution was present predominantly in reduced form (H_2S and HS^-), although SO_4^{2-} may have been locally important in some of the Thames mineralisation where barite was also deposited. The presence of arsenopyrite in some of the Te Ahumata stibnite mineralisation indicates conditions of relatively low $f\text{S}_2$.

Mineral Deposition

The instability of antimony sulphide complexes in solution and subsequent deposition of stibnite appears to have occurred at Te Ahumata, Whangapoua and Thames because of decreasing pH, coupled with boiling at Whangapoua and oxidation at Thames.

Barite

Geochemical Environment

The temperature of barite deposition appears to have been quite variable and spans a considerable range. Merchant (1978) noted fluid inclusion filling temperatures ranging from 330 - 105°C (but mainly between 260°C and 230°C) for samples from the Monowai Vein and Stokes Reefs north of Thames and a range of 288 - 132°C was recorded here for plates of barite coating Stage 3 vug quartz crystals from Tui Mine. In contrast, with the exception of one inclusion at 196°C, filling temperatures for similar barite from Waiorongomai were between 98°C and 128°C.

Robinson (1974), using oxygen isotope fractionations, calculated temperatures of $210 \pm 30^\circ\text{C}$ for barite grown with Stage 3 vug quartz and $150 \pm 30^\circ\text{C}$ for barite coating Stage 3 quartz of Tui Mine.

Fluid inclusions in Broken Hills barite have not been investigated, however temperatures of deposition are probably between 200°C and 250°C (c.f. Broken Hills quartz).

Figure 11-6: Depth zonation model for epithermal deposits (see text for explanation).

Kaolinite and sericite occur in the wall rocks of the barite mineralisation indicating that the hydrothermal fluids were acidic, particularly at low temperatures. Oxygen fugacities were relatively high with the fluids containing approximately equal proportions of sulphate and sulphide, or sulphate predominating over sulphide.

Mineral Deposition

Late stage barite deposition at Tapu - Thames, Tui Mine and Waiorongomai appears to have occurred as a result of falling temperature and generally oxidising conditions.

Deposition of barite during gold - silver mineralisation at Broken Hills and Thames (gold - pyrargyrite association of Merchant, 1978) was probably related to boiling, oxidation and a decreasing pH.

MODEL OF EPITHERMAL VEIN MINERALISATION

Introduction

The hydrothermal fluids responsible for the epithermal vein deposits originated as deeply circulating meteoric water, which in some instances penetrated to sufficient depth to mix with magmatic fluid. Components such as sulphur, carbon and the metals were derived from the magmatic fluid and by wall rock leaching; the relative importance of these two sources varying according to depth of fluid circulation and proximity to the igneous heat source.

The formation of the various vein mineral assemblages is modelled on a hypothetical depth zonation scheme illustrated in Fig. 11-6. Deposition of the various vein mineral assemblages occurs in response to the changing physicochemical environment, resulting from the inter-reactions of the hydrothermal fluid with the wall rocks as the fluid ascends through the veins to the surface. The occurrence of specific mineral assemblages depends on the presence of favourable structural environments in addition to suitable physicochemical conditions. Therefore, the presence of a particular mineral assemblage in a deposit does not necessarily imply that with changing elevation there should be a transition into the adjacent mineral assemblages shown in the model.

Three aspects of the model are elaborated in the following sections.

Hydrology

Three major hydrological zones are shown in Fig. 11-6: (a) a deep mixing zone where magmatic fluid mixes with deeply circulating meteoric

water, (b) an intermediate zone in which the changing composition of the hydrothermal fluid is predominantly related to inter-reactions with the wall rocks (but not mixing), and (c) a near surface mixing zone where the hydrothermal fluid mixes with cooler and oxygenated near surface water.

If the magmatic fluid has a vapour component (c.f. Chapter 10) the first zone may represent a boiling horizon (c.f. Cu - Bi Association of Tapu - Thames; Merchant, 1978). Boiling may occur at other horizons if the outflow of the hydrothermal system exceeds the recharge (c.f. vapour dominated systems of White *et al.*, 1971) or as a result of pressure release following dislodgement of vein obstructions (e.g. explosive clearing of veins necked due to crystallisation) and hydraulic brecciation of porous wall rocks (e.g. breccia pipes at Broken Hills and Neavesville). The most frequent location of boiling appears to be near or above the junction of zones (b) and (c).

Hydrothermal Alteration and Solution Chemistry

Introduction

The sequence of hydrothermal alteration assemblages, in order of decreasing depth, is: quartz - sericite, argillic (clay - sericite), propylitic, argillic and advanced argillic.

The highest grade of alteration encountered in some deposits is propylitic, suggesting that some water circulation cells did not penetrate to sufficient depth to acquire the physicochemical characteristics necessary for quartz - sericite and deep argillic alteration capability. Therefore, at least two starting points occur in the model, one in the quartz - sericite environment (high degree of magmatic input) and the other in the propylitic environment (low degree of magmatic input).

Quartz - Sericite Zone

Fluid - wall rock reactions in the quartz - sericite zone produce secondary quartz, sericite and pyrite in the wall rocks by hydrogen (dominant) and potassium (subordinate) metasomatism accompanied by release of Na^+ , Ca^{2+} and Mg^{2+} to the fluid. Consequently the Na/K and KCl/HCl ratios of the fluid increase through the zone.

At high temperatures (i.e. above 400°C) oxidised sulphur is present in the fluid as SO_2 . With decreasing temperature the SO_2 hydrolyses to H_2S and H_2SO_4 (equation 10-1, Chapter 10) and the resulting increase in H_2S activity may be a major mechanism for sulphide deposition.

The quartz - sericite environment is depicted in Fig. 11-6 as the zone where magmatic fluid mixes with meteoric water. Sulphide deposition may therefore also result from the effects of dilution and a decrease in

temperature.

Deep Argillic Zone

The production of HCl during sulphide deposition in the quartz - sericite zone (c.f. equation 10-3, Chapter 10), coupled with increasing dissociation of acids such as HCl and H_2SO_4 with decreasing temperature, results in a decrease in the KCl/HCl ratio in the hydrothermal fluid and possibly a shift of the fluid - mineral equilibria from sericite to kaolinite or pyrophyllite. The resulting increase in hydrogen metasomatism of the wall rocks (argillic alteration) tends to neutralise the fluid, increasing the KCl/HCl ratio. Therefore this zone may be equivalent to Giggenbach's (1981) "Primary Neutralisation Zone".

Dr R.L. Brathwaite (pers. comm.) considers that deep argillic alteration in the sense used here is not well developed in the Hauraki Gold - Silver Province but that quartz - sericite alteration generally passes into propylitic alteration zones without an argillic intermediary. He considers that the intermediate argillic alteration zones adjacent to medium temperature (i.e. 250 - 320°C) vein deposits (e.g. Maratoto) may be retrograde assemblages formed by late stage overprinting on original propylitic alteration assemblages. Therefore in these cases the decrease in KCl/HCl ratio of the fluid, from sulphide deposition in the quartz - sericite zone and dissociation of acids, did not reduce the pH sufficiently for kaolinite deposition. The absence of appreciable acid dissociation (e.g. H_2SO_4) implies a low sulphate/sulphide ratio in the fluid.

Propylitic Zone

With decreasing temperature and acidity (increasing KCl/HCl ratio) the alteration changes to propylitic and minerals such as chlorite, epidote, calcite and adularia become stable in addition to pyrite, quartz and sericite. The specific alteration mineral assemblage depends on fCO_2 (e.g. epidote, wairakite and/or calcite; Appendix V), pH (kaolinite, sericite or adularia; c.f. Fig. V-4, Appendix V) and temperature (e.g. heulandite or wairakite).

The hydrothermal fluid passing through the propylitic zone is of the alkali chloride type (c.f. Ellis & Mahon, 1977). The main fluid - wall rock reactions involve CO_2 , hydrogen, calcium and potassium metasomatism with concomitant release of Na^+ , Mg^{2+} , and Al^{3+} to the fluid. Giggenbach (1981) stressed the importance of the plagioclase + CO_2 = calcite + clay reaction in modern geothermal fields as a controlling reaction of water chemistry.

The predominance of sericite and calcite in most propylitic zones of the Hauraki Gold - Silver Province suggests that this reaction was similarly important there.

Propylitic alteration is the most widely recognised type of hydrothermal alteration in the province and is generally accompanied by deposition of metal sulphide [±] electrum mineral assemblages in veins. Some veins contain abundant calcite and a few also contain adularia, suggesting that near neutral pH is favoured for this type of mineralisation.

Near Surface Argillic and Advanced Argillic Zones

Mixing of the hydrothermal fluid with near surface oxygenated water causes progressive oxidation of the remaining H_2S in solution to SO_4^{2-} and a decrease in pH. This may be compounded in some cases by condensation of CO_2 and H_2S (with subsequent oxidation to SO_4^{2-}), emanating from lower boiling zones, forming acid sulphate waters (c.f. Ellis & Mahon, 1977).

A second cycle of hydrogen metasomatism occurs producing argillic and advanced argillic alteration. Kaolinite dominates the clay mineralogy of these zones although montmorillonite sometimes occurs. In areas where the concentration of sulphate is high in the fluid, alunite may be produced.

Mineralisation

The various vein mineral assemblages are shown in a depth zonation sequence in Fig. 11-6 and are grouped into four metal zones: Mo zone, Cu zone, Cu-Pb-Zn zone and Au-Ag zone.

The generalised vertical metal zonation: W, Mo, Cu, Bi, Pb, Zn, Au, Ag, Sb, and Hg, is believed to reflect increasing solubility of the metal carrying complexes (least soluble deposited first, most soluble deposited last) coupled with the changing role of chloride and sulphide complexes as transporters of the metals and the different responses of these complexes to the vertically changing physicochemical environment (upward decreasing temperature, decreasing pH and increasing oxidising conditions).

Deposition of metallic minerals in the Mo, Cu and Cu-Pb-Zn vein zones is believed to occur from metals transported in solution as chloride complexes. In contrast, deposition of metallic minerals at lower temperatures in the Au-Ag zone occurs from metals transported in solution as sulphide complexes. Because these different types of complexes respond differently to specific changes in some of the principal physicochemical parameters (viz. mS^{2-} , fO_2 and pH) this property is a major contributing factor to the zonation. For example, deposition in the Mo, Cu and Cu-Pb-Zn

zones is considered to have predominantly occurred due to an increase in pH (because of reactions with the wall rocks or boiling) and reduction, whereas decreasing pH, oxidation and decreasing $m_{S^{2-}}$ (due to boiling off of H_2S) caused mineral deposition in the Au-Ag zone.

Decreasing temperature, although not considered the principal cause of metal deposition, determines the overall metal zonation because it controls the solubility trend and also the relative importance of chloride and sulphide complexes of gold and silver.

Some overlap between the chloride complexed metal and sulphide complexed metal zones occurs, particularly if mineral deposition results from some factor which causes instability of chloride and sulphide complexes equally (e.g. dilution without significant oxidation).

CHAPTER 12

MINERALISATION AND VOLCANISM

MINERALISATION ASSOCIATED WITH ANDESITIC VOLCANISM

The Relationship Between Andesitic Volcanism and Mineralisation

The porphyry copper and some of the epithermal vein deposits are considered to have been deposited as a result of hydrothermal activity associated with the emplacement and cooling of intrusive magma bodies now represented by the intrusive rocks of the Coromandel Group.

The mineralising environment envisaged is an andesitic volcanic terrain similar to the present Tongariro Centre of the Taupo Volcanic Zone (c.f. Cole, 1979). Magma bodies occur at various levels beneath the cones of the modern composite andesite volcanoes. The occurrence of parasite cones and flank eruptions of lava indicate the presence of various auxillary necks, plugs and dikes of magma within the cone, in addition to the main neck supplying the central vent (c.f. Williams & McBirney, 1979). The main magma reservoir occurs at deeper levels and recent work has demonstrated that a complex series of hypabyssal and plutonic magma bodies may underlie the volcanoes, in contrast to the classic simplistic picture of a single large magma chamber. For example, on consideration of geophysical evidence, Latter (1981) postulated the existence of magma bodies at various depths below the volcanoes of the Tongariro Volcanic Centre.

Extrapolating this environment to the Coromandel Group rocks readily accounts for the multiplicity of intrusive bodies comprising the Kai-iti Porphyrites, Whangapoua Intrusives and Tainui Intrusives in the volcanic environment and Paritu Plutonics and some Kai-iti Porphyrites in the hypabyssal environment.

The epithermal vein deposits were probably formed in shallow (<2 km) geothermal systems generated by the general intrusive activity in a volcanic centre (i.e. a suite of hypabyssal and volcanic intrusives), whereas the porphyry copper deposits were associated with specific hypabyssal intrusions emplaced at depths greater than 1.5 km.

The different mechanisms and depths of formation give rise to the contrasting spacing relationships between porphyry copper and epithermal vein deposits suggested by Sawkins (1980). Porphyry copper deposits are spaced in the order of tens of kilometres (Sawkins suggested an average

Figure 12-1: Porphyry copper style deposits (at all locations shown except for Cuvier Island where the intrusives are unmineralised) of the North Island occur in a chain from Knuckle Point, south to Tainui (Tapu - Thames). K-Ar ages (shown) of the associated intrusive rocks suggest two periods of formation: 20 - 16 m.y. (Knuckle Point, Kauri Mountain?, Copper Mine Island, Miners Head, Paritu and Manaia?) and 13 - 9 m.y. (Tainui).

Source of K-Ar ages: Paritu and Cuvier Island are from Richards *et al* (1966), whereas the remainder are from Dr C.J.D. Adams and others (pers. comm.).

of 50 km), probably representing sites of major uprise of magmas, whereas epithermal vein deposits are spaced only a few kilometres apart (Sawkins cited examples averaging approximately 5 km) representing the dimensions of the convective cells. The specific location of the vein deposits also depends on the presence of suitable structural environments. Upward movement of the hydrothermal fluid via fault fissures produces the mushroom cross-sectional shape that is typical of most modern geothermal systems (c.f. Elder, 1965; 1966). The largest convective cells penetrated deep levels (to the quartz - sericite zone of Fig. 11-6) and probably interacted with magmatic fluids, whereas the magmatic component of the shallow convective cells (penetrating to the propylitic zone of Fig. 11-6) was probably minor.

Sequence of Events During Andesitic

Volcanism in the Hauraki Province

During the early Miocene (c.a. 20 - 16 m.y.), volcanism probably initially comprised several widely spaced andesite strato-volcanoes fed from chambers of granodiorite and quartz diorite magma in the underlying greywacke. The latter are represented by a chain of mineralised intrusives (Fig. 12-1) consisting of the porphyry copper style deposits at Cape Karekare, Kauri Mountain, Copper Mine Island, Miners Head, Paritu and Manaia, in addition to the unmineralised intrusives of Cuvier Island.

The first extrusive rocks of this series are represented in the Hauraki Gold - Silver Province by the group of volcanics at the north-eastern end of the Colville Peninsula comprising Port Charles Andesite, Omoho Formation, Kokumata Dacite and Te Karaka Andesite (Fig. 2-3). The Omoho Formation consists of large pyroclastic flow deposits and probably originated by caldera collapse of one of the volcanoes.

The early Miocene volcanic episode ended with the eruption of the Beesons Island Volcanics and Tuatēawa Andesite in the Coromandel - Whangapoua area and the Tui Andesite (dated at 16.1 m.y. by Adams *et al.*, 1974) at Te Aroha. Early andesitic volcanism in the Thames (Premier Andesite) and Waihi areas may also have occurred around this time (c.a. 16 m.y.).

These various volcanic formations (particularly the Beesons Island Volcanics) contain numerous intrusive stocks, plugs, necks and dikes which were probably contemporaneous with extrusive volcanism and are believed to have caused the hydrothermal alteration and epithermal mineralisation in the Colville and Coromandel areas, and possibly at Waihi.

During the mid Miocene the volcanic sequence in the northern area

continued with the Whangapoua Andesite, Materangi Andesite, Parakete Formation, Te Tutu Andesite, Ruaporoa Basaltic Andesite and Mahinapua Andesite, the latter dated at 13.8 and 11.4 m.y. (Dr C.J.D. Adams, pers. comm.). Some of these formations have been intruded by various small stocks and dikes of the Whangapoua Intrusives which probably generated the epithermal veins in the Whangapoua and Kuaotunu areas.

In the southern region, the Tararu Andesite of Tapu - Thames was erupted between approximately 13 and 9 m.y. and was intruded by high level quartz diorite stocks of the Tainui Intrusives (12.9 - 9.3 m.y.; Dr C.J.D. Adams, pers. comm.), possibly related to caldera resurgence. Porphyry copper and epithermal vein mineralisations of the Tapu - Thames area occurred at this time.

In the late Miocene volcanoes began erupting in the vicinity of Maratoto, Komata and Paeroa (K - Ar ages of 9.7, 7.0 and 7.0 m.y. respectively; Stipp, 1968). The Maunaupaki Andesite and andesites in the vicinity of Karangahake, Golden Cross and Waihi (second phase) may also have formed during this period. The phase ended between 5 and 4 m.y. (c.f. 4 m.y. K - Ar age date for Coromandel Group andesites from the western end of the Kaimai Tunnel by Stipp, 1968). Taurahue Andesite probably formed at the end of this period, around 5 m.y..

The relationship between andesite volcanism and mineralisation in this southern region is complicated by the overlap with Whitianga Group rhyolite volcanism which may also have contributed to the mineralisations (e.g. Thames, Karangahake and Tui Mine). Nevertheless, whether these southern mineralisations are due to andesite or rhyolite volcanism they appear to have occurred less than 9 m.y. ago.

The Coromandel Group sequence ended in the Late Pliocene with the intrusion and extrusion of basic andesites of the Omaha Andesite (3.8 m.y.; Stipp, 1968).

MINERALISATION ASSOCIATED WITH RHYOLITIC VOLCANISM

The Relationship Between Rhyolitic Volcanism and Mineralisation

The deposits at Te Ahumata, Kapowai, Broken Hills, Phoenix Hill, Neavesville, Luck at Last and Waihi Beach can be related to hydrothermal activity associated with Pliocene rhyolitic volcanism because they occur partly or completely within Whitianga Group rocks. Several deposits that occur only in andesites are also considered to be related to rhyolite

Fig. 12-2A

Fig. 12-2B

Figure 12-2: Models for hydrothermal systems during andesitic volcanism (Fig. 12-2A) and rhyolitic volcanism (Fig. 12-2B). During andesitic volcanism hydrothermal systems, centered approximately 5km apart, are generated by many intrusive bodies. The close proximity of the magma to the ground water (meteoric) convective cells allows a high degree of magmatic input. The hottest systems may be associated with porphyry copper type systems beneath strato volcanoes or calderas. In contrast, during rhyolitic volcanism the magma chambers are probably deep plutons (-batholiths) which generate widely spaced (approximately 10km) hydrothermal systems. The magmatic input, apart from heat and CO_2 , into the ground water convective cells is probably small.

volcanism on the evidence of stratigraphy, stable isotopes, K - Ar age data, or hydrothermal alteration of the overlying rhyolite rocks. In this group are the deposits at Thames, Karangahake and Tui Mine.

The deposits associated with rhyolite volcanism are considered to represent centres of fossil geothermal areas analogous to present day geothermal activity in rhyolite rocks of the Taupo Volcanic Zone. The validity of this comparison is supported by the similar tectonic setting and geology of the two rhyolite terrains and the presence of precious and base metal mineralisation in some of the modern geothermal fields (c.f. Weissberg *et al*, 1979). Also they have similar spacing relationships: the deposits that occur in continuous rhyolite terrain of the Coromandel Peninsula (viz. Kapowai, Phoenix, Broken Hills, Neavesville and Luck at Last) have an average spacing of approximately 11 km (range: 8 - 12 km) compared with the modern Taupo Volcanic Zone geothermal field spacing of 12 - 15 km (Latter, 1980).

The convective cell systems generated by rhyolite volcanism are considered to differ from those formed during andesite volcanism in their dimensions and type of interaction with the intrusive magmas (Fig. 12-2). In the previous section it was suggested that during andesitic volcanism, large intrusive bodies of magma penetrated very shallow levels (within 1.5 km of the surface) and in many instances directly interacted with circulating ground water (both porphyry copper and epithermal deposits). In contrast, available evidence for the genesis of the Taupo Volcanic Zone rhyolites suggests that the rhyolite magma reservoirs are probably granite batholiths at a depth of greater than 5 km (c.f. Ewart *et al*, 1975). Pyroclastic flow and rhyolite lava (dome building) eruptions appear to directly tap these deep reservoirs without intermediate shallow chambers. Drilling in modern geothermal fields of the Taupo Volcanic Zone, to depths greater than 2 km, has penetrated rhyolite pyroclastics, lavas and sediments, some andesites, and greywacke basement, but apparently no intrusive sub-volcanic rhyolite magma reservoirs. Also the geothermal (heat) gradients in these systems are too low for the magmas to be in close proximity.

Therefore the hydrothermal convective cells operating during rhyolite volcanism are considered to be large but relatively decoupled from the magmatic heat source (Fig. 12-2). Apart from heat the magmatic contribution to the hydrothermal system is probably small with most of the fluid components being derived by leaching from the sedimentary and volcanic country rocks.

Figure 12-3: Negative isostatic vertical gradient gravity anomalies (after Woodward, 1971), beneath the Whitianga Group, which may represent centres of rhyolitic volcanism (Dr D.N.B. Skinner, pers. comm.). Anomalies associated with non-rhyolitic rocks in other parts of the Province are not shown. Anomaly values in Eöt vös units (10^{-9} s^{-2}).

Sequence of Events During Rhyolitic
Volcanism in the Hauraki Province

During the late Miocene an extensional tectonic regime was initiated in the region following the migration of the subduction zone to the south-east. A series of grabens (comprising the Coromandel Depression) formed in the eastern part of the region with concomitant rhyolite volcanism.

Skinner (pers. comm.) considers that several volcanic centres (Fig. 12-3) may be represented by negative gravity anomalies in the Isostatic Vertical Gradient Anomaly Map (Woodward, 1971). These may be analogous to the rhyolite volcanic centres of the Taupo Volcanic Zone, the latter representing multiple caldera collapse structures with each major pyroclastic flow eruption having been followed by collapse of the vent area and eruption of lava (domes) and tephra (Cole, 1981). A similar eruptive sequence is recognised in some sections of the Whitianga Group (c.f. Table Mountain; Hayward, 1974) but cyclic volcanic events have left a more complicated sequence in others.

Although rhyolite volcanism may have begun in the northern part of the province and proceeded southward (c.f. Fig. 2-9), the ages of the associated mineralisations may not necessarily follow this trend. If the hydrothermal systems were generated by heat from deep batholiths, as suggested previously, then geothermal activity may have been contemporaneous throughout most of the region, analogous to the widespread geothermal activity in the Taupo Volcanic Zone today.

CHAPTER 13

COMPARISON OF THE EPITHERMAL DEPOSITS OF THE HAURAKI PROVINCE WITH SIMILAR DEPOSITS IN OTHER PARTS OF THE WORLD

INTRODUCTION

The geology and geochemistry of some types of epithermal deposits have recently been reviewed by Sillitoe (1977) and Boyle (1979), while White (1981) and Henley & Ellis (in press) have related the formation of epithermal deposits to modern geothermal processes.

This chapter gives a brief introduction to the occurrence, characterisation and classification of epithermal deposits and compares the deposits of the Hauraki Province with some overseas examples in terms of size, specific mineralogical and physicochemical features, and genetic models.

GOLD PRODUCTION

Epithermal deposits have accounted for approximately 5% of the world's total gold production, ranking third after placer deposits (approximately 65%) and deposits in Archean greenstone belts (approximately 18%). Production from the major deposits in the Hauraki Province and some other famous epithermal deposits, is listed in Table 13-1.

GEOGRAPHIC OCCURRENCE OF EPITHERMAL DEPOSITS

The largest group of epithermal gold and silver deposits occurs around the circum-Pacific volcanic belt and includes New Zealand, Fiji, the Philippines, Indonesia, Japan, Colorado - Nevada, Mexico, Ecuador, Columbia and Peru. However, deposits also occur in U.S.S.R., Romania (Transylvania) and Spain.

TYPES OF EPITHERMAL DEPOSITS

A mineralogically based classification of epithermal deposits, partly after Lindgren (1933) and Boyle (1979) is given in Table 13-2. The overseas examples cited are historically large gold and silver producers (Table 13-1) and therefore in classifying the Hauraki deposits only Waihi, Karangahake and Thames are of similar economic significance. These latter deposits

TABLE 13-1: Gold production of some famous epithermal deposits.

	<u>Mine or district</u>	<u>Kg of gold</u>
NEW ZEALAND*	Waihi	200,000
	Thames	40,000
	Karangahake	35,000
FIJI	Emperor Mine	111,700
INDONESIA	Benkoelen	34,100
PHILIPPINES	Accupan and Antomok Mines	205,000
MEXICO	Guanajuato	124,400
PERU	Finlandia	1,600
U.S.A Nevada	Comstock	226,300
	Goldfield	130,000
	Tonopah	58,000
	Silver City	28,000
	Round Mountain	12,000
	Jarbridge	7,000
Colorado	Cripple Creek	622,000
	Sunnyside	13,000
Washington	Republic	15,200

* Au production figures from Downey's (1935) Au + Ag bullion totals corrected by the estimated Au:Ag ratio.

TABLE 13-2: Classification of epithermal mineral deposits, modified after Lindgren (1933) and Boyle (1979).

Class	Minerals*				Notes
	Principal Au mineral	Principal Ag mineral	Other metallic minerals	Gangue	
Gold-silver	el	ac	py,sp,gn,cp,thd,pg,pb, Au-Ag tellurides, Ag sulphosalts and Ag selenides	qtz,ad,carb,fl	el is a major constituent
Silver-Gold	el	ac	py,sp,gn,cp,thd,hm,mc, sulphosalts, Ag-Au tellurides and selenides, po,pg,pb,bi,wo,mo,sch	qtz,carb,ad,fl, ba,sc,cl	Strong development of adularia
Silver	-	ac	py,pb,pg,sp,gn,cp,thd, apy,po, Ag selenides	qtz,carb,ad, ba,fl	el is a minor constituent, whereas ac and base metals are major constituents. Tellurides and selenides sometimes abundant
Gold-telluride	cal,ptz or syl	hs	py,sp,gn,cp,thd, Au-Ag tellurides native Te,mc,apy, mo,wo	qtz,ad,carb,fl roscelite	Virtually no el or other Au minerals
Gold-selenide	el	rm or agu	apy,py,sp,gn,cp,ac,pb, thd,gn,Ag-Au tellurides, po	qtz,carb	Au occurs predominantly as a telluride mineral. el-gold is rare but when it occurs it has high fineness. Tellurium content of the deposits is 5-20 times that of gold.
Lead, zinc and copper ("Base metal deposits")	-	(thd)	py,gn,sp,cp,sulphosalts, mc,apy,po,hm,mo	qtz,carb,fl, ba	Ag occurs predominantly as a selenide mineral
Antimony ("Stibnite deposits")	-	-	sb,py,sp,apy,thd,cb	qtz	
Mercury ("Cinnabar deposits")	-	-	cb,py,mc,sb	qtz,ca	

* See list of abbreviations

Examples (Au/Ag ratios)

Brad and Baia Mare Districts, Romania (0.5 to 0.2)

Hauraki, N.Z. (0.4)

El Oro, Mexico (0.05)

Black Mountain, Arizona

De Lamar, Idaho (0.05)

Tonopah (0.01)

Comstock Lode (0.03)

Creede Colorado (0.01)

Pachua } Mexico

Real de Monte } (0.01)

Guanaquato (0.01)

Cripple Creek, Colorado (10)

Vatukoula, Fiji (1)

Goldfield, Nevada (3)

Acupan, Philippines (1)

Republic, Washington

Radjang-Lebong, Indonesia (1-0.01)

Kushikino, Kagoshima Prefecture Japan (1-0.25)

Casapalca, Peru

Paarl, Mexico

Hunan Province, China

Uncia and Porco, Bolivia

Almaden, Spain

Idria, Italy

Redington } California

New Almaden }

Chisos, Texas

belong to the gold - silver category*, as suggested by Lindgren (1933). If smaller deposits of the Hauraki Province are considered, some of the other classes of epithermal deposits are also represented, e.g.: silver - gold, Maratoto; gold - telluride, Monowai and Sylvia (Tapu - Thames); lead - zinc - copper, Tui Mine; and mercury, Mackaytown and Kauaeranga Valley.

CHARACTERISTIC FEATURES OF EPITHERMAL GOLD AND SILVER DEPOSITS

Sillitoe (1977) noted that epithermal deposits are characterised by the following features:

1. They are commonly emplaced in volcanic sequences ranging from andesite to rhyolite which are mid- to late Cenozoic in age.
2. Veins occupy pre-existing tension fractures, including faults, and occur in branching patterns which are commonly increasingly complex upwards.
3. The host rocks are altered to propylitic assemblages on a regional scale, whereas the more restricted alteration haloes bounding the veins consist of either sericitisation and silicification (commonly with adularia) or argillic and advanced argillic alteration (with clays, alunite, pyrophyllite, diaspore, etc.) accompanied by widespread silicification.
4. The deposits contain principally precious metals in various proportions, but also base metals. Silver occurs as acanthite and arsenic- or antimony-bearing sulphosalts; gold as native gold, electrum or as tellurides; lead as galena, and zinc as sphalerite. Copper is plentiful, but commonly occurs as enargite where advanced argillic alteration is developed. Stibnite, cinnabar and selenides can also occur. The main gangue is quartz, commonly as aphanitic chalcedony, accompanied by varying quantities of pyrite, calcite, dolomite, barite, adularia, rhodochrosite and fluorite.
5. Low confining pressure is indicated by vein features such as drusy cavities, filling, comb, colloform and crustiform textures and inter-mineral breccias. Ore and gangue minerals are commonly fine - grained.
6. The shallow depths of emplacement, perhaps from 100 to 1000m beneath the surface, are emphasized by the abrupt downward termination or 'bottoming' of mineralisation or the downward increase of base metal sulphides at the expense of gold and silver. Ore shoots in veins have rarely been worked for more than 600m vertically.

* Footnote: Although the veins at Thames contain gold and silver telluride minerals they are not gold - telluride deposits because the predominant gold mineral is electrum rather than a gold or gold - silver telluride.

ZONE	SURFACE	Au/Ag RATIO	PERSISTENT ELEMENTS	INDEX ELEMENTS	PERSISTENT MINERALS	INDEX MINERALS	REMARKS
1		Low	SiO ₂ , Fe, Ca, Mg, Mn, S	Ba, Sr, F	Quartz (chalcedony), pyrite, marcasite, carbonates	Barite, fluorite, (cinnabar)	This zone is rare in most veins. Generally barren of gold and silver
2			SiO ₂ , Fe, Ca, Mg, Mn, S	Hg, Sb, As, Ba, Sr, F	Quartz (chalcedony), pyrite, marcasite, carbonates	Cinnabar, realgar, orpiment, stibnite, barite, fluorite	In certain veins this zone may be auriferous and argentiferous
3			SiO ₂ , Fe, Ca, Mg, Mn, S	Ag, Au, As, Sb, Cu, Zn, Pb, Bi, Te, Se	Quartz (chalcedony), pyrite, carbonates, galena, sphalerite, chalcopryite, gold (electrum), (molybdenite)	Acanthite, gold, stibnite, sulphosalts, tellurides, selenides, bismuthinite and other bismuth minerals, adularia, alunite, Mn-silicates, Mn-carbonates, fluorite, barite, (scheelite), (wolframite)	Constitutes bonanza section of most epithermal gold-silver deposits. Passes with decrease in gold and silver into zone 4. Generally absent in deep-seated deposits.
4			SiO ₂ , Fe, Ca, Mg, Mn, S	Cu, Zn, Pb	Quartz, pyrite, carbonates, galena, sphalerite, chalcopryite	Chalcopryite, pyrite, sphalerite, galena, barite	Commonly low or barren in gold and silver. Represents the bottoms of many epithermal Au-Ag veins.
5		Medium	SiO ₂ , Fe, Ca, Mg, Mn, S	Au, Ag, Cu, Pb, Zn, As, Sb, Te	Quartz, pyrite, arsenopyrite, carbonates, galena, sphalerite, chalcopryite, gold, (molybdenite)	Galena, sphalerite, tetrahedrite-tennantite, (acanthite), sulphosalts, (scheelite), (wolframite), tellurides, gold	Sphalerite commonly increases with depth.
6			SiO ₂ , Fe, Ca, Mg, Mn, S	Au, Ag, Cu, As, Sb	Quartz, pyrite, arsenopyrite, carbonates, gold, (molybdenite)	Chalcopryite, tetrahedrite- tennantite, enargite, uraninite (pitchblende), scheelite, wolframite, tellurides, gold, (tourmaline)	Merges into zone 7
7			SiO ₂ , Fe, Ca, Mg, Mn, S	Au, Ag, As, Te, Cu, W	Quartz, pyrite, arsenopyrite, carbonates, feldspar, gold, (molybdenite)	Arsenopyrite, chalcopryite, scheelite, wolframite, tourmaline, tellurides, gold	Merges into zone 8
8		High	SiO ₂ , Fe, Ca, Mg, Mn, S	Au, Ag, Cu, W	Quartz, pyrite, pyrrhotite, feldspar, carbonates, tourmaline, gold, (molybdenite)	Pyrite, pyrrhotite, chalcopryite, arsenopyrite, scheelite, wolframite, gold, tourmaline	
9			SiO ₂ , Fe, S	W, Sn, Mo, Bi, B, F, As	Quartz, feldspar, pyrite, pyrrhotite, molybdenite	Pyrite, pyrrhotite, bismuth, molybdenite, arsenopyrite, bismuthinite, wolframite, scheelite, cassiterite, tourmaline, topaz	Generally barren of gold and silver

Figure 13-1: Idealised vertical zonation of elements and minerals in epigenetic gold deposits, after Boyle (1979). Although many specific minerals and some zones of the illustrated scheme are absent from the epithermal deposits of the Hauraki Gold - Silver Province, the general elemental and mineral trends are similar.

The deposits of the Hauraki Gold - Silver Province have generally similar features to those described above, but differ in some points of detail. For example, fluorite is absent and enargite has been noted from only the deposits at Thames.

MINERALOGICAL ASPECTS OF EPITHERMAL GOLD AND SILVER DEPOSITS

Mineral Zoning and Paragenesis

The generalised depth zonation scheme proposed here for the Hauraki Gold - Silver Province resembles Boyle's (1979) idealised vertical mineral zonation for gold deposits (Fig. 13-1), particularly zones 1 to 4.

Similarly, the mineral paragenetic trends recognised in the individual deposits of the Hauraki Gold - Silver Province generally conform to Boyle's (1979, pp 415 - 417) suggested paragenesis for gold deposits:

1. pyrite and arsenopyrite, 2. wolframite and scheelite, 3. molybdenite, 4. native bismuth and bismuthinite, 5. sphalerite, 6. uraninite and/or brannerite, 7. chalcopyrite, tennantite, tetrahedrite, enargite, cubanite and bornite, 8. galena, 9. acanthite, 10. stibnite and various sulphosalts (e.g. pyrargyrite), 11. native bismuth and bismuthinite, 12. precious metal and base metal tellurides, 13. native gold and electrum, 14. aurostibite, and 15. cinnabar, orpiment and realgar. Stages 6, 11 and 14 have not been recognised in the Hauraki Province and Stages 10, 12 and 13 are reversed.

Gold/Silver Ratios and Gold Fineness

The gold/silver ratio of gold deposits generally decreases with decreasing depth (Boyle, 1979) because of the increasing proportion of silver minerals near the surface (c.f. Karangahake and Waiorongomai). Similarly the fineness of gold (-electrum) decreases with decreasing depth but this trend is directly related to physicochemical factors (fS_2 and temperature, see Appendix V).

Although native gold is rare in gold - telluride deposits, when found it usually has a high fineness (Boyle, 1979) indicating that the equilibrium reaction:

trends more strongly to the right than the analogous sulphide reaction [equation (V-30)].

Figure 13-2: Minerals of the system Au - Ag - Te. (From Kelly & Goddard, 1969.)

Telluride Minerals

The phase relations in the system Au - Ag - Te were investigated experimentally by Markham (1960) and Cabri (1965) and empirically by Kelly & Goddard (1969). The stoichiometric compositions of the naturally occurring minerals in the system are shown in Fig. 13-2.

Apart from hessite, gold and silver tellurides generally occur in only small quantities in epithermal gold - silver, silver - gold and silver deposits. However gold - telluride deposits are characterised by the dominance of Au and Au - Ag telluride minerals (calaverite, krennerite, sylvanite and petzite) over electrum.

Hessite has been noted from several mining centres in the Hauraki Province (Table 4-1) but representatives of the Au and Au - Ag telluride minerals (and native Te) have been identified only in the Tapu - Thames and Thames areas (by Merchant, 1978 and Ramdohr, 1980). The quantity of sylvanite and petzite, relative to electrum - gold, in some deposits of the Tapu - Thames area (e.g. Monowai and Sylvia; c.f. Merchant, 1978) may justify their classification as gold - telluride deposits (mineralogically but without any economic conotation).

In his classification of telluride deposits, Markham (1960) suggested that telluride mineralisation in Tertiary volcanic settings (equivalent to gold - telluride epithermal deposits) are characterised by an abundance of native tellurium, rarity of native gold (electrum), predominance of krennerite over calaverite, and a paucity of tellurides, other than those of gold and silver. However, Kelly & Goddard (1969) noted that these features were not consistent for all epithermal gold - telluride deposits. In the Acupan vein (Philippines) for example, electrum is common, native tellurium absent and calaverite predominates over krennerite. These authors considered that "At present, there does not appear to be any consistent scheme of classification of telluride deposits inherent in the tellurium mineralogy per se" (Kelly & Goddard, 1969 p 186).

In Chapter 11 and Appendix V the occurrence of gold and silver telluride minerals is related to the concentration of total Te in solution; gold - telluride deposits probably result from fluids relatively rich in tellurium. Physicochemical factors (e.g. temperature) may determine whether gold and silver or other tellurides (e.g. Bi - tellurides) are deposited (e.g. tetradyomite at high temperature and hessite at moderate temperature). Detailed thermodynamic investigations of these aspects is not possible at present with the current state of knowledge of aqueous tellurium species and telluride metal complexes.

Seliniferous and Selenide Minerals

It may be demonstrated empirically, with some thermodynamic basis, that at medium and high temperatures selenium isomorphously substitutes for sulphur in sulphide minerals, whereas selenide minerals are precipitated at low temperatures and under relatively oxidising conditions. Therefore gold - selenide deposits would be expected to form at low temperatures and from solutions with oxidised/reduced aqueous sulphur species ratios greater than 1.

Naumannite is the only selenide mineral that has been identified from the Hauraki Province and it occurs at Te Ahumata and Broken Hills in association with various seleniferous sulphide minerals. The relative abundance of naumannite in these deposits however is insufficient to classify them in the gold - selenide category. Both deposits were formed at relatively low temperatures but only the mineralisation at Broken Hills appears to have been deposited under relatively oxidising conditions. The $\frac{\Sigma \text{Se}}{\Sigma \text{S}}$ ratio of the hydrothermal fluid may have been the controlling parameter at Te Ahumata.

In epithermal deposits, isomorphous substitution of selenium for sulphur is most notable in acanthite (e.g. Kieft & Oen, 1973; Petruk *et al.*, 1974; Shikazono, 1978; this study) although it also commonly occurs, but generally to a lesser extent, in other sulphides such as galena, and sphalerite, and in the Hauraki Province, tetradymite and tellurobismutite (Merchant, 1978).

PHYSICOCHEMICAL ASPECTS

Introduction

Although recent fluid inclusion and stable isotope studies have provided temperature and apparent salinity data for a large number of epithermal deposits (c.f. Sillitoe, 1977; Boyle, 1979) only a few studies have included a detailed thermodynamic interpretation of the chemistry of the depositional environment. Most of the latter are summarised in Table 13-3.

Temperature

The temperature of formation of overseas epithermal deposits, determined by fluid inclusion and stable isotope studies, are generally in the 200 - 300°C range (Fig. 13-3) although temperatures up to 385°C (Slack, 1980; Lake City, Colorado; not shown in Fig. 13-3) have been recorded. The

Figure 13-3: Fluid inclusion filling temperatures from epithermal deposits. (From Sillitoe, 1977.)

TABLE 13-3: Geochemical parameters for some overseas epithermal deposits calculated by previous workers

TABLE 13-3: Geochemical parameters for some overseas epithermal deposits calculated by previous workers																	
Location		Mine/vein	Reference	Class ^{*1} (Au/Ag)	Ore minerals ^{*2}	Gangue minerals ^{*2}	Pressure ^{*3} (depth)	t °C ^{*4,5}	Salinity ^{*6}	pH ^{*4}	≤S ^{*4}	Log f S ₂ (bars)	Log f O ₂ (bars)	CO ₂ (bars)	Aqueous ^{*7} S species	Mechanism of ore deposition	
Colorado (San Juan Mountains)	Eureka District	Sunnyside Mine	Casadevall & Ohmoto (1977)	Ag-Au (0.04)	(1)sp,gn,py,thd, el,ptz,cal,bo, aikinite,hm (2)sp,gn,cp	(1)qtz,pym,rho (2)qtz,fl,ca,rho	(1)110-220 (1450-2000) (2) 33 (400)	(1)250-320 (300) (2)170-245, B at 240	(1)0 to 3.6 (2) 1	4.3-5.9	0.03-0.07 (0.05)	-6.6 to -8.0	(1)-31.1 to -28.3	0.5 to 4	o > r	decreasing temperature and increas- ing pH	Eureka District
"	Lake City District	Ute - Hidden Treasure vein system	Slack (1980)	Ag-Au	(1)py,sp,gn,cp, thd,apy,hm,el (2)py,thd,gn,sp,cp, apy,sulphosalts, hm,mg,pitchblende Au-Ag tellurides,el	(1)qtz,rho,ca,sc, fl (2)ba,qtz,rho,sc, clays	40	(1)260-185 (2)206-385 B at 250 (250)	(1)0.1 to 4 (2)1.3 to 12.4	5.4	0.01	-11.2	-34.4	2 to 40	o ≈ r	boiling and throttling	Lake City District
"	Creede District	OH vein	Barton et al (1977)	Ag-Au (0.01)	gn,sp,cp,py,hm,thd, el,ss	qtz,cl,ad,ba,rho, fl,ss	40-50 (500-600)	190-268 B (250)	4-12	4.9 to 5.9 (5.4)	0.018 to 0.30 (0.02)	-9 to -13	-34 to -13	-	o > r	*8	Creede District
Peru	Colqui District	Finlandia vein	Kamilli & Ohmoto (1977)	Ag-Au	(1)thd,Ag sulphosalts, el,sp,gn,py (2)sp,gn	(1)qtz,mu,ss (2)qtz,late ba	74 (>1000)	(1)250-290 B (270) (2)260-140	(1)0.2- 8.2 (2)4.5- 13	4.7 to 5.5 (5.1)	0.03 to 0.0003 (0.003)	-9.6 to -10.8	-33.2 to -36.0	15 to 29	o ≈ r	boiling	Colqui District
Japan	Yatani Mine	(i) Yatani Pb-Zn vein (ii) Kanizawa Au-Ag vein	Hattori (1975)	Ag-Au	{ sp,gn,cp,po,mc ac,el sp,gn,cp,el,ac,py }	{ qtz,cl,mu,ad Mn-silicate Mn-carb. qtz,ad }	-	200 to 250 (250)	0.7 to 1.3	{ ≤ 6 ≥ 6 }	0.01 to 0.001 (0.01)	{ -12 to -14 -11 }	{ -37 to -40 -34 to -39 }	- -	o << r o ≈ r	oxidation	Yatani Mine
"	Toyoha Mine	(i)Soya vein (ii)Tajima vein	Shikazono (1975)	Ag-Au	py,sp,gn,cp,hm,po	qtz,carb,cl alabandite	-	150 to 250	0.2 to 3.7	7	0.01 to 0.001 (0.01)	-13.5 to -16.5	-38 to -44.5	> 0.1	(1) o << r (2) o > r	reduction	Toyoha Mine
Philippines	Baguio District	Antamok and Acupan veins	Sawkins et al (1979)	Au - telluride (1)	py,el,sp,gn,cp	qtz,ca,an	73 (900)	250-300 B	0 to 6	-	-	-	-	-	-	-	Baguio District
Fiji	Vatukoula	Emperor Mine	Ahmad (1979)	Au - telluride (1 to 0.4)	py,sp,thd,cp, Au-Ag tellurides, native Te,el,mc, apy	qtz,ad, roscoelite an,do,ca	20-32 (200-350)	170-317 B (250)	4.6 to 7.1	5 to 6 (5.5)	0.001	-10.5 to -12	-35 to -37	0.25 to 2.5	o ≈ r	boiling	Vatukoula

*1 See Table 13-2.

*2 See list of abbreviations.

*3 Pressure in bars, depth in metres.

*4 Value used for thermodynamic model is given in brackets

*5 B = Boiling

*6 Salinity in equivalent weight % NaCl, from fluid inclusion
freezing temperature data.

*7 o = oxidised, r = reduced

*8 Not stated specifically "but probably involve decreasing
temperature and rising pH" (Barton et al 1977 p 22).

Hauraki mineralisations were deposited over a similar temperature range although the temperature of deposition for the early pyrite - chalcopyrite mineral assemblage at Tapu - Thames and Tui Mine may have been slightly higher (approximately 400°C).

Fluid inclusion studies have also indicated that precious metal deposition in a number of epithermal deposits was accompanied by boiling and this is thought to be a characteristic feature of the bonanza type deposits (c.f. Kamilli & Ohmoto, 1977).

Salinity

The apparent salinity of fluids during deposition of precious metal stages in epithermal deposits are generally low, predominantly in the range of 0 to 4 eq. wt. % NaCl (c.f. Table 13-3; Sillitoe, 1977; Boyle, 1979), although much higher values have been recorded for mixed precious metal - base metal assemblages: 7.1 eq. wt. % NaCl from Vatukoula (Ahmad, 1979) and 12.4 eq. wt. % NaCl from Lake City District (Slack, 1980). However, some of these high values may result from the increase in concentration of the components remaining after steam separation during boiling (c.f. Slack, 1980).

In individual deposits apparent salinities of fluids present during deposition of base metal stages are generally higher than during precious metal stages although as a group they overlap and have similar maximum values (e.g. 13 eq. wt. % NaCl during sphalerite - galena deposition in the Finlandia vein; Kamilli & Ohmoto, 1977).

The difference in ranges of true salinity between the precious and base metal stages may be greater than indicated by the apparent salinities because of the larger relative effect of dissolved CO_2 on the low salinity results (because liquid CO_2 is generally not present in fluid inclusions of epithermal deposits, the corrections required for the concentration of dissolved CO_2 are less significant with increasing apparent salinity).

Precious metal stages of the deposits in the Hauraki Province have similar apparent salinities to those of overseas deposits (i.e. 0 to 4 eq. wt. % NaCl), however salinities recorded from the base metal stages (e.g. Northern Colville Peninsula, Petote Stream, Tapu - Thames and Tui Mine) are generally low compared with their overseas counterparts, the maximum recorded value being 6.1 eq. wt. % NaCl from Tui Mine.

pH

The widespread occurrence of adularia as a vein mineral and wall rock alteration product suggests that most epithermal gold and silver deposits

formed under conditions of near neutral (i.e. pH = 5.5 to 5.7 at the temperatures of deposition) or slightly alkaline pH. Goldfield (Nevada) is a notable exception, where acidic conditions are indicated by the occurrence of abundant alunite.

Shikazono (1978) noted that in Japan adularia is commonly found in Au - Ag vein type deposits while sericite is common in Pb - Zn vein type deposits indicating different pH ranges for the formation of the two different types of deposits. However, such a consistent relationship is not found in all epithermal districts of the world with exceptions to the Japanese trend occurring in both Au - Ag (exemplified by Goldfield) and Pb - Zn type deposits.

Aqueous Sulphur Species, Oxidised/Reduced S Species Ratio

Thermodynamic studies of overseas epithermal deposits by previous workers (Table 13-3) indicate that in the majority of cases mineral deposition appears to have occurred from solutions containing approximately equal proportions of aqueous sulphate and sulphide species, and in two (Sunnyside Mine and Creede) the concentration of oxidised species is believed to have exceeded that of the sulphide species. Fluids containing predominantly reduced sulphur species have been identified from only two deposits of the group listed in Table 13-3, both Japanese Pb - Zn type deposits.

In contrast many of the deposits in the Hauraki Province are believed to have formed from fluids containing sulphur predominantly in reduced form and this appears to be the case with the largest economic deposits: Waihi, Thames and possibly also Karangahake. Relatively oxidised fluids were present mainly in the deposits believed to have been formed in relatively shallow environments and the deeper, predominantly base metal, deposits at Tui Mine and Waiorongomai.

SPECIFIC MECHANISMS OF ORE DEPOSITION

Introduction

Various mechanisms of ore deposition have been proposed by previous studies to explain the localisations of ore in epithermal deposits (c.f. Table 13-3; Boyle, 1979). They include:

- (i) decrease in temperature
- (ii) mixing with other fluids
- (iii) changes in fluid chemistry as a result of fluid - wall rock reactions

- (iv) boiling
- (v) fluctuating concentrations of volatile constituents

Some of these processes may be modelled thermodynamically and by comparison with modern geothermal systems.

Mixing

Mixing of the hydrothermal fluid with ground water is an attractive mechanism for ore deposition in the epithermal environment because it causes instability of both chloride and sulphide complexed metals in solution (see Chapter 11). Drummond (1981) modelled the process thermodynamically and concluded that the most important effect on the hydrothermal fluid, with regard to mineral deposition, is the resulting decrease in temperature.

Henley & Seward (in prep, cited in Henley & Ellis, in press) consider that the relatively high oxygen fugacity of the ore deposition environment (where $\text{HSO}_4^- \rightarrow \text{H}_2\text{S}$) of many epithermal ore deposits is most likely the result of mixing with steam-heated acid sulphate waters generated above the boiling zone of the hydrothermal systems. This is analogous to environments in modern geothermal systems where deep alkali chloride type waters mix with shallow acid sulphate type waters. Henley & Ellis (in press) cite examples in modern geothermal fields where acid sulphate waters occur at deep levels (deeper than 500m at Matsuo and 700m at Matsukaua).

Boiling

Drummond (1981) thermodynamically modelled the effects of boiling in hydrothermal solutions and concluded that open boiling under isoenthalpic conditions (i.e. boiling accompanied by cooling) tends to oxidise solutions by removing reduced components (H_2S , CH_4 , H_2 , etc.) from solution more rapidly than their less volatile counterparts (SO_4^{2-} , SO_2 , CO_2 , etc.). Closed boiling has little effect on the oxidation state of the solution since all of the redox components are confined within the liquid - vapour system. Boiling also tends to increase pH by removing acid volatile species (i.e. H_2CO_3 , H_2SO_4) from solution. The relative importance of the resulting oxidation versus increasing pH effects on the deposition of metals from chloride and sulphide complexes in solution probably depends on the original composition of the solution and the quantity of gas separation. The decrease in temperature accompanying boiling may also be important in causing mineral deposition in some instances, however a large fraction of the water must be boiled off to produce a significant drop in the temperature (c.f. Drummond, 1981).

Kamilli & Ohmoto (1977) suggested that the advent of boiling at a particular elevation may be caused in at least three different ways: by an increase in volatile constituents, a drop in total pressure, or an increase in temperature. In the case of the Finlandia Vein they considered that boiling was caused by a process of gas effervescence.

A drop in total pressure may be caused by tectonic effects (e.g. sudden opening of the vein by fault movement) or by sudden explosive clearing of blocked channels. In the latter case, gas pressures may build up in sealed systems leading to hydraulic fracturing and hydrothermal explosions with subsequent boiling, gas loss (with associated increase in fluid pH) and temperature drop, causing mineral deposition, resealing of the system and the beginning of another cycle (Hedenquist, 1981). Similar effects may also occur in porous rocks in the near surface environment, forming hydrothermal breccia pipes (e.g. breccia pipes in rhyolite tuffs at Kapowai, Broken Hills and Neavesville).

Temperature data for epithermal deposits are generally not sufficiently detailed to evaluate whether temperature increases are an important mechanism for the 'initiation' of boiling.

Fluctuating Concentrations of Volatile Constituents

Carbon dioxide is generally the dominant gas component in modern hydrothermal systems (c.f. Ellis & Mahon, 1977; Ellis, 1979) and its concentration is important in regulating the fluid pH [equation (11-4)] and the maximum depth (pressure) of boiling (i.e. position of the boiling point of water versus depth curve). Wide ranges of apparent salinity in fluid inclusions in epithermal deposits (Tables 6-2 and 13-3) and geothermal systems (e.g. Browne *et al.*, 1974; Christie, 1980; Hedenquist, in prep.) may indicate that large fluctuations in gas content occur. These may be important mechanisms, via their influence on pH or the initiation of boiling, of mineral deposition.

Summary

No single deposition mechanism cited above accounts for the formation of all types of epithermal deposits and in reality probably all of the mechanisms operated individually in different deposits. The depth zonation model proposed by the writer (Chapter 11) uses most of the previously described mechanisms, separately in different parts of the hypothetical system, and suggests that the different environments in which the different mechanisms operate deposit generally characteristic mineral assemblages.

COMMON GENETIC FEATURES OF EPITHERMAL DEPOSITS

In Sillitoe's (1977) review of epithermal deposits, he concluded that in individual deposits:

- (a) A suitable structural environment for vein deposition is created by volcanism.
- (b) Ore deposition commonly follows the deposition of the host volcanic rock by 1 to 3 m.y. (although it may be up to 15 m.y.).
- (c) The composition of the host volcanic rock is not a crucial feature.
- (d) Intrusions are sometimes spatially related to mineralisation.
- (e) The ore fluid generally had a low salinity and was at a moderate to low temperature. The water was predominantly meteoric in origin.
- (f) The metals, carbon and sulphur were derived from either a magma or by leaching from basement rocks.

These statements are generally equally applicable to the epithermal deposits of the Hauraki Gold - Silver Province except that with regard to point (c) andesites have provided better ore forming environments than rhyolites both in terms of structure and, as suggested here, proximity to heat source. Also, regarding point (a): many overseas deposits, particularly those in Colorado, are structurally, although generally not temporally, related to caldera formation; however caldera land forms have been recognised in only two or three locations in the Hauraki Province and their genetic relationship to nearby gold - silver deposits has not been definitely established.

CHAPTER 14CONCLUSIONS

The metaliferous mineral deposits of the Hauraki Gold - Silver Province may be grouped into porphyry copper and epithermal - vein associations.

The porphyry copper deposits are associated with quartz diorite stocks of lower and mid Miocene age, intruded into Jurassic greywacke suite rocks and Miocene andesites. They are 'diorite' model, hypabyssal and volcanic types. Surface geological mapping, stream sediment and rock chip geochemistry, together with limited subsurface drill hole analysis by mineral exploration companies, has indicated that the deposits are small and presently uneconomic.

Fluid inclusion and sulphur isotope studies of one of the porphyry deposits, Miners Head, suggest that copper mineralisation occurred at a temperature of approximately 425°C from fluids with apparent salinities up to 15.5 eq. wt. % NaCl and containing sulphur of magmatic origin. The low values of ΣS , fS_2 and fO_2 indicated for the depositional environments of some of the deposits may explain the absence of abundant copper mineralisation.

The epithermal deposits range in age from Miocene to Pleistocene and occur as fault fissure fillings in greywacke, andesite, dacite and rhyolite rocks. Some small deposits in rhyolite tuff host rocks occur cementing hydrothermal breccias.

The historically profitable epithermal deposits are gold - silver types although silver - gold, silver, gold - telluride, Cu - Pb - Zn and mercury type deposits are also found in the province. Acanthite and electrum dominate the precious metal assemblages although tellurides (mainly hessite), seleniferous sulphide and selenide minerals are locally important. The base metals; sphalerite, galena, pyrite and chalcopyrite, occur in most deposits. Gangue minerals are mainly quartz and calcite.

Wall rock alteration assemblages are generally propylitic and characterised by sericite and/or adularia indicating that the pH of the hydrothermal fluids was near neutral or slightly alkaline. Argillic assemblages, dominated by kaolinite, are considered to have formed by reactions with late acidic fluids as retrograde stages or, if primary, in the near surface environment.

Temperatures derived from fluid inclusion and stable isotope studies indicate that base metal deposition occurred predominantly in the range of 320 - 280°C, whereas precious metal deposition occurred between 280 and 200°C. Late barite precipitation in some deposits occurred generally below 200°C. Boiling during mineralisation is indicated in some deposits by the occurrence of vapour rich and vapour filled fluid inclusions.

Salinities of epithermal fluids were predominantly in the range of 0 to 4 eq. wt. % NaCl. No consistent difference in apparent salinity between the different types of epithermal deposits was recognised, although the highest maximum values (up to 6.1 eq. wt. % NaCl) were recorded from the base metal deposit at Tui Mine.

The concentration of CO₂ averages 1 mole % in the deposits in which this aspect was studied and it is believed to be below 3 mole % (possibly below 1.5 mole %) in all deposits except the Garbo Mine (Thames) where Merchant (1978) reported the occurrence of liquid CO₂ in fluid inclusions.

Moderate values of fS₂ and fO₂ are indicated for base metal and mixed base metal - precious metal assemblages of most deposits by the predominance of pyrite + chalcopyrite over other iron-bearing phases; primary bornite is absent, whereas pyrrhotite, hematite and magnetite rarely occur in the veins.

The largest gold - silver deposits formed from solutions in which the sulphur species in solution were predominantly reduced. Near surface environments and some deep, predominantly base metal, deposits were formed from solutions with approximately equal concentrations of oxidised and reduced sulphur species.

A variety of mechanisms of deposition are recognised, viz: (a) fluid - wall rock reactions with their associated effects on fluid pH, (b) mixing with other types of fluids, (c) boiling, and (d) varying concentrations of CO₂ in solution. These mechanisms are believed to operate at specific horizons within the hydrothermal system and deposit generally characteristic mineral assemblages.

The combination of specific depositional mechanism with favourable structural environment in the andesites has formed two different types of large gold - silver deposits. The bonanza gold deposits of Thames and Coromandel are considered to result from near surface boiling of hydrothermal fluids in a complexly faulted terrain. In contrast, the large comparatively low grade, gold - silver deposits of Waihi and Karangahake formed over a wide vertical range in a small number of major fault fissures with similar strike. Several different depositional mechanisms operated locally, but probably the most important overall were changes in pH resulting from

reactions of the fluid with wall rocks and varying concentrations of CO_2 .

Telluride minerals were formed in some deposits from solutions with relatively high concentrations of total tellurium, whereas selenide and seleniferous sulphide minerals were generally precipitated because of favourable physicochemical conditions: oxidising low temperature environments.

Deuterium/hydrogen ratios of water extracted from fluid inclusions indicate that the hydrothermal fluids mostly originated as meteoric water.

Sulphur isotope ratios of sulphide and sulphate minerals, in association with the thermodynamic relations of the mineral assemblages, indicate that the sulphur was derived from at least two different sources; sedimentary sulphate and magmatic SO_2 , the relative importance of each varying from one deposit to another.

Two types of hydrothermal systems are postulated for the formation of the epithermal deposits of the Hauraki Province. During andesitic volcanism in the Miocene - early Pliocene hydrothermal fluid convective cells were generated by heat from near surface small intrusive bodies of magma, whereas during rhyolitic volcanism in the late Miocene - Pleistocene the heat sources were larger plutons at greater depth.

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ANTHONY BARRY CHRISTIE

FLUID INCLUSIONS, STABLE ISOTOPES AND GEOCHEMISTRY
OF PORPHYRY COPPER AND EPITHERMAL VEIN DEPOSITS
OF THE HAURAKI GOLD - SILVER PROVINCE,
NEW ZEALAND

VOLUME 2

APPENDIX 1

A REVIEW OF THE INDIVIDUAL DEPOSITS
OF THE HAURAKI GOLD - SILVER PROVINCE

August 1982

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APPENDIX IA REVIEW OF THE INDIVIDUAL DEPOSITS
OF THE HAURAKI GOLD - SILVER PROVINCEINTRODUCTIONPREAMBLE

This appendix reviews the deposits of the Hauraki Gold - Silver Province individually in a geographical order from north to south (Fig. I-1). It combines both the writers work and information from previous studies.

INTRODUCTORY NOTESOre Petrography

Where detailed descriptions of the ore petrography of individual deposits are available in previous works this aspect is only briefly mentioned here. However, some areas have not been investigated recently and where samples were available for study detailed descriptions are given. Because of the large number of specimens investigated from Waihi, Karangahake and Waiorongomai, samples from these areas are described separately in Appendices VI, VII and VIII respectively.

Mineral and Rock Chemistry

Aspects of mineral and rock chemistry (e.g. EPMA, XRD and XRF analyses) are generally not reviewed here unless pertinent to some particular discussion.

EPMA analyses of metallic minerals made during this study are listed in Appendix II and summarised in Chapter 5. Those made by previous studies are referenced in Table 5-1.

Thermochemistry

The information and methods used to calculate the thermochemical parameters discussed in this appendix are described in Appendix V.

Figure I-1: Location of areas described in sections I-A to I-V.

Scope of Bibliographies

The bibliographies at the end of each deposit section refer to the relevant Geological Survey Bulletin of the early 1900's and subsequent works. References to earlier works are not included because they are listed in the bulletins as follows (see Fig. 1-7 for locations):

Coromandel Subdivision; Fraser & Adams (1907)

pages 9 to 11

Thames Subdivision; Fraser (1910) pages 4 to 7

Waihi - Tairua Subdivision; Bell & Fraser (1912)

pages 4 to 6

Aroha Subdivision; Henderson & Bartrum (1913)

pages 5 to 9

Waihi District; Morgan (1924) pages 11 to 13

Additional Sources of Information

Kitt (1978) listed all assays of mineral samples for gold, silver and platinum carried out at Chemistry Division, DSIR between 1922 and 1976. Chemical analyses of rocks made between 1917 and 1957 are listed in Challis (1971).

In addition to the geological sources referenced in this appendix, mine plans, photographs and historical accounts of the mining can be important to the geological interpretation of the mineralisations.

Detailed mine plans for many of the old workings are held at the Huntly branch of the Mines Division (Ministry of Energy).

Historical photographs of the mines and mining subjects are held by the Alexander Turnbull Library, Auckland Museum, Coromandel School of Mines Museum and the Waihi Art Centre and Museum.

Historical accounts of the mines and mining in the province include Bale (1971), Chapman (?), Gwilliam (1968), Isdale (1967), Kennedy (1964), McCara (1978), McNeil (1967),

Nolan (1977), Read (1965), Simpson (1971), Sommerville (1969) and Sparke & Cameron (1965).

Details of mine development and production for the major mines are given in a series (generally annual) of Mines Statements (Parliamentary Papers; copies are held in the Library of the Mines Division, Wellington) and Galvin (1986).

A detailed bibliography of published and unpublished works relating to the mines in State Forest areas is given by Slane & White (1980).

I-A

MINERS HEAD AND THE NEEDLESINTRODUCTION

Between 1857 and 1867 approximately 50,000 tonnes of rock were mined from Miners Head, from which 2300 tonnes of copper ore were concentrated and exported.

Brief descriptions of the Miners Head area were given by Hutton (1869), Park (1897), Bartrum (1921) and Henderson (1931, 1939), whereas a detailed report on the geology was given by Gregg et al (1970). The geology of the area north of Miners Head was mapped by Rabone (1971) and d'Auvergne (1974a). Weigel (1978) briefly described the sulphide mineralogy of the deposits at Miners Head and the Needles.

The mine at Miners Head consists of a chamber 45m x 12m, accessible by adit from the south, with a 22m deep shaft in one corner (Figs I-A-1 and I-A-2).

GEOLOGY

Miners Head is a composite breccia body intruding greywacke suite rocks (mostly argillite) of the Manaia Hill Group. It consists of an argillite (-greywacke) breccia "stock" cemented by quartz and quartz diorite porphyry (Fig. I-A-3) separated from the mainland by a pair of dikes; a western mineralised breccia dike (1.5 - 15m wide) and an eastern quartz diorite porphyry dike.

Quartz diorite and andesite-dacite porphyry dikes occur in the argillite and greywacke to the north of Miners Head (Rabone, 1971; d'Auvergne, 1974a) and at the Needles mineralised breccia and pebble dikes also occur (Weigel, 1978). The latter contain fragments and pebbles of greywacke-argillite and andesite porphyry.

Figure I-A-1: Map of the mine and adjacent rocks, at Miners Head. (Modified from Gregg *et al.*, 1970.)

Figure I-A-2: Inside the mine at Miners Head looking south along the strike of the mineralised breccia dike. The roof of the mine above the camera position has collapsed forming the hill of rubble in the foreground. The log fence surrounds a 22m deep shaft, now filled with water. The walls of the mine are stained with oxidation products (mainly malachite and azurite) of the mineralisation.

Figure I-A-3: Geological map of Miners Head. (Modified from Gregg et al., 1970.)

K - Ar AGE

Biotite from the quartz diorite at Miners Head was dated at 18.1 ± 0.2 m.y. by the K - Ar method (Dr. C.J.D. Adams and Prof. P.M. Black pers. comm.).

HYDROTHERMAL ALTERATION

The hydrothermal alteration of the igneous and greywacke suite rocks is generally propylitic (secondary quartz, chlorite, sericite, pyrite, epidote, calcite, prehnite and zeolites; Gregg *et al*, 1970), however Weigel (1978) considered that phyllic alteration also occurs and Prof. P.M. Black (pers. comm.) identified secondary biotite ("potassic" style alteration) at Miners Head.

MINERALISATION

Miners Head

Environment

Chalcopyrite with minor pyrite and sphalerite mineralisation is exposed on the walls of the mine chamber, around the shaft, and on the southern coast of the headland in and around three small adits (Fig. I-A-3). It occurs in a quartz cemented argillite breccia dike separating the breccia "stock" from a quartz diorite porphyry dike and the mainland.

The breccia dike is divisible into four parts based on the degree of silicification and mineralisation (Fig. I-A-4). The mineralised zones (zones 3 and 4) consist of brecciated argillite and greywacke fragments (50mm dia.) cemented by quartz veinlets ranging from 2 to 20mm thick. Vugs containing quartz crystals up to 7mm long occur frequently.

Henderson (1931) reported several analyses of the copper ore, ranging up to 23% Cu. One sample, with 7.74% Cu, also contained 3oz.9dwt.7gr. (106 ppm) Ag.

Hypogene Mineralogy

Weigel (1978) described the sulphide mineralogy as

Figure I-A-4: Diagrammatic cross-section of the southern coastal exposure of the mineralised breccia dike at Miners Head. (From Gregg *et al.*, 1970.)

Zone 1: brecciated argillite, occasionally mineralised and very siliceous.

Zone 2: brecciated argillite, less siliceous, occasionally mineralised.

Zone 3: brecciated argillite and dike rock. Not very siliceous, but abundant mineralisation.

Zone 4: Pockets of chalcopyrite mineralisation.

chalcopyrite containing inclusions of "skeletal - flagellate (exsolution?) sphalerite; zoned pyrite; mackinawite (cubanite?) occurs as fine skeletal inclusions, tiny prisms, flames and threads".....; "pyrrhotite occurs as coarser anhedral inclusions" (Weigel, 1978 p565). Wolframite was "tentatively" identified in altered greywacke containing fine chalcopyrite disseminations.

Samples examined by the writer consisted predominantly of chalcopyrite with minor pyrite (av. 0.5mm, max. 0.7mm), sphalerite (max. 0.3mm) and pyrrhotite (max. 0.5mm). Small (max. 50 micrometres) inclusions of argentian pentlandite (Weigel's mackinawite - cubanite?) and rare galena occur in the chalcopyrite. Sphalerite, pyrite and pyrrhotite were not in complete equilibrium as demonstrated by the iron content of sphalerite (Appendix V).

Supergene Mineralogy

The walls of the chamber (Fig. I-A-2) and the cliffs of the headland at the outcrop of mineralisation are stained with malachite, azurite and limonite (goethite). In polished section, covellite replaces chalcopyrite, whereas goethite replaces pyrite.

The Needles

Weigel (1978) mentioned several sulphide assemblages occurring in the Needles area either disseminated in the wall rocks adjacent to altered pebble and breccia dikes or within the dikes cementing the pebbles or breccia fragments. He suggested a paragenetic sequence of: bornite + chalcopyrite + rutile followed by bornite + chalcopyrite + sphalerite + galena + Ag-Ge-Se sulphosalts + rutile. The gangue mineral is quartz.

FLUID INCLUSIONS

Merchant (in Weigel, 1978 p515) determined filling temperatures between 260 and 338°C and salinities of 4.5 - 9.5 eq. wt. % NaCl for two phase primary and secondary inclusions

in quartz from Miners Head. In contrast, vug quartz crystals collected by the writer from the mineralisation beside the shaft in the chamber, have filling temperatures of primary inclusions between 365 and 402°C (Fig. I-A-5), with a peak in the 390 to 400°C range. Freezing temperature results group in two narrow ranges; -2.7 to -2.8°C and -10.4 to -10.7°C indicating salinities of around 4.5 and 14.5 eq. wt. % NaCl respectively.

Assuming a depth of mineralisation of approximately 1.5 - 2 km, and a lithostatic to partly hydrostatic pressure regime, a total pressure of 400 bars is indicated. At this pressure the pressure - salinity correction which must be added to filling temperatures of 395°C is approximately 30°C for a 10% NaCl solution or 25°C for a 15% NaCl solution. Therefore a temperature of 425°C is assigned to the Miners Head mineralisation.

SULPHUR ISOTOPES

$\delta^{34}\text{S}$ values of chalcopyrite and pyrite are presented in Table 9-1. Two cp - py pairs were analysed. Their fractionations of 0.1 per mil and 0.4 per mil suggest disequilibrium because of the unrealistically high temperatures indicated.

DEPTH OF MINERALISATION

There is no positive evidence to indicate the depth at which mineralisation occurred at Miners Head and the Needles, however comparison with other deposits of a similar type suggests that mineralisation occurred at depths greater than 1 km, possibly greater than 2 km. A depth between 1.5 and 2 km is used here.

THERMOCHEMISTRY

The geochemical environment of the quartz, chalcopyrite, pyrite, sphalerite and pyrrhotite mineralisation at Miners Head is illustrated in Fig. I-A-6.

The environment is limited by the presence of pyrite,

Figure I-A-6: fS_2 versus fO_2 diagram at 425°C showing the geochemical environments for (A): Miners Head quartz-chalcopyrite-pyrite-pyrrhotite-sphalerite-argentian pentlandite mineralisation, and (B) the Needles chalcopyrite + bornite mineralisation. $\pm S = 0.5m$, $\text{pH} = 5.5$, $\log fS_2$ from sphalerite compositions (Miners Head only) = -6.2 , and $\log fS_2$ from pyrrhotite compositions (Miners Head only) = -6.6 . Details of construction are given in Appendix V.

chalcopyrite and pyrrhotite but absence of bornite, magnetite and hematite. fS_2 is defined by the pyrite/pyrrhotite boundary ($\log fS_2 = 6.4$) and the FeS content of sphalerite ($\log fS_2 = -6.2$).

Contours of $\log m \leq S$ in the H_2S region, constructed for a pH of 5.5, indicate that $\log m \leq S$ was greater than -2, or magnetite would be the stable iron phase rather than pyrite and pyrrhotite. Because $\log m \leq S$ values greater than -1 are generally considered unlikely for hydrothermal deposits (Barnes & Czamanske, 1967; Ohmoto, 1972) a value of -1.3 (0.05m) is chosen.

At $\log fS_2 = -6.3$ and $\log m \leq S = -1.3$, $\log fO_2$ is fixed at approximately -28.0. Fig. I-A-7 indicates that under these conditions H_2S predominates over SO_2 in solution, the concentration of the latter probably being negligible.

The probable environment of quartz, chalcopyrite and bornite mineralisation of the Needles is also shown in Figs I-A-6 and I-A-7. The presence of bornite requires a much higher sulphur fugacity than present during the Miners Head mineralisation and also indicates a higher concentration of SO_2 in the hydrothermal fluid (Fig. I-A-7) although H_2S still predominates over SO_2 .

GENESIS

The igneous and hydrothermal breccia dikes and "stock" at the northern end of Great Barrier Island are similar to features typically found above hypabyssal plutons and they may therefore indicate the presence of larger igneous bodies at depth. The quartz diorite porphyry cemented argillite breccia "stock" at Miners Head may represent the apex of such an intrusive.

The sequence at Miners Head began with the intrusion of a pluton and stoping of the roof rocks to form the breccia pipes. Intrusion of porphyry dikes into the surrounding

Figure I-A-7: fO_2 versus temperature diagram showing the proposed geochemical environments of (A): Miners Head quartz-chalcopyrite-pyrite-pyrrhotite-sphalerite-argentian pentlandite mineralisation and (B) the Needles chalcopyrite + bornite mineralisation. The base diagram, from Fig. 4 of Burnham & Ohmoto (1980), shows the stability fields of pertinent iron bearing mineral assemblages at 1 kbar, and the SO_2/HSO_4^- and HSO_4^-/H_2S boundaries for unit activity ratios at $pH = 4$.

argillite occurred during this phase or later, accompanying solidification of the pluton. Lastly, the magmatic aqueous phase, formed by retrograde boiling (c.f. Phillips, 1973; Burnham, 1979), was expelled explosively from the solidifying pluton to form the hydrothermal breccia dikes. The copper mineralisation was probably formed in the zone of mixing of the magmatic hydrothermal fluid with meteoric water (the moderate salinity of the fluid inclusions suggests that the hydrothermal fluid was not purely magmatic).

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TE AHUMATAINTRODUCTION

The epithermal Ag - Au veins of the Te Ahumata region of Great Barrier Island (Fig. I-B-1) were mined predominantly between 1892 and 1908, producing 1.3 million grams (41,640 ounces) of bullion from 17330 tonnes of quartz (Downey, 1935). Most of the production was from Lees Reef.

Consolidated Silver Mining Co. prospected the area in the late 1960's to the early 1970's (Hancock, 1970; Consilver, 1973; d'Auvergne, 1974a, 1974b) excavated an unknown quantity of mineralised quartz from one of the deposits (Iona Quarry) and transported it to their treatment plant at Maratoto. Because of the short period of this operation it is assumed that the mineralisation proved to be of too low grade for profitable mining. During this time the geology and mineralisation of the deposits were described by Ramsay (1971) and Ramsay & Kobe (1974).

The area was reinvestigated by AMOCO and Erceg (1981) and in 1980 AMOCO drilled three diamond drill holes from the top of the plateau at Te Ahumata. The holes passed through mainly Whitianga Group rocks but two penetrated the underlying Coromandel Group andesites.

GEOLOGY

Three rock types outcrop in the area (Fig. I-B-1). A poorly bedded sequence of Coromandel Group andesite lava flows and pyroclastics (in a ratio of 2:1) is intruded by a quartz diorite porphyry termed the Orville Quartz Porphyrite by Ramsay & Kobe (1974). These authors considered that the latter formation was a correlative of the Kai-iti Porphyrites at the northern end of the Coromandel Peninsula. The andesites and quartz diorite porphyry are unconformably overlain by the Ahumata Sinter Formation (Ramsay & Kobe, 1974); a 100 - 230m thick (Ramsay & Kobe, 1974; and Erceg, 1981 respectively) massively bedded sequence of siliceous sinter,

Figure I-B-1: Geological map (top left) and cross-section (bottom) of the Te Ahumata area, Great Barrier Island (top right). Detailed mine plans and locations were given by Ramsay (1971). (Maps compiled from Thompson, 1960; Ramsay & Kobe, 1974; Erceg, 1981. Cross-section from Erceg, 1981.)

rhyolite pyroclastics and carbonaceous shales. Ramsay & Kobe considered that the Ahumata Sinter Formation was deposited in a lake during the Pliocene - Pleistocene.

HYDROTHERMAL ALTERATION

Erceg (1981) described the hydrothermal alteration mineral assemblage of the Ahumata Sinter Formation as: quartz, kaolinite, sericite (illite and interlayered illite - montmorillonite) metahalloysite, siderite and a single occurrence of adularia. The alteration may therefore be classified as intermediate argillic. He considered that there was originally a zonal pattern of alteration around fluid channelways consisting of an inner adularia/illite zone, a central interlayered illite - montmorillonite zone and an outer Ca-montmorillonite zone. However, this was later overprinted by "acid oxidative leaching" producing quartz and kaolinite.

Ramsay & Kobe (1974) studied the hydrothermal alteration of the underlying andesites and quartz diorite porphyry. They recognised a zonal pattern of hydrothermal alteration around the areas of mineralisation. Propylitic alteration (chlorite, sericite, carbonate, and pyrite) is present as initial or fringe alteration, intermediate argillic alteration (quartz, interlayered illite - montmorillonite, kaolinite and rare non-expanding chlorite and pyrite) occurs closer to the veins and in the more porous rocks, whereas advanced argillic alteration (kaolinite) and silicification are characteristic of fissures and veining.

MINERALISATION

Epithermal mineralisation occurs in three areas; Barrier Reefs, Iona and Sunbeam (Fig. I-B-1). Ramsay (1971) and Ramsay & Kobe (1974) studied Ag - Au and base metal mineralisation in quartz veins of all three areas, whereas Erceg (1981) described Ag - Au mineralisation from a quartz vein exposed at the surface in the Iona area and a base metal mineralised fault breccia intersected in one of the AMOCO drill holes (139 - 144m in DDH 2).

The veins and mineralised breccia studied by these authors

Figure I-B-2: Paragenetic sequence of minerals at Te Ahumata. (Compiled from: Ramsay, 1971; Ramsay & Kobe, 1974; Erceg, 1981; this study.)

occur in andesite but Ramsay & Kobe (1974) noted that some extend up into the overlying Ahumata Sinter Formation.

The paragenesis (Fig. I-B-2) was compiled from Ramsay (1971), Ramsay & Kobe (1974), Erceg (1981) and the writers own field observations. A base metal stage (Stage 1), predominantly consisting of pyrite and marcasite, is followed by a silver sulphosalt (Stage 2a) or a stibnite (Stage 2b) stage. The exact time relationship of the stages 2a and 2b is not clear because they are not found together, but they are arbitrarily placed in this order. The silver sulphosalts of Stage 2a are dominated by pyrargyrite although proustite, polybasite (-pearceite), seleniferous argyrodite, aguilarite and naumannite also occur. The stibnite stage (Stage 2b) is best developed in the Barrier Reefs region where stibnite occurs in quartz and kaolinite gangue, either solitary in veins and vugs or with other sulphides in veins.

Quartz is mainly chalcedonic in the Iona region (Fig. 4-4) but commonly finely crystalline in the Sunbeam and Barrier Reefs regions. Also found in the latter regions are epimorphous quartz on calcite and quartz pseudomorphs after calcite. Ramsay (1971) suggested that these features indicated an early stage of calcite deposition followed by quartz, dissolution of calcite (hydrothermal leaching) and finally, deposition of the base and precious metal mineralisation with quartz.

FLUID INCLUSIONS

Both the writer and Erceg (1981) studied fluid inclusions in samples of quartz from Te Ahumata. Erceg (1981) studied individual samples from Barrier Reefs, Iona and Sunbeam areas, whereas the writer studied one sample from the Barrier Reefs area, and two from the Sunbeam (Fig. I-B-1). The paragenetic positions of the writers samples are shown in Fig. I-B-2.

The fluid inclusions are two phase, liquid plus vapour,

Figure I-B-3: Histograms of filling temperatures and apparent salinities for primary fluid inclusions in quartz samples: 13952 and 13953, Stage 1 Sunbeam Region; 13954, Stage 2b Barrier Reefs Region. The individual measurements are listed in Appendix III.

normal types with no evidence of boiling. Erceg (1981) determined filling temperatures predominantly in the range of 200 - 230°C, whereas the writers results (Fig. I-B-3) indicate temperatures generally 10 to 20°C higher, partly due to different paragenetic positions of some samples.

The writers samples from the Sunbeam area have apparent salinities between approximately 0.5 and 2 eq. wt. % NaCl, whereas Erceg measured anomalously high apparent salinities (one result of approximately 8 eq. wt. % NaCl, whereas the rest were between 2.5 and 4.1 eq. wt. % NaCl) in samples from the Barrier Reefs and Iona areas. Erceg's results are considered to be in error.

The filling temperatures require the addition of a pressure - salinity correction which, considering the shallow level of mineralisation (see later), is probably less than 5°C. Therefore, based on my filling temperature results, the average depositional temperature for Stage 1 is considered to be 240°C, whereas Stage 2b formed around 230°C. Two of Erceg's samples indicate that Stage 2a mineralisation occurred at 220°C.

SULPHUR ISOTOPES

$\delta^{34}\text{S}$ values of pyrite, chalcopyrite and stibnite samples are listed in Table 9-1. They range from -0.2 per mil (stibnite) to +1.3 per mil (pyrite).

DEPTH OF MINERALISATION

The Ahumata Sinter Formation was considered by Ramsay & Kobe (1974) to be a lake deposit and the top of the formation was regarded by them as being equal to the former land surface at the time of mineralisation. The depth reconstruction illustrated in Fig. I-B-4 uses a surface datum 150m above Te Ahumata Trig and assumes a value of 230m for the original thickness of the Ahumata Sinter Formation (c.f. Fig. I-B-1 and Erceg, 1981).

Figure I-B-4: Diagrammatic representation of the depth relations, at the time of mineralisation, for the Te Ahumata deposit. The position of the surface datum is based on an assumed thickness of 230m for the Ahumata Sinter Formation (c.f. cross-section in Fig. I-B-1).

The absence of evidence for boiling of the hydrothermal fluids in the fluid inclusions investigated by the writer and Erceg (1981) is consistent with the reconstruction (hydrostatic pressure would allow boiling to maximum depths of 250m at 220°C and 370m at 240°C; Haas, 1971).

THERMOCHEMISTRY

Introduction

Three mineralisations are modelled: Stage 1 base metal, Stage 2a silver - gold and Stage 2b stibnite. Table I-B-1 lists several parameters of these mineralisations.

The descriptions of hydrothermal alteration by Ramsay (1971), Ramsay & Kobe (1974) and Erceg (1981) indicate that the early fluids (Stage 1) were in equilibrium with wall rock assemblages containing sericite and possibly adularia, but that late fluids (Stage 2b) were in equilibrium with kaolinite.

Stage 1

The log fS_2 versus pH diagram for Stage 1 base metal mineralisation (Fig. I-B-5) was constructed for a total sulphur in solution concentration of 0.005m ($\log m \leq S = -2.3$). The mineralogy (Fig. I-B-2) limits the geochemical environment to the pyrite plus chalcopyrite stability field. Log fS_2 values around -12.4 are indicated by the iron content of sphalerites and therefore contours of log fS_2 for values of -12 and -13 are shown in Fig. I-B-5. A pH near that of the sericite/K-feldspar boundary (6.1) limits log fO_2 between approximately -39 and -40 as shown by the shaded area in Fig. I-B-5. The general value of +1.5 for log fCO_2 is precluded and a value around 0 seems more appropriate. Sulphur was present in solution predominantly in reduced form.

Stage 2a

Stage 2a silver - gold mineralisation plots in the pyrite plus chalcopyrite field of the fO_2 versus pH diagram (Fig. I-B-6) constructed for a total sulphur in solution concentra-

TABLE I-B-1: General thermochemical parameters
for the depositional environments
of the epithermal vein mineralisa-
tions at Te Ahumata.

	Stage 1 (base metal)	Stage 2a (Au-Ag)	Stage 2b (Stibnite)	Reference
Temperature °C	240	220	230	Table V-1
True ionic strength	0.15	0.15	0.15	" " "
Salinity (mNaCl eq.)	0.17	0.17	0.17	" " "
mK ⁺ (room temp.)	0.023	0.020	0.022	" " "
pH	6.0	6.0	4.9	see text
pH of kaolinite/ sericite boundary	4.7	4.8	4.9	Table V-1
pH of sericite/K- feldspar boundary	6.1	6.2	6.2	" " "
Total S (log m _S)	-2.3	-3.0	-3.0	see text
Log fS ₂ (sphalerite comp.)	-12.4			Table V-4A
Log fS ₂ (electrum comp.)		-12.9 to -13.5		Table V-6B
Log fO ₂	-39to-40 (FigI-B-5)	-40to-41.5 (FigI-B-6)	-38to-41 (FigI-B-8)	figures cited
Log fCO ₂	+1.5	+1.5	+1.5	Table V-1

Figure I-B-5: fO_2 versus pH diagram at 240°C showing the geochemical environment (shaded) of Stage 1 quartz + pyrite + marcasite + chalcopyrite + sphalerite + galena + tetrahedrite mineralisation in veins of the Te Ahumata area. (see Table I-B-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-B-6: fO_2 versus pH diagram at 220°C showing the geochemical environment (shaded) of Stage 2a quartz + pyrite + chalcopyrite + silver sulphosalts + electrum mineralisation in veins of the Te Ahumata area. (See Table I-B-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

tion of $0.001m$ ($\log m \leq S = -3$). Values of $\log fS_2$ between -12.9 and -13.5 are indicated by the mole fraction of silver in electrum analysed by Ramsay (1971) and Erceg (1981), confining the mineralisation to the reduced sulphur species field of Fig. I-B-6 in the absence of magnetite and hematite. Like the other stages of mineralisation at Te Ahumata, low CO_2 fugacities are indicated, probably around $\log fCO_2 = 0$. Sulphur was present in solution predominantly in reduced form.

Stage 2b

The fS_2 versus fO_2 diagram used to model the stibnite mineralisation (Fig. I-B-7) is similar to Fig. 55 of Ramsay (1971) but much lower values of fS_2 and fO_2 are considered here for the mineralisation.

The mineralisation occupies the area to the left of the stibnite/ Sb_2S_2O boundary in the pyrite plus chalcopyrite field of Fig. I-B-7. The presence of minor arsenopyrite, reported by Ramsay, limits fS_2 to values below the arsenopyrite/pyrite + arsenic boundary at $\log fS_2 = -13.3$ when arsenopyrite is present.

On the fO_2 versus pH diagram (Fig. I-B-8) stibnite + Pyrite + arsenopyrite mineralisation occupies the lower end of the shaded area and indicates that H_2S was the predominant sulphur species in solution. Wider ranges of fluid composition in terms of fS_2 and fO_2 (up to the oxidised/reduced S species boundary in Fig. I-B-8) are possible for stibnite + pyrite, without arsenopyrite, mineralisation but a fluid containing sulphate > sulphide is precluded by the Sb_2S_2O field and possibly also by the absence of barite (Fig. I-B-8).

The general $\log fCO_2$ value of +1.5 is precluded and a value of around 0 is required to shift the graphite/ CO_2 boundary below the shaded area and $\log fCO_2$ values possibly as low as -2 may be required for arsenopyrite + CO_2 stability (c.f. Fig. I-B-7).

Figure I-B-7: fS_2 versus fO_2 diagram at 230°C showing the geochemical environment (line of crosses) of Stage 2b quartz + stibnite $\pm$ kaolinite $\pm$ pyrite $\pm$ marcasite $\pm$ arsenopyrite mineralisation in veins of the Te Ahumata area. (See Table I-B-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-B-8: fO_2 versus pH diagram at 230°C showing the geochemical environment (shaded) of Stage 2b mineralisation. $mBa^{2+}=0.0001$. (See Table I-B-1 for other relevant thermochemical parameters and Appendix V for methods of construction.)

GENESIS

The epithermal vein deposits of Te Ahumata were formed in a geothermal system generated by rhyolitic volcanism in the Pliocene - Pleistocene.

$\delta^{34}\text{S}_{\text{S}}$ of the hydrothermal fluid was probably near 0 per mil because sulphur was present in solution predominantly in reduced form (Figs. I-B-5, I-B-6 and I-B-8) and $\delta^{34}\text{S}_{\text{S}}$ may therefore be represented by $\delta^{34}\text{S}$ of the sulphide minerals (e.g. $\delta^{34}\text{S}_{\text{cp}} = +0.7$ per mil). The sulphur was probably of magmatic origin.

The mineral paragenesis (Fig. I-B-2) resulted from general decreases in fluid temperature and pH. Early stage mineral deposition probably occurred as a result of fluid - wall rock reactions and their effects on the fluid chemistry (e.g. fCO_2 and pH), however mixing with near surface water, and later acidic conditions, are thought to be responsible for the subsequent stages. All stages are characterised by antimoniferous minerals (Stage 1: miargyrite and tetrahedrite-freibergite; Stage 2a: pyrargyrite and polybasite; Stage 2c: stibnite) and may indicate a relatively high concentration of antimony in solution. Similarly, seleniferous and selenide minerals of Stage 2a (aguilarite, seleniferous argyrodite and naumannite) suggest a relatively high Se/S ratio because of the low dissolved sulphate/dissolved sulphide ratio (see Appendix V).

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I-C

NORTHERN COLVILLE PENINSULAINTRODUCTION

Skinner (1967) drew attention to the possibility of a porphyry copper orebody being associated with the Paritu Pluton at the northern end of the Coromandel Peninsula. Subsequently, Mitsui Mining and Smelting Co. Ltd carried out a geochemical exploration survey and in 1970 diamond drilled three holes (hole 1 = 150m, hole 2 = 57m and hole 3 = 150m; Akiyama, 1970) in a zone of Cu anomalous soils (250 - 1700 ppm Cu compared to background values of 20 - 40 ppm) in the Ongohi Stream area (Fig. I-C-1). The recovered core contained disseminated pyrite and chalcopyrite mineralisation, averaging 0.16% Cu (maximum analysis of 0.337% Cu) in hole No.1.

In 1973 a joint venture by Southern Cross Minerals Exploration Ltd and Fletcher Mining and Exploration Co Ltd (Brown & Hancock, 1973) discovered another zone of Cu anomalous soils, in Stony Bay Creek, however this area has not been drilled.

In addition to porphyry style mineralisation, several base metal quartz veins occur associated with the intrusive rocks. Also, small silver - gold veins in Hope Stream, Okatutahi Stream (Eva Mine) and Tangiaro Stream were mined in the late 1800's but produced only a few thousand grams of gold and silver.

GEOLOGY

The geology of the Colville Peninsula was described by Fraser & Adams (1907) and Skinner (1962, 1967, 1976), whereas the Paritu Pluton was specifically studied by Black (1967) and Skinner (1975a). A geological map compiled from these sources is presented in Fig. I-C-1.

Figure I-C-1: Geology of Northern Colville Peninsula. (Compiled from Skinner, 1967; 1976; Brown & Hancock, 1973.)

The Paritu Pluton is a composite body of quartz diorite, granodiorite and aplite intruding a Jurassic greywacke suite of the Moehau Formation (Manaia Hill Group) and Miocene Port Charles Andesite (Coromandel Group). Plugs and dikes of andesite and dacite porphyry (Kai-iti Porphyrites) are also found intruding these formations and although many are contemporaneous with, some are considered to predate and others, postdate the intrusion of the pluton. Brown & Hancock (1973) mention the occurrence of diorite breccia dikes in quartz diorite at several localities.

Contacts between the pluton and country rock are generally discordant. Near contacts with the Moehau Formation the pluton contains recrystallised xenoliths of greywacke producing a marginal tonolite zone.

Skinner (1976) described the Port Charles Andesite as andesite pyroclastic and flow rocks with rare carbonaceous layers but locally abundant petrified logs. The pyroclastics were deposited subaerially and subaqueously and consist mainly of tuff to lapilli tuff although breccias with a tuff to lapilli tuff matrix are also found.

K - Ar AGE DATA

K - Ar ages of 16 to 17.1 m.y. were determined from biotite and hornblende concentrates of the plutonic rocks by Richards et al (1966).

METAMORPHISM

Black (1972) described an isochemical metamorphic aureole in Moehau Formation, defined up to 900m from the contact with the pluton by porphyroblastic quartz, orthoclase, albite, epidote, biotite, hypersthene, hornblende, actinolite, magnetite, almandine and tourmaline.

Skinner (1975a) considered that the common occurrence of yellow porphyroblastic epidote in granodiorite from Sorry Mary Stream resulted from metamorphism induced by intrusion of later quartz diorite.

DEUTERIC ALTERATION

Wodzicki (1970) and Skinner (1975a) described the alteration of hornblende in the plutonic rocks to a secondary green fibrous amphibole, urallite. Both authors ascribe this alteration to a deuteric phase.

HYDROTHERMAL ALTERATION

Propylitic alteration is ubiquitous and has resulted in partial and occasionally complete replacement of hornblende and urallite by chlorite, epidote and calcite, minor replacement of plagioclase by sericite, epidote and occasionally adularia, and replacement of oxides by pyrite, leucosene and minor chalcopryrite (Wodzicki, 1970). Skinner (1975a) also recognised secondary albite and sphene as alteration products. Skinner considered that hydrothermal alteration was only slight in the quartz diorite but intense in the granodiorite.

Potassic alteration may be represented by the occurrence of secondary orthoclase replacing plagioclase in some igneous phases of the pluton (c.f. Skinner, 1975a p341) and in druses with quartz and later epidote and calcite. Skinner (1975a) attributed the latter to a pegmatitic phase of the pluton. The formation of thin veinlets of tourmaline, some containing sulphides (c.f. Skinner, 1967), was correlated with the plagioclase alteration by Skinner (1975a).

MINERALISATION

Disseminated Mineralisation

Skinner (1967) described disseminated chalcopryrite, pyrite, wolframite, pyrrhotite and marcasite in the igneous and hornfels rocks of the coastal section south of Paritu (Fig. I-C-1). He considered that pyrrhotite replaced wolframite and was itself replaced by marcasite.

Wodzicki (1970) described disseminated pyrite, chalcopryrite and magnetite mineralisation in drill cores

from Ongohi Stream. Most of the mineralisation occurred in a biotite quartz diorite phase of the pluton, found only in core of hole No.1. The biotite quartz diorite is the least altered of a suite of rocks in the drill holes and nearby surface exposure, being unaffected by uralitisation and only slightly propylitised.

Brown & Hancock (1973) note that the matrix of diorite breccia dikes in the quartz diorite contain disseminated pyrite and chalcopyrite.

Vein Mineralisation

Veinlets commonly occur infilling joints and shears in the igneous rocks and surrounding greywacke and contain quartz, pyrite and occasionally epidote, chlorite and calcite. Veinlets and veins containing sulphides other than pyrite occur less frequently. Known examples are described below, west to east.

South Coast

Minor molybdenite, pyrrhotite, marcasite, sphalerite, chalcopyrite and arsenopyrite mineralisation occurs in quartz veinlets filling shears and joints in the igneous and hornfels rocks along the coast south of Paritu (Fig. I-C-1). In some instances this mineralisation is associated with the disseminated mineralisation described from the same area (Skinner, 1967).

Sorry Mary Stream

Skinner (1967) noted quartz boulders with sulphide mineralisation in Sorry Mary Stream. The vein outcrop (Fig. I-C-1) was later discovered by Brown & Hancock (1973) and its location noted on their Map 1 (S).

The vein consists of a 0.4m wide zone of quartz cemented wall rock breccia. The host rock and breccia fragments are quartz diorite of the Paritu Plutonics. Concentrations of quartz veinlets occur near the hanging wall and footwall.

The latter zone, approximately 80mm wide, contains most of the sulphides. The quartz veinlets, up to 30mm thick, surround breccia fragments up to 50mm in diameter.

Pyrite occurs disseminated in the wall rocks and breccia fragments.

Two stages of quartz, pyrite, sphalerite, chalcopyrite and galena occur; the first, fine grained and the second, medium to coarse grained. The latter stage has also grown into vugs with quartz crystals up to 10mm long with rare coatings of sulphides near their bases.

Textures of the sulphide mineralisation are simple as a result of the brecciated nature of the vein. Individual grains of sulphides occur surrounded by quartz; contacts between different sulphides are rare. Quartz is generally euhedral to the sulphides and sphalerite characteristically contains abundant inclusions of chalcopyrite, sometimes arranged along grain boundaries or zones.

Hope Stream

Fraser & Adams (1907) noted that an east-west striking quartz vein in Hope Stream was prospected by aditing in the late 1800's. Although they were unable to view the vein due to collapse of the adits, they noted that blocks of quartz on the dump ranged in size up to 0.6m and contained pyrite, galena and sphalerite. A single sample assayed 1dwt. 6 gr. Au and 9 ounces 14dwt. 8 gr. Ag per ton (1.9ppm Au and 297ppm Ag).

Stony Bay Creek

Skinner (1967) described mineralisation occurring in a number of quartz stringers (generally less than 10mm but up to 100mm thick) crossing a plunge pool in Stony Bay Creek (Fig. I-C-1). Epidote occurs as an early phase followed by galena, chalcopyrite, sphalerite and pyrite. The texture of the mineralisation is similar to the Sorry Mary Stream vein.

The country rock is greywacke of the Moehau Formation.

Doctors Creek

Brown & Hancock (1973) noted on their Map 4 the occurrence of a quartz vein, containing sulphides, in the western branch of Doctors Creek. The vein was relocated by the writer and found to be a 1m wide zone of quartz cemented wall rock breccia.

The country rock is a porphyry dike which intrudes greywacke of the Moehau Formation.

Sphalerite, galena, chalcopyrite and pyrite (in order of abundance) occur in quartz veinlets up to 7mm thick cementing the breccia fragments (up to 120mm in diameter). Later brecciation of the first stage was followed by further quartz deposition with rare sulphides. Vugs lined with quartz crystals up to 7mm are common in this late stage.

The texture of the sulphide mineralisation is similar to the Sorry Mary Stream vein (e.g. Fig. 4-19).

Eva Mine

Downey (1935) noted that the only recorded production from the Eva Mine in Okatutahi Stream was 15,000 grams (477 ounces) of bullion during 1887 and 1888. The mineralisation has not been described. Skinner (1976) shows the location of the mine in Port Charles Andesite.

Tangiario Stream

The mineralisation in Tangiario Stream, also in Port Charles Andesite, occurs in a 1m wide quartz and kaolinite cemented breccia vein striking 325° and dipping 74° to the west (Skinner 1967). Marcasite, pyrite and arsenopyrite occur in the central part of the vein, whereas later pyrite, arsenopyrite, tetrahedrite, chalcopyrite, sphalerite and rare galena and electrum occur in quartz stringers and conchy quartz between the hanging wall and central zone.

Although Fraser & Adams (1907) suggested that acanthite was present it was not identified by Skinner. Instead Skinner considered that the silver occurred in tetrahedrite. Analyses

240 260 280 300 320 340 360 0 1 2

13972 + 13973

240 260 280 300 320 340 360 0 1 2

Filling Temperature °C

Salinity
eq. wt % NaCl

Single values: =

□

Figure I-C-2: Histograms of filling temperatures and apparent salinities for primary fluid inclusions in quartz from the base metal sulphide veins in Doctors Creek (sample 13971) and Sorry Mary Stream (samples 13972 and 13973). The individual measurements are listed in Appendix III.

of vein material were reported by McKay (1897) as 105 ounces to 110 ounces Ag and a trace to 17 dwt. Au per ton (3214 to 3367 ppm Ag and ? to 26 ppm Au), whereas a sample taken by Fraser & Adams assayed only 19 ounces 1 dwt. 5 gr. Ag and 22 gr. Au per ton (583 ppm Ag and 1.4 ppm Au).

Supergene Mineralogy

Covellite and limonite are the predominant supergene minerals found replacing the sulphides in the veins although chalcocite, in addition to covellite and limonite, occurs in specimens from Sorry Mary Stream and Skinner (1967) noted hematite in material from Tangiaro Stream.

FLUID INCLUSIONS

The results of filling and freezing temperature measurements on fluid inclusions in vug quartz crystals from the veins in Sorry Mary Stream and Doctors Creek are presented in Fig. I-C-2 and Appendix III.

The filling temperatures, with a 15°C pressure-salinity correction (assuming a depth of 1 km and lithostatic - partly hydrostatic pressure), indicate depositional temperatures of approximately 290°C for second stage sulphides in the Sorry Mary Stream vein and 310°C for post - sulphide mineralisation quartz in the Doctors Creek vein. Salinities are 1.2 - 1.7 and 1.9 eq. wt. % NaCl respectively.

SULPHUR ISOTOPES

$\delta^{34}\text{S}$ values of sulphide minerals from the veins in Sorry Mary Stream, Doctors Creek and Tangiaro Stream are presented in Table 9-1. They range from +0.4 (galena) to +3.9 (pyrite) per mil.

Three depositional temperatures for the Sorry Mary Stream mineralisation are derived from sp - gn pairs (320, 340 and 370°C), whereas temperatures from a py - cp pair (320°C) and a py - gn pair (280°C) are calculated for the Doctors Creek mineralisation in addition to two sp - gn pairs of 350°C and 460°C. The 460°C temperature seems in error

TABLE I-C-1: General thermochemical parameters for the depositional environments of the Paritu coastal section porphyry copper mineralisation and the base metal quartz vein mineralisations in Sorry Mary Stream, Stony Bay Creek and Doctors Creek.

	Porphyry Copper Coastal Section	Pb-Zn-Cu Veins	Reference
Temperature °C	425	325	Table V-1
True ionic strength	0.12	0.19	"
Salinity (mNaCl eq.)	1.2	0.27	"
mK ⁺	0.35	0.057	"
pH	5.5	5.4	See text
pH of kaolinite/sericite boundary	4.3	4.1	Table V-1
pH of sericite/K-feldspar boundary	5.6	5.6	"
Total S (log m S)	-1.3	-2.0	See text
Log fS ₂ (sphalerite comp.)		-7.9to-9.0	Table V-4A
(calculated)	-5.5to-6.5 (Fig.I-C-3)		
Log fO ₂	-25.5to-26.5 (Fig.I-C-3)	-30.5to-32.0 (Fig.I-C-5)	figures cited
Log fCO ₂	+1.5	+1.5	Table V-1

and is rejected on the grounds of possible non-equilibrium.

LEAD ISOTOPES

Cooper & Richards (1969) measured lead isotope ratios in samples of galena from the base metal veins in Sorry Mary Stream and Stony Bay Creek. Comparison of these values with lead isotope ratios in samples of greywacke (Armstrong & Cooper, 1971) and andesite and rhyolite (Cooper & Richards, 1969) from other locations in the Coromandel Peninsula suggests that the lead in the galena is affiliated with lead in the greywacke and rhyolite rocks but has a different parentage from lead in the andesites (c.f. Fig. 5 of Robinson, 1974). Cooper & Richards (1969) concluded that lead in the veins and rhyolite rocks was derived from the Mesozoic greywacke suite rocks.

DEPTH OF MINERALISATION

Skinner (1962; 1975a; 1976) considered that the volcanic rocks intruded by the Paritu Pluton (Port Charles Andesite) may have been only about 1 km thick. Black (1972) and Skinner (1975, 1976) therefore postulated that the total thickness of rock cover above the pluton at the time of intrusion was slightly less than 1 km (i.e. approximately 900m). Presumably porphyry copper and base metal vein mineralisations occurred at similar depths although precious metal vein mineralisations in Okatutahi Stream (Eva Mine) and Tangiaro Stream probably occurred at shallower levels.

THERMOCHEMISTRY

Table I-C-1 lists some parameters of the geochemical environments responsible for the two high temperature mineral assemblages modelled here (a) the quartz, pyrite, chalcopyrite, pyrrhotite, marcasite, sphalerite, arsenopyrite, molybdenite and wolframite disseminated and vein mineralisation of the Paritu coastal section and (b) the quartz, pyrite, sphalerite, galena and chalcopyrite vein mineralisations in Sorry Mary Stream, Stony Bay Creek and Doctors Creek. fS_2 versus fO_2 diagrams for these mineralisations are presented in Figs I-C-3 and I-C-4 respectively.

Figure I-C-3: fS_2 versus fO_2 diagram at 425°C showing the geochemical environment (star) for the disseminated and vein porphyry style mineralisation of the Paritu coastal section. The arrow indicates the paragenetic sequence of quartz + pyrite + chalcopyrite $\pm$ wolframite followed by quartz + pyrrhotite $\pm$ chalcopyrite $\pm$ molybdenite $\pm$ arsenopyrite $\pm$ sphalerite. (See Table I-C-1 for relevant thermochemical parameters and Appendix V for details of construction.)

Figure I-C-4: fS_2 versus fO_2 diagram at 325°C showing the general field of stability (shaded) for the quartz + pyrite + sphalerite + galena + chalcopyrite vein mineralisations in Sorry Mary Stream, Stony Bay Creek and Doctors Creek. (See Table I-C-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-C-5: fO_2 versus pH diagram at 325°C and $\Sigma S=0.01m$ showing the geochemical environment (shaded) for the quartz + pyrite + sphalerite + galena + chalcopyrite vein mineralisations in Sorry Mary Stream, Stony Bay Creek and Doctors Creek. (See Table I-C-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

The sulphur fugacity of the coastal section vein mineralisation is defined by the pyrite - pyrrhotite and arsenopyrite - arsenic plus pyrite boundaries in Fig. I-G-3. A $\log fS_2$ value of -6.3, equivalent to the pyrite - pyrrhotite boundary, is chosen to represent this mineralisation.

The stability relations of wolframite are discussed in Appendix V, where it is concluded that the Paritu wolframite should plot in the pyrite field near the pyrite - pyrrhotite - magnetite triple point of Fig. I-C-3. The disseminated pyrrhotite is later than the wolframite and records the changing conditions of fS_2 with a move into the pyrrhotite stability field (represented by the arrow in Fig. I-C-3).

Assuming a $\log m \leq S$ value of -1.3 (c.f. Section I-A Miners Head) the sulphur and oxygen fugacities of the coastal section mineralisation can be defined as follows:

	$\log fS_2$	$\log fO_2$
Early disseminated mineralisation (wolframite)	-5.5	-25.5
Late disseminated mineralisation (pyrrhotite)	-7.0	-27.0
Vein mineralisation	-6.3	-26.0

The occurrence of sericite and minor K-feldspar in the hydrothermal alteration accompanying the base metal vein deposits in Sorry Mary Stream, Stony Bay Creek and Doctors Creek suggests a pH of around 5.6 (pH of the sericite/K-feldspar boundary, Table I-C-1). Comparison of the $\log m \leq S$ contours, constructed at this pH in Fig. I-C-4, with the $\log fS_2$ values defined by the FeS content of sphalerites indicates that $\log m \leq S$ was approximately -2.0. An fO_2 versus pH diagram for this value of $m \leq S$ is presented in Fig. I-C-5. The region of mineral deposition is shown by the shaded area and suggests that the fluid contained dissolved sulphur predominantly in reduced form.

GENESIS

The porphyry mineralisations of the Paritu coastal section and in the Ongohi drill holes may each represent different mineralising episodes.

The coastal section mineralisation mainly occurs in the hornfelsed rocks of the contact between the unmetamorphosed greywacke suite country rocks and the quartz diorite phase of the pluton. It was deposited from a hydrothermal fluid with relatively low fS_2 , fO_2 and $m \leq S$, possibly in a convective ground water system generated during the intrusion of the magma (c.f. Cathles, 1977).

In contrast, the style of mineralisation in the biotite quartz diorite phase of the Ongohi drill holes is more typical of porphyry copper deposits. It was probably deposited after hydraulic brecciation (c.f. Phillips, 1973; Burnham, 1979; Burnham & Ohmoto, 1980) of the biotite quartz diorite by a magmatic hydrothermal fluid generated by retrograde boiling (c.f. Burnham, 1979) in an underlying magma chamber. The chalcopyrite-pyrite-magnetite mineralisation may have been deposited at the site where the magmatic hydrothermal fluid encountered ground water or due to changes in the chemistry of the magmatic hydrothermal fluid accompanying fluid - wall rock reactions.

The vein mineralisations (e.g. Sorry Mary Stream, Stony Bay Creek, Doctors Creek, Okatutaki Stream and Tangiaro Stream) may represent concurrent deposits peripheral to the porphyry copper mineralisation or deposits formed at a much later stage during a different intrusive (-volcanic) episode. In either case they were probably deposited from fluids consisting predominantly of meteoric water. The lead isotope results of Cooper & Richards (1969) suggest that the lead in galena of these veins was derived from the greywacke suite rocks.

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I-D

KUAOTUNUINTRODUCTION

Two large quartz veins, the Bald Spur Lode (also known as the Try Fluke) and the Waitaia Vein, were mined between 1889 and the 1930's. Mines on the Bald Spur Lode (principally the Great Mercury, Kapai Vermont and Try Fluke Mines) produced 2.2 million grams (71,985 ounces) of bullion from 88,039 tonnes of quartz, whereas the Waitaia and Mountain King Mines on the Waitaia Vein produced only 620,000 grams (19,949 ounces) of bullion from 10,789 tonnes of quartz. Production from other workings in the Kuaotunu area accounted for only 109,000 grams (3,508 ounces) of bullion.

The veins were mined from adits which with the exception of an upper level of the Waitaia Mine have collapsed or been filled in.

Parkinson (1980) studied the geology and mineralisation of the area in association with a geochemical exploration program by Gold Mines of New Zealand Ltd.

GEOLOGY

The geology of the Kuaotunu area has been recently mapped by Skinner (1976) and Parkinson (1980). A geological map compiled from these sources is presented in Fig. I-D-1.

A large block of Jurassic greywacke suite rocks (Manaia Hill Group) outcrops in the Kuaotunu area, flanked by Upper Miocene Coromandel Group andesites: Te Tutu Andesites to the west and Mahiapua Andesite to the south and east. Contemporaneous Upper Miocene - Lower Pliocene lacustrine and hydrothermal deposits (Black Jack Formation and Waitaia Sinter respectively) occur overlying the greywacke east of Kuaotunu. Parkinson (1980) recommended that Waitaia Sinter should be renamed Waitaia Silica Deposit because the formation includes silicified volcanic breccia and sediments in addition to chemical precipitates.

Figure I-D-1: Geology of the Kuaotunu area (after Skinner, 1976).

HYDROTHERMAL ALTERATION

Parkinson (1980) identified the following hydrothermal alteration minerals associated with the gold - silver mineralisation in the Kuaotunu area: secondary quartz, clays (kaolinite, illite, montmorillonite and interlayered illite - montmorillonite), chlorite (minor abundance), zeolite (rare abundance) and calcite.

Alteration is most intense close to the major quartz veins.

The clay mineralogy has a depth related zonal distribution with a progression of the assemblages kaolinite, sericite (illite) [†] kaolinite, and sericite (illite) corresponding to increasing depth.

Two other types of alteration have locally restricted occurrences. A red clay deposit occurs in volcanic breccia of Te Tutu Andesite in the northern part of Waitaia Ridge. It is gradational to surrounding quartz, kaolinite [†] chlorite alteration. Parkinson attributed its formation to localised sulphate alteration. Skinner (1968, 1976) noted alunite and kaolinite associated with plugs of Waitaia Sinter.

MINERALISATION

Gold - silver mineralisation occurs in two widely separated, semi parallel, easterly dipping veins, the Bald Spur Lode and the Waitaia Vein (Fig. I-D-1). Both veins are predominantly in greywacke of the Moehau Formation although they extend southwards into adjacent Mahinapua Andesite (Coromandel Group). They each range up to 4m wide with average thicknesses of 0.3m (Waitaia) and greater than 0.8m (Bald Spur Lode), and dip steeply.

Quartz is the only recorded gangue mineral although in the Bald Spur Lode, quartz pseudomorphs after calcite predominate, indicating that calcite was originally a major mineral.

Fraser & Adams (1907) noted only manganese oxides,

Minerals \ Stages	1	2	3	4	5
Quartz					
Calcite					
Pyrite					
Marcasite					
Arsenopyrite					
Electrum					
Sphalerite					
Galena					
Hessite					
Pyrrhotite					
Titanomagnetite					
Sericite					
Kaolinite					

Figure I-D-2: Paragenetic sequence of vein minerals in the Kuaotunu area (based on descriptions by Fraser & Adams, 1907, and Parkinson, 1980).

hematite (forming pseudomorphs after calcite) and electrum mineralisation in the Bald Spur Lode but pyrite, arsenopyrite, galena, sphalerite and electrum (average Au:Ag ratio = 1:0.4) are recorded from the Waitaia Vein. Electrum in both veins (but especially the Bald Spur) was very fine grained and widely dispersed in the quartz causing considerable problems with the early treatment methods.

Parkinson's (1980) vein paragenesis for the region is as follows: (1) calcite and quartz (now represented by quartz pseudomorphs after calcite) followed by brecciation, (2) microcrystalline quartz, (3) grey quartz often accompanied by brecciation, and lastly (4) quartz and clay. The last stage is represented by large euhedral quartz crystals, in the central part of the veins, set in a quartz clay (kaolinite near surface, illite below 100m) pug.

Parkinson identified pyrite, arsenopyrite, pyrrhotite, sphalerite, galena and titanomagnetite in a single polished mount of the grey quartz material (phase 3 of above). An unidentified Ag - Te mineral, probably hessite, occurs with galena inclusions in pyrite of this specimen.

In an earlier section of his thesis (p97) Parkinson mentions the occurrence of quartz, pyrite, marcasite, arsenopyrite veins crosscutting the veins of quartz pseudomorphs after calcite. Their relation to the other stages is not stated although on p128 they are listed after the veins of quartz pseudomorphs after calcite and before the grey quartz mineralised veins. Fig. I-D-2 summarises this information with considerable inference by the writer.

FLUID INCLUSIONS

Fluid inclusions were examined in three samples of quartz (unmineralised except for pyrite) from the Kuaotunu area: 14007 (K3), 14008 (K4) from the Waitaia Ridge Mine (Waitaia Vein) and 14009 (GL1) from the Golden Link Mine. Fluid inclusions in all three samples are two phase, liquid plus vapour, normal types.

Figure I-D-3: Histograms of primary fluid inclusion filling temperatures for samples of quartz from the Waitaia Ridge Mine (14007 and 14008) and Golden Link Mine (14009). The individual measurements are listed in Appendix III.

Primary fluid inclusions are rare and of small size in the Waitaia Vein samples, hence only a few filling temperatures could be determined from these samples. The results are presented in Fig. I-D-3. Pressure - salinity corrections of between 5 and 10°C must be added to the filling temperatures which indicate a probable temperature range of mineralisation between 250 and 270°C.

SULPHUR ISOTOPES

Three samples of pyrite from the Waitaia Mine have $\delta^{34}\text{S}$ values between +0.6 and +1.0 per mil (Table 9-1).

THERMOCHEMISTRY

Parkinson (1980) related the depth zoned distribution of alteration minerals at Kuaotunu (kaolinite and montmorillonite at the surface giving way to sericite at depth) to the pH of the hydrothermal fluids, suggesting that the near surface waters were acidic, whereas the deeper waters were neutral or slightly alkaline. A pH value of 5.5 (neutral pH at 250°C) was used to construct the contours of $\log m \leq S$ shown in Fig. I-D-4.

Stage 2 mineralisation is defined by the presence of pyrite and arsenopyrite but absence of bornite, pyrrhotite, magnetite and hematite. $f\text{S}_2$ of this mineralisation is therefore limited between the pyrite/pyrrhotite and arsenopyrite/pyrite plus arsenic boundaries.

Pyrrhotite and titanomagnetite are present in Stage 3 mineralisation suggesting close proximity to the pyrite-pyrrhotite-magnetite triple point in Fig. I-D-4. Because graphite is absent from this mineralisation a $\log f\text{CO}_2$ value of +1.5 (the general value used where $m\text{CO}_2$ has not been measured) is precluded. A value close to 0 for this parameter seems more reasonable and is also plotted in Fig. I-D-4.

The concentration of total sulphur in solution during Stage 3 mineralisation was approximately 0.002m ($\log m \leq S = -2.7$) and by using the same value for Stage 2 mineralisation

Figure I-D-4: fS_2 versus fO_2 diagram at 250°C showing the geochemical environment for Stage 4 quartz + pyrite + electrum deposition (star) and the transition from Stage 2 quartz + pyrite + marcasite + pyrrhotite to Stage 3 quartz + pyrite + arsenopyrite + sphalerite + galena + pyrrhotite + titanomagnetite (arrow). $\pm S=0.002\pi$, $\text{pH}=5.5$, $\log fS_2$ from electrum composition (Stage 4 only, see text) = -10.1 . Details of construction are given in Appendix V.

the progression from Stage 2 to Stage 3 can be represented by the arrow in Fig. I-D-4.

Therefore if temperature remained constant, fO_2 and fS_2 decreased from Stage 2 to Stage 3. Alternatively a similar change in mineralogy can be caused by a slight increase in temperature (20°C) at constant fO_2 and fS_2 . A decreasing temperature, fO_2 and fS_2 regime seems more likely.

Fraser & Adams (1907) recorded an average gold:silver ratio of 1:0.4 for the Waitaia ore. Silver minerals other than electrum were not reported by them. Equating the gold:silver ratio to the average composition of electrum, a $\log fS_2$ value of -10.1 at 250°C may be calculated. If a silver mineral were present (for example hessite as tentatively identified by Parkinson) the proportion of silver in electrum would be less and indicate a higher value of fS_2 . Nevertheless, whether a silver mineral is present or not the sulphur fugacity derived for electrum deposition is much higher than indicated for Stage 2 and Stage 3 and by the possible presence of arsenopyrite with the electrum as suggested by Fraser & Adams' description of the mineralisation. Either, conditions were very different during electrum deposition with much higher sulphur fugacities or the gold to silver ratio reported by Fraser & Adams is not representative of the electrum composition. In the former case a hydrothermal fluid containing approximately equal concentrations of sulphate and sulphide is indicated (Fig. I-D-4).

In conclusion, the base metal mineralisation at Kuaotunu is characterised by a relatively low concentration of total sulphur in solution and low fugacities of O_2 , S_2 and CO_2 . Electrum deposition may have occurred at higher fugacities of O_2 , S_2 and CO_2 .

GENESIS

Parkinson (1980) postulated that the epithermal Au - Ag veins in the Kuaotunu area were near surface deposits of a fossil geothermal system. They were considered to occur at

the boundary between quartz - illite and quartz - kaolinite wall rock alteration which Parkinson interpreted as marking the change of fluid pH from alkaline to acidic and metal carrying complexing ions in solution from dominantly chloride to dominantly bisulphide.

Developing Parkinson's latter hypothesis, Stage 3 mineralisation was probably deposited as a result of reduction of the fluid (as represented by the decrease in fO_2 and fS_2 from Stage 2 to Stage 3) or increases in pH due to wall rock reactions. Conversely electrum deposition (Stage 4) was initiated by decreasing pH and possibly oxidation (suggested by the high fS_2 and fO_2 values indicated by electrum compositions).

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I-E

TOKATEA, COROMANDELINTRODUCTION

Several veins occur in the Tokatea-Success range immediately to the east of Coromandel township. The largest is the Tokatea Big Reef, a generally unmineralised quartz vein, approximately 4km long and up to 45m wide. Veins containing Au - Ag and base metal mineralisation occur on the footwall (eastern) side of the Tokatea Big Reef and were mined in the Tokatea - Royal Oak and Success mines.

Downey (1935) recorded a total production of 3.9 million grams (125,688 ounces) of which 1 million grams (31,775 ounces) were produced from 7,788 tonnes of quartz.

Skinner (1967) briefly described the Tokatea Big Reef but apart from a geochemical exploration program carried out by ASARCO (Neilsen, 1968) no geological work has been reported on the mineralisations since Fraser & Adams (1907).

GEOLOGY

The section of the Tokatea Success range of interest here (Fig. I-E-1) comprises greywacke of the Tokatea Hill Formation (Moehau Group) and andesites of the Beesons Island Volcanics (Coromandel Group).

The Tokatea Big Reef occurs in both rock types, whereas veins of the Tokatea - Royal Oak mines occur only in Tokatea Hill Formation and veins of the Success Mine occur only in Beesons Island Volcanics. Fraser & Adams (1907) thought that the latter was tuffaceous in the vicinity of the Success Mine. These authors also considered that the most productive portions of veins in the Tokatea Mines occurred where tuffaceous sediments (of the Tokatea Hill Formation) were found inter-stratified with the ordinary sandstone and argillites of the Tokatea Hill Formation.

Workings on the Tribute vein in the Royal Oak Mine

Figure I-E-1: Geology of the Coromandel and Tokatea areas (after Skinner, 1976).

encountered a hornblende porphyry dike approximately 7.5m wide and dipping eastwards (normal to the strike of the vein). The dike occurs in Tokatea Hill Formation. The Tribute vein crossed the dike but at a reduced width or by breaking into a few small stringers.

HYDROTHERMAL ALTERATION

Fraser & Adams (1907) noted that the sedimentary rocks in the Tokatea Mines were silicified, pyritised and bleached. They described the alteration of the Beesons Island Volcanics in the Success Mine as propylitic with no further qualification.

Neilsen (1968) considered that the andesites surrounding the Success Mine were only moderately altered.

MINERALISATION

Tokatea Big Reef

The Tokatea Big Reef extends southwards from the Waverly Fault along the west flanks of the Tokatea Range, branches into two veins in the vicinity of the Buffalo Mine and ends on the Cadman Fault (Fig. I-E-1). Skinner (1967, 1976) considered that the veins outcropping in Cadman Stream, Aitken Stream, Hutt Creek and Petote Stream (described in Section I-G; Petote Stream Area, Coromandel) are continuations of the Tokatea Big Reef on the southern side of the Cadman Fault.

The Tokatea Big Reef varies in width between 10 and 45m and dips to the west 40 to 75° (Skinner, 1976). Outcrops contain cross cutting veins of comby and vuggy amethystine quartz with crystals commonly 100mm long. Very minor base metal sulphide mineralisation occurs at a few localities (e.g. Buffalo Mine) but gold and silver are absent.

Tokatea Mines

Veins containing gold and silver occur on the footwall side of the Tokatea Big Reef near Tokatea Saddle. The largest mine was the Royal Oak which consisted of seven adit levels

and two lower levels worked from a shaft. Most of the ore taken from this mine came from the Tokatea and Tribute veins which strike east-north-east and east respectively. The following description of these veins is summarised from Fraser & Adams (1907).

The major vein constituents are quartz, calcite (far more abundant than in the Kauri Block and Kapanga mines, see Section I-F), pyrite and electrum. Manganese oxides (e.g. pyrolusite), native arsenic, arsenolite, orpiment and realgar were also noted. The latter three occurred as coatings on the wall of the veins and are probably of supergene origin as was also the manganese oxides. In the West Tokatea and other mines situated south of Tokatea Saddle the arsenic was usually in the form of reniform nodules. Geodes exceeding 150mm in diameter were not uncommon and often enclosed filaments of electrum.

Electrum occurred in bonanza shoots related to supposedly more permeable layers in the greywacke termed "mineral heads" or "bars". In the lower levels the bonanzas generally occurred at the intersection of "flinties" (so called because of their fine grained siliceous nature) with the veins, or occasionally in connection with faults of slight displacement.

Vugs lined with crystals of quartz and calcite were common, some exceeding 3m long by 0.3m wide, and were often associated with bonanza ores. Electrum was usually associated with quartz and pyrite but some visible grains and threads occurred in cleavages of calcite crystals. The quartz and calcite in the veins were "often irregularly associated" but Fraser & Adams described a crustified specimen consisting of 1) pyritised wall rock, 2) white crystalline quartz containing fine dispersed electrum, 3) comby crystalline quartz, and 4) large rhombohedral calcite crystals.

Fraser & Adams (1907 p122) state that "the gold occurs with silver in the average proportion of 100 to 50 by weight". It is not clear whether this refers to the overall Au:Ag ratio in the ore or the electrum composition as quoted by them for some other deposits.

Three samples originating from the Tokatea mines were obtained from institutional collections. A sample of bonanza gold ore (sample 13961) contains fine grained hessite, electrum and minor chalcopyrite scattered in quartz euhedral to the metallic minerals. The following banded sequence occurs:

- quartz plus hessite
- quartz plus hessite, electrum and minor chalcopyrite
- quartz plus electrum
- vug quartz (crystals up to 2mm long)

The other two samples contain quartz, sphalerite, galena, pyrite and chalcopyrite. Sample 13960 (TK6) contains medium to coarse grained sulphides in the order (textural interpretation):

- quartz plus pyrite
- quartz plus sphalerite and galena
- quartz plus chalcopyrite and pyrite
- quartz

The sphalerite is characterised by abundant inclusions of (interstitial and exsolved?) chalcopyrite (Fig. 4-17).

Sample 13959 (TK1) exhibits an unusual texture, consisting predominantly of large masses of sphalerite, with abundant chalcopyrite inclusions, seamed (Fig. 4-21) by fine grained galena, chalcopyrite, pyrite and quartz (subhedral to the sulphides). Replacement of pyrite by galena is indicated by poikilitic texture (Fig. 4-14).

Success Mine

The principal veins in the Success Mine were the Jubilee Nos 1 and 2, Success Nos 1 and 2 and James "East and West Reef". Little is known of the mineralisation other than that the electrum occurred in bonanzas and that in the upper levels "sheets of 'gold' (electrum) without any admixture of gangue-minerals were found enclosed in open cavities in the vein fissure. These were described to the writers 'as hanging from the top of the cavity like leaves of a book' " (Fraser & Adams, 1907 p124).

Figure I-E-2: Histograms of filling temperatures and apparent salinities for primary fluid inclusions in samples of quartz: 13955, 7 Level Royal Oak Mine; 13956 Royal Oak Mine (unlocated); 13957 Tokatea Big Reef, Tokatea Saddle; 13958, Buffalo Mine. The individual measurements are listed in Appendix III.

FLUID INCLUSIONS

Fluid inclusions in samples from 7 level of the Royal Oak Mine (samples 13955 quartz and 13956 calcite), Tokatea Big Reef near Tokatea Saddle (13957) and the Buffalo Mine tip head (13958) are normal two phase, liquid plus vapour types. These locations are shown in Fig. I-E-1. Histograms of filling temperatures and salinities for the samples are presented in Fig. I-E-2.

Similar depositional temperatures for the two samples from the Royal Oak Mine and the sample from the Tokatea Big Reef are indicated by the similar ranges of their filling temperatures. Pressure - salinity corrections are probably less than 5°C and therefore a depositional temperature of 220°C is assigned to these samples.

The sample from the Buffalo Mine has generally higher filling temperatures and a pressure - salinity correction of up to 10°C may be required, giving a depositional temperature of approximately 265°C. This higher temperature is to be expected because the Buffalo Mine is at a lower level in the Tokatea Big Reef than the Tokatea Saddle (approximately 300m).

Apparent salinities of the Tokatea Big Reef sample may be higher than those of the Royal Oak sample although this difference may not be significant considering there is only one result for the latter.

Partial chemical analyses of fluid inclusions in samples 13957 (TK2), 13958 (B02) and 13962 (R03), determined by crushing and leaching experiments, are presented in Table 7-7. All three samples have Na/K ratios around 2, considerably lower than theoretical values, between 5 and 7.5, predicted by the Na/K geothermometer for the depositional temperatures considered.

SULPHUR ISOTOPES

Sulphides in a sample of ore from the Tokatea Mines have $\delta^{34}\text{S}$ values of +2.6 per mil (pyrite) +2.3 per mil (chalcopryrite)

TABLE I-E-1: General thermochemical parameters for the depositional environments of the epithermal base metal and gold - silver mineralisations in the Tokatea Mines, Coromandel.

	Stage		Reference
	Base metal	Gold - Silver	
Temperature °C	280	220	Table V-1
True Ionic Strength	0.21	0.17	"
Salinity (mNaCl eq.)	0.26	0.23	"
mK ⁺	0.045	0.025	"
pH	5.5	5.9	See text
pH of kaolinite/sericite boundary	4.3	4.8	Table V-1
pH of sericite/K-feldspar boundary	5.8	6.1	"
Total S (log m _± S)	-2.0	-2.0	See text
Log fS ₂ (sphalerite comp.)	-10.9		Table V-4A
(electrum comp.)		-12.3	Table V-6A
		-11.7	Table V-6C
Log fO ₂	-35.0to-37.0 (Fig I-E-3)	-38.5to-40.0 (Fig. I-E-5)	Figures cited
Log fCO ₂	+1.5	+1.7	Table V-1

and +2.0 per mil (sphalerite). The minerals are not in isotopic equilibrium as indicated by their failure to observe the normal fractionation trend $py > sp > cp$ and therefore depositional temperatures calculated from their fractionations are not realistic.

HYDROGEN ISOTOPES

Water from fluid inclusions in samples 13957 (TK2), 13958 (B02) and 13962 (R03) was extracted under vacuum and the hydrogen separated and analysed by mass spectrometer. δD values were measured as -33.2 (13962), -34.1 (13957) and -36.3 (13958). These values are consistent with a meteoric water origin (possibly during a cooler climate than present) although other types of water could be involved by invoking various modification processes.

THERMOCHEMISTRY

Two mineralisations are modelled for the Tokatea Mines, an early relatively high temperature (280°C) base metal stage and a later lower temperature (220°C) gold - silver stage.

Table I-E-1 lists some of the parameters characterising the geochemical environments of these mineralisations. An fO_2 versus pH diagram for the high temperature mineralisation is presented in Fig. I-E-3, whereas fS_2 versus fO_2 and fO_2 versus pH diagrams for the low temperature mineralisation are presented in Figs I-E-4 and I-E-5 respectively.

Fraser & Adams (1907) described the hydrothermal alteration of the greywacke wall rocks as silicification. The presence of the pH diagnostic potassium minerals was not noted. Therefore regions of mineral deposition over a range of approximately 1 pH unit either side of neutral (pH of 5.5) are shown in Figs I-E-3 and I-E-5.

Because of the absence of hematite and magnetite, the hydrothermal fluids plot in the reduced sulphur species region of the high temperature fO_2 versus pH diagram (Fig. I-E-3), whereas fluids with dissolved sulphur in solution predominantly

Figure I-E-3: f_{O_2} versus pH diagram at 280°C and $\Sigma S = 0.01m$ showing the broad geochemical environment (shaded) for quartz + pyrite + chalcopyrite + sphalerite + galena ($\pm$ electrum?) mineralisation in the Tokatea Mines. (See Table I-E-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-E-4: fS_2 versus fO_2 diagram at 220°C showing the probable chemical environment (shaded) for quartz + pyrite + electrum + hessite + argentite (acanthite) + native arsenic deposition in the veins of the Tokatea Mines. (See Table I-E-1 for relevant thermochemical parameters and Appendix V for details of construction.)

Figure I-E-5: fO_2 versus pH diagram at $220^\circ C$ and $\Sigma S = 0.001m$ showing two possible geochemical environments (A and B, shaded) for quartz + pyrite + electrum + hessite + argentite (acanthite) + native arsenic deposition in the veins of the Tokatea Mines. Environment B, consistent with the higher temperature base metal mineralisation, is preferred here. The pH of the calcite soluble/insoluble boundary = 4.9. (See Table I-E-1 for other relevant thermochemical parameters and Appendix V for details of construction.)

as sulphate (field "A" of Fig. I-E-5) or sulphide (Field 'B' of Fig. I-E-5) are possible at 220°C. To be consistent with the high temperature fluid and because sulphate minerals (e.g. barite) are absent, field B in the reduced sulphur species region is preferred. At both temperatures $\log f\text{CO}_2$ may be less than initially suggested (i.e. the general $\log f\text{CO}_2$ value of +1.5 for the high temperature mineralisation, and the measured value of +1.7 for the low temperature mineralisation), possibly as low as $\log f\text{CO}_2 = 0$ at 280°C.

GENESIS

The occurrence of sulphur in solution predominantly in reduced form indicates that $\delta^{34}\text{S}_{\text{S}}$ is equivalent to $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ which in turn is approximately equal to $\delta^{34}\text{S}$ of the sulphide minerals such as chalcopyrite and sphalerite. Therefore a value of +2 per mil is assigned to $\delta^{34}\text{S}_{\text{S}}$ and is indicative of a magmatic source for the sulphur. In contrast, a meteoric origin for the water is suggested by δD values of the fluid inclusions.

There is insufficient information to define the specific causes of mineral deposition in the Tokatea area or why precious and base metal mineralisation is essentially absent from the Tokatea Big Reef.

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KAURI BLOCK AND KAPANGA, COROMANDELINTRODUCTION

The mineralisations considered here are those mined in the immediate vicinity of Coromandel township; the Hauraki and Bunkers Hill mines of the Kauri Block to the west of the town and the Kapanga Mine to the north (Fig. I-F-1).

Like the deposits at Thames, the Coromandel deposits differed from other mineralisations in the province by having bonanza style mineralisation with very high Au:Ag ratios. The Coromandel deposits were also unusual in the number and diverse strike of their veins and the general absence of silver minerals other than electrum.

The three mines produced a total of 7.4 million grams (238,402 ounces) of bullion from 66,845 tonnes of quartz (Downey, 1935).

The mines were worked from shafts and are now inaccessible. The only geological investigation of the mineralisation was made by Fraser & Adams (1907) although the descriptions of the mines by Downey (1935) give some insight to the style of mineralisation.

GEOLOGY

The mineralisations occur in hypersthene andesite and hornblende dacites of the Beesons Island Volcanics of the Coromandel Group (Fig. I-F-1).

Fraser & Adams (1907) noted that the rocks encountered in the upper levels of the Kapanga and Scottys (grouped here with the Kapanga) mines were fine grained tuffs interstratified with solid flows of andesite and dacite, whereas from approximately 220m to 370m below surface (150 to 300m below sea level) the country rock consisted entirely of tuff beds (dipping at low angles to the west and south-west) and an 0.6m thick carbonaceous layer (dipping southwards), encountered at

Figure I-F-1: Location of veins and workings in the Kauri Block and Kapanga areas. Detailed plans of some of the mines are held at the Huntly Branch of Mines Division.

approximately 287m (213m below sea level).

The rocks of the Kauri Block are predominantly andesite flows although fragmental rocks also occur. A hornblende porphyry dike formed a hard bar in workings of the Golden Pah Mine and Fraser & Adams (1907) considered that it probably extended into the Union Beach section of the Hauraki Mine.

HYDROTHERMAL ALTERATION

Fraser & Adams (1907) described a depth zoned pattern of alteration in the country rocks of the Kapanga and Hauraki Mines. In the top 120m of the Kapanga Mine (from surface to 50m below sea level) the andesitic rocks were altered "to a bluish white pyritised kaolinitic-like mass" in which "silicification is not an uncommon feature" (Fraser & Adams, 1907, p100). Between 120m and 270m (50m and 200m below sea level) "the andesites penetrated were harder, and of a dark-greenish colour; alteration in this zone apparently resulting mainly in the development of chlorite and, in a lesser degree, of carbonates" (Fraser & Adams, 1907, p100). From 270m to 370m (200 to 300m below sea level) another zone of intense alteration was encountered.

Similarly the rocks in the upper levels of the Hauraki Mine were intensely altered but passed into less altered "hard dark-greenish" rocks with depth. Intensely altered rocks were again encountered at approximately 120m below sea level (below the 400 foot level).

MINERALISATION

Kauri Block

A large number of veins of diverse strike were worked in the Hauraki and Bunkers Hill mines. The veins averaged 150mm in width but varied from "mere stringers to strong ore-bodies" 1.5m wide. The most productive vein was Legges Reef (also known as No. 2 Hauraki) in which the ore shoot measured 45m in length and extended from the surface down to a depth of 80m.

The major vein constituents were quartz (bluish-white colour), pyrite, sparse calcite, arsenopyrite and manganese

oxides. Native arsenic (generally massive), stibnite (Hauraki and Blagrove's Mines), pyrrargyrite (Golden Pah Mine) and kermesite (Hauraki Mine) were also found. Vugs lined with drusy quartz were "abundant" and wall rock breccias occurred "occasionally". The vein material was sharply separated from the smooth slickensided surfaces of the wall rocks by a narrow "pug" (fault breccia) zone. Electrum (averaging 74% gold and 26% silver) occurred in bonanza shoots generally related to vein intersections. Ore containing "three ounces to the pound" (200g/kg) was "not uncommon", and many tonnes of ore were mined averaging over "an ounce to the pound" (70g/kg). Although workings were sunk to 120m and the lowest bonanza was mined at 90m, most of the gold was won from within 65m of the surface. The bonanza sections of the mines occurred in intensely altered country rock.

Kapanga

Two north striking, but very sinuous, veins known as Kapanga and Scotty's were mined to below 180m from the surface in the Kapanga Mine. Their westerly dip of 25 to 35° in the upper levels increased with depth at a point where the country rock became harder and "less altered". In the deeper levels this pair of veins were not identified, with mining on the 940 foot (287m) and 1000 foot (305m) levels being on two westerly striking veins known as Hartridge's and Anniversary. The latter veins were not located above the 940 foot level and therefore the relationship between the two pairs of veins is not known.

All four veins were very narrow with maximum widths less than 0.5m. Quartz and pyrite predominate over calcite. Electrum (averaging 70% gold and 30% silver), often visible, occurred in bonanza shoots at bends and elbows in the veins or at the intersections with cross veins. Native arsenic (reniform nodules and massive forms) and arsenopyrite were common in the rich ore. Aragonite was found in Scotty's Reef. Strong pyrite mineralisation and hydrothermal alteration of the wall rocks accompanied the bonanza mineralisation. The richest bonanza in Hartridge's vein occurred in the 940 foot level (287m) near Larnach Shaft where the vein contacted the

Figure I-F-2: fS_2 versus fO_2 diagram at 220°C showing the geochemical environment (line of crosses) of quartz + pyrite + electrum $\pm$ arsenopyrite $\pm$ native arsenic deposition in the veins of the Kauri Block and Kapanga Mines Coromandel. Log fS_2 from electrum compositions = -10.7 to -11.3, and log fCO_2 (estimated) = +1.5. (See Appendix V for methods of construction.)

0.6m carbonaceous layer mentioned earlier. The latter was strongly pyritised.

THERMOCHEMISTRY

The Kauri Block and Kapanga mineralisations are modelled at a temperature of 220°C in the fS_2 versus fO_2 (Fig. 12-2) and fO_2 versus fH_2O (Fig. 12-3).

Figure I-F-3: fO_2 versus pH diagram at 220°C and $a_S=0.001m$ showing the geochemical environment (shaded) of quartz + pyrite + electrum + arsenopyrite + native arsenic deposition in the veins of the Kauri Block and Kapanga Mines, Coromandel. $\bar{I}=0.15$, $mK^+=0.02$, $pH=5.1\pm0.6$, log fS_2 from electrum composition = -10.7 to -11.3 , log fS_2 for native arsenic deposition = <-12.3 , log fS_2 for arsenopyrite deposition = <-13.8 . (See Appendix V for methods of construction.)

Electrum deposition predominantly occurred at $\log fS_2$ values around -11 but values as low as approximately -14 occurred. $\log fO_2$ was approximately between -38 and -42. A fluid containing sulphur in solution in reduced form is indicated, probably with H_2S predominating over HS^- .

GENESIS

The bonanza mineralisations of the Kauri Block and Kapanga mines are related to structural features in a near surface environment and in this respect resemble the gold deposits of Thames. Electrum deposition probably resulted from boiling of the hydrothermal fluid and loss of H_2S , causing instability of the gold transporting sulphide complexes. Variations in the concentration of H_2S may also account for the wide range of fS_2 and fO_2 indicated by the mineral assemblages.

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PETOTE STREAM AREAINTRODUCTION

Quartz veins containing base metals outcrop in Cadman Stream, Aitken Stream, Hutt Creek and Petote Stream (Fig. I-G-1) and were considered by Skinner (1967, 1976) to be extensions of the Tokatea Big Reef. They were described by Fraser & Adams (1907) and Skinner (1967) and recently re-examined by Edwards (1979).

Although minor prospecting by the excavation of small trenches and short adits was carried out in the late 1800's and early 1900's, the deposits were found to be small and no mines were established in the area.

GEOLOGY

A geological map of the area is presented in Fig. I-G-1

The veins occur in greywacke of the Tokatea Hill Formation. Intrusives (Coromandel Group Kai-iti Porphyrites), ranging from dikes one metre across to stocks 150m across, also occur in the area and were classified by Edwards (1979) as follows:

- (i) Intrusives predating regional hydrothermal alteration, Lower to Mid Miocene; small diorite plutons and quartz diorite and aplite dikes.
- (ii) Intrusives contemporaneous with regional hydrothermal alteration, Mid to Upper Miocene; quartz diorite, and to a lesser extent diorite, porphyries, forming dikes and small stocks.
- (iii) Intrusives postdating regional hydrothermal alteration, Upper Miocene; predominantly andesite and dacite porphyries and intrusive andesites.

HYDROTHERMAL ALTERATION

Edwards (1979) described the hydrothermal alteration of the greywacke country rocks, in order of increasing grade, as follows:

Figure I-G-1: Geology of the Petote Stream area (after Skinner, 1967; 1976).

1. Propylitic; pyrite, epidote, chlorite, secondary quartz, calcite and clays.
2. Sericitic; sericite, quartz and pyrite.
3. Quartz-sericitic; quartz, sericite and pyrite.
4. Silicic; quartz, pyrite, minor sericite, chalcopyrite and covellite.

MINERALISATION

Several mineralised quartz veins up to 2m wide occur in the area (Fig. I-G-1) and consist of quartz and sulphide cemented wall rock breccias (Fig. 4-3). The sulphides are generally medium grained. Comb and vug quartz are common in some of the veins. The ratio of sulphide to quartz varies but is high in the Hutt Creek vein, Galena Lode and Chalcopyrite Lode, Sphalerite is generally the most common sulphide, followed by galena but chalcopyrite is particularly abundant in the Chalcopyrite Lode.

A generalised paragenesis (Fig. I-G-2) consists of the following:

1. Repetative sequences of brecciation with subsequent quartz and sulphide depositions (in some veins the resulting texture consists of individual grains of sulphides separated by quartz).
2. Comb and vug quartz with pyrite and sometimes chalcopyrite.
3. Late calcite followed by kaolinite deposition on quartz crystals in vugs (only present in the Chalcopyrite Lode).

The detailed paragenesis within Stage 1 of the Hutt Creek, Galena Lode and Chalcopyrite Lode is complex with some specimens exhibiting banded textures (Fig. I-G-3, and also Plates 105 and 110 of Skinner, 1967). The absence of unweathered vein sections at Hutt Creek and the Galena Lode makes elucidation of the complete Stage 1 sequence at these locations impossible but Skinner (1967) described the banded sequence in half of a symmetrical crustified veinlet (originally 30mm wide) from the Chalcopyrite Lode as follows:

country rock + pyrite
 quartz + pyrite
 pyrite + minor sphalerite

Minerals \ Stages	1	2	3	4
Quartz	—	—		
Pyrite	—	—		
Chalcopyrite	—	—		
Sphalerite	—			
Galena	—			
Calcite			—	
Kaolinite			—	
Chalcocite				—
Covellite				—
Goethite				—

Figure I-G-2: Paragenetic sequence of minerals in the veins of the Petote Stream area.

Figure I-G-3: Banded, breccia, medium to coarse grained, sulphide mineralisation from the Hutt Creek vein (Sample 13989, 5.5cm wide x 5cm high).

Figure I-G-4: Histograms of primary fluid inclusion filling temperatures and apparent salinities for samples of Stage 2 quartz (13980, 14006, 14005 and Chalcopryrite Lode quartz: 13992 + 13993q + 13995 + 13996 + 13997) and Stage 3 calcite (13991 + 13993c) from the Petote Stream area. The individual measurements are listed in Appendix III.

chalcopyrite + minor sphalerite + galena (irregular)
 sphalerite + minor galena (irregular)
 chalcopyrite
 galena cubes
 quartz
 calcite
 sequence repeated in reverse order

The latter quartz and calcite (centre of vein) equate with Stage 2 and Stage 3 respectively of Fig. I-G-2.

Covellite replaces chalcopyrite along fractures and rims in some specimens from the veins in Aitken Stream and Petote Creek examined by the writer. Supergene minerals were not identified in samples from the Hutt Creek vein. Skinner (1967) noted limonite, in addition to covellite, in some of his samples and Edwards (1979) also reported replacement of chalcopyrite by chalcocite in the Aitken Stream vein.

FLUID INCLUSIONS

Fluid inclusions in Stage 2 quartz and calcite from Aitken Stream and Petote Stream are normal two phase liquid plus vapour types except for a few inclusions in samples 13996 (PS10) and 14006 (PS26) which also contain a fibrous solid phase (see Chapter 6).

Histograms of filling temperatures and apparent salinities are presented in Fig. I-G-4. A pressure - salinity correction of approximately 10°C must be added to the filling temperatures. Some of the histograms are broad and lack well defined modes, however depositional temperatures are assigned as follows:

Aitken Stream	Stage 2 quartz	: 290°
Petote Stream north	Stage 2 quartz	: 310°
Galena Lode, Petote Stream,	Stage 2 quartz	: 270°
Chalcopyrite Lode, Petote Stream,	Stage 2 quartz	: 290°C
Chalcopyrite Lode, Petote Stream,	Stage 3 calcite	: 250°C

Partial chemical analyses of fluid inclusions in samples

13907 (Hutt 2), 13980 (AS1) and 13998 (PS15), determined by crushing and leaching experiments are presented in Table 7-7. The Na/K ratios of all these samples (13907 = 24, 13980 = 15.3 and 13998 = 10) are much higher than the theoretical values, between 4 and 6, predicted by the Na/K geothermometer.

HYDROGEN ISOTOPES

Fluid inclusions in samples of quartz contain waters with δD values of -36.7 per mil (sample 13998), -45.7 per mil (sample 13980) and -48.9 per mil (sample 13907). These values probably result from a meteoric water origin (during a cooler climate), however the latter two values are close to the -50 to -85 per mil range considered characteristic of primary magmatic waters (Taylor, 1979) and may indicate the presence of a magmatic water component.

SULPHUR ISOTOPES

The $\delta^{34}S$ values of samples from the Petote Stream area are listed in Table 9-1 with depositional temperatures derived from sp - gn pairs. Two of the samples from Hutt Creek (samples 13986 and 13989) give unrealistic temperature estimates and a third (sample 13987) also appears to be too high in comparison with the remaining 6 temperature estimates. Therefore it is concluded that Stage 1 sulphide deposition occurred at temperatures around 290 to 320°C.

LEAD ISOTOPES

Cooper & Richards (1969) measured the lead isotope ratios in a sample of galena from the Chalcopyrite Lode in Petote Stream. Comparison with lead isotope ratios in samples of vein galena, andesite, rhyolite (Cooper & Richards, 1969) and greywacke (Armstrong & Cooper, 1971) from other areas of the Coromandel Peninsula (c.f. Fig. 5 of Robinson, 1974) suggests that the lead in the Petote Stream veins was derived from the greywacke suite rocks.

THERMOCHEMISTRY

The geochemical environment of the Petote Stream mineralisation is limited on the fS_2 versus fO_2 diagram

Figure I-G-5: fS_2 versus fO_2 diagram at 300°C showing the geochemical environment (shaded) of Stage 1 quartz + sphalerite + galena + pyrite + chalcopyrite mineralisation in veins of the Petote Stream area. $\leq S=0.01m$, pH=5.6, log fS_2 from sphalerite compositions = -9.0 to -9.4, and log fCO_2 from fluid inclusion measurements = +1.6. (See Appendix V for details of construction.)

(Fig. I-G-5) by the presence of pyrite and chalcopyrite but absence of pyrrhotite, magnetite, hematite and bornite. Log fS_2 values between -9.0 and -9.4 are indicated by the sphalerite compositions and at these sulphur fugacities log fO_2 is limited between -34.4 and -31.0 by the absence of graphite and magnetite respectively.

Sericite occurs in the wall rocks, whereas K-feldspar and kaolinite are absent (although kaolinite occurs as a late stage vein mineral). Therefore a pH of around 5.6 (near neutral) is indicated.

An fO_2 versus pH diagram, constructed for a total sulphur in solution concentration of 0.01m ($\log m \leq S = -2$), is presented in Fig. I-G-6. The shaded area of the diagram (and also in Fig. I-G-5) represent the region of mineralisation. A fluid with HS^- as the predominant sulphur species in solution is indicated. Values of log fO_2 are between -33.0 and -33.5 at a pH of 5.6

GENESIS

Edwards hypothesized that the main period of regional hydrothermal alteration in the Petote Stream area was related to deep porphyry copper mineralisation during the mid to upper Miocene and that vein mineralisations now exposed at the surface were related to a later second period of porphyry mineralisation in the late Miocene to early Pliocene.

The former mineralisation is conjecture, however the vein mineralisations are undoubtedly associated with a period of intrusion of Kai-iti Porphyrites and their deeper equivalents. The writer envisages a geothermal system initiated by the intrusives. The mineralising fluid was deeply circulating meteoric water which leached most of the mineralising components from the greywacke basement rocks. Sulphide deposition was probably a result of decreases in fluid pH due to reactions with the wall rocks.

The uncertainty of the dissolved sulphate/dissolved

Figure I-G-6: fO_2 versus pH diagram at $300^\circ C$ and $\Sigma S = 0.01m$ showing the geochemical environment (shaded) of Stage 1 quartz + sphalerite + galena + pyrite + chalcopyrite mineralisation in veins of the Petote Stream area. $\bar{I} = 0.11$, $mK^+ = 0.006$, pH 5.6, $\log fS_2$ from sphalerite compositions = -9.0 to -9.4, $\log fCO_2$ from fluid inclusion measurements = +1.6, and the pH of the calcite soluble/insoluble boundary = 5.6. (See Appendix V for methods of construction.)

sulphide ratio of the hydrothermal fluid (c.f. Fig. I-G-6) prevents definition of $\delta^{34}\text{S}_{\text{S}}$ and the origin of the sulphur.

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WHANGAPOUA AND THE OPITONUI MINE

INTRODUCTION

The Opitonui Mine produced 1 million grams (30,972 ounces) of bullion (57,137 tonnes of quartz mined), predominantly between 1895 and 1904, from three east-west striking veins known as Maiden, Carvill and Hilda. Several northerly striking veins such as the Opitonui, although auriferous, proved unprofitable. The veins were mined on two adit levels and 4 shaft levels, all now inaccessible.

Robson (1979) recently investigated the geology, hydrothermal alteration and mineralisation of the Whangapoua area concurrently with a stream sediment and rock chip geochemical exploration program by AMOCO (reported in Moore, 1979a).

GEOLOGY

The geology of the Whangapoua area (Fig. I-H-1) consists of andesites of the Tuataewa Andesite, Beesons Island Volcanics and Whangapoua Andesite formations, intruded by stocks of hornblende diorite porphyry and hornblende microdiorite porphyry termed Whangapoua Intrusives by Robson (1979). Several dikes of andesite porphyry cut the diorite porphyry stocks and andesites. All formations belong to the Coromandel Group.

Fraser & Adams (1907) described the rocks in the Opitonui Mine area as andesites although they noted that the presence of hornblende porphyry was indicated by a specimen found on the tip head.

HYDROTHERMAL ALTERATION

Robson (1979) classified the hydrothermally altered rocks of the Whangapoua area into five groups as follows (in order of increasing intensity of alteration):

1. Weak propylitic: chlorite, calcite and magnetite
2. Advanced propylitic: chlorite, epidote, laumontite, pyrite, sericite (interlayered illite - montmorillonite), minor calcite, minor sphene, magnetite and rare adularia.
3. Magnetite-chlorite-calcite: magnetite, chlorite, calcite, sericite (interlayered illite - montmorillonite), pyrite and chalcoppyrite.
4. Clay-sericite (equivalent to argillic alteration): sericite (illite and interlayered illite - montmorillonite), chlorite, pyrite, quartz, and accessory sphene.
5. Quartz-sericite (equivalent to phyllic alteration): quartz, pyrite, sericite (illite and interlayered illite - montmorillonite), minor chlorite and accessory sphene.

Kaolinite is restricted to shear zones and veins where it occurs with sericite. For example, it is associated with vein stibnite mineralisation.

A concentric zonal pattern of the different alteration types is not well developed because of the pronounced structural control which offsets the alteration zones and induces limited superposition or telescoping of assemblages (Robson, 1979). However, two centres of intense alteration were defined (Fig. I-H-2).

MINERALISATION

The most productive vein of the Opitonui Mine, the Maiden vein ranged from 0.6m to 4.3m in width with an average of about 1.8m (Fraser & Adams, 1907). In the lowest mine level (4 level at 113m below surface) the width of the Maiden vein contracted to 0.3m on intersecting a "hard bar" which Fraser & Adams postulated to be a dike of hornblende porphyry.

Downey (1935) considered that the economic mineralisation of the Opitonui Mine was concentrated in comparatively restricted shoots near the surface, with poor grades in the lower levels.

Fraser & Adams described the mineralisation as consisting of electrum, with approximately equal proportions of gold and

□ Alluvium

COROMANDEL GROUP

Extrusive Rocks

WHANGAPOUA ANDESITE FORMATION

▨ porphyritic andesite dike

△△ glomeroporphyritic pyroxene andesite flows.

BEESENS ISLAND VOLCANICS FORMATION

▽▽ hornblende-pyroxene andesite flows

TUATEAWA ANDESITE FORMATION

◊◊ augite-hypersthene andesite flows

Undifferentiated

△△ Volcaniclastics

◊ hypersthene augite andesite dike

Intrusive Rocks

WHANGAPOUA INTRUSIVES FORMATION (Informal unit.)

◎ Dacite porphyry (Goat Rock)

■ Andesite porphyry dike

◊◊ Hornblende-microdiorite porphyry

◊◊ Diorite porphyry

— Vein - - - Fault / Road

Figure I-H-1: Geology of the Whangapoua area (after Robson, 1979).

Figure I-H-2: Generalised distribution of hydrothermal alteration zones in the Whangapoua area (after Robson, 1979).

Minerals	I	II	III	IV
	Fe	Pb-Zn-Ag-As-Sb-Cu(Fe)	As (Fe)	Sb
pyrite	_____	_____	_____	_____
marcasite	_____			
miargyrite		_____		
tetrahedrite		_____		
freibergite		_____		
famatinite		_____		
sphalerite		_____		
chalcopryrite		_____		
galena		_____		
antimony (native)		_____		
rutile/anatase			_____	
arsenopyrite			_____	
arsenic (native)			_____	
stibnite				_____

Figure I-H-3: Paragenetic sequence of minerals in veins of the Whangapoua area. (From Fig. 5.2 of Robson, 1979.)

silver, fairly evenly disseminated throughout the quartz vein although some concentrations occurred "in certain thin partings in the vein" (Fraser & Adams, 1907 p130).

Robson (1979) studied samples from a 0.2m wide quartz vein and float in Waingaro Stream, approximately 2.5km west of the Opitonui Mine. The mineralisation consisted of various assemblages of pyrite, marcasite, stibnite, arsenopyrite, miargyrite (AgSbS_4), tetrahedrite, freibergite (argentian tetrahedrite), famatinite (Cu_3SbS_4), sphalerite, chalcopyrite, galena, native antimony, rutile/anatase and native arsenic. Robson's proposed paragenesis is shown in Fig. I-H-3. Stibnite associated with banded and vug quartz and occasionally also pyrite is the only assemblage found commonly in float of Waingaro Stream.

Rare isolated occurrences of chalcocite, molybdenite and pyrrhotite were recorded from a few localities by AMOCO (Moore, 1979a).

FLUID INCLUSIONS

Robson (1979) determined fluid inclusion filling temperature ranges of $270 - 370^\circ\text{C}$ and $220 - 360^\circ\text{C}$ for an unmineralised 1m wide quartz vein and unmineralised quartz float respectively in upper Waingaro Stream. Histograms of the filling temperatures (Figs 5.5 and 5.6 of Robson) have modes at approximately 300°C . Robson correlated his Stage 2 mineralisation with $270 - 330^\circ\text{C}$ groupings in the filling temperature histograms.

A float sample from Waingaro Stream, studied by the writer, contained needles of stibnite intergrown with vug quartz crystals on earlier vein quartz and pyrite. The sample is correlated with Robson's Stage 4 mineralisation. The quartz crystals contain many vapour filled primary inclusions indicating that the hydrothermal fluid was boiling at the time of crystal growth. Two normal type primary inclusions gave filling temperatures of 190°C . This sample was also crushed and leached (Chapter 7) to determine the chemical composition of the inclusion fluids. The results indicate the

TABLE I-H-1: General thermochemical parameters for Stage 2 and Stage 4 quartz vein mineralisation in the Waingaro Stream area Whangapoua.

	Stage 2 Cu-Pb-Zn	Stage 4 Sb 200 (fluid boiling)	Reference
Temperature °C	280		Table V-1
True ionic strength	0.21	0.11	"
Salinity (m NaCl eq.)	0.26	0.11	"
mK^+	0.045	0.012	"
pH	5.1	5.2	See text
pH of kaolinite/sericite boundary	4.3	5.2	Table V-1
pH of sericite/K-feldspar boundary	5.8	6.5	"
Total S ($\log mS$)	-2.0	-3.0	See text
$\log fS_2$ (sphalerite comp.)	-9.7 to -9.9		Table V-4B
$\log fO_2$	-33.5 to -35.8 (Fig. I-N-5)	-39 to -41.5 (Fig. I-N-6)	figures cited
$\log fCO_2$	+1.5	+2.0	Table V-1

presence of 2300 ppm Na^+ , 450 ppm K^+ , 3700 ppm Cl^- and 0.8 moles/kg of CO_2 .

SULPHUR ISOTOPES

Stage 4 stibnite and pyrite from float in Waingaro Stream have $\delta^{34}\text{S}$ values of +1.5 and -2.1 per mil respectively.

HYDROGEN ISOTOPES

Fluid inclusions in quartz (sample 13910) from the Stage 4 quartz plus stibnite mineralisation contain water with a δD value of -47.6 per mil. This value is close to the upper limit of the δD range considered characteristic of primary magmatic water (-50 to -85 per mil) although considering the paragenetic position of the sample a predominantly meteoric water origin is considered more likely.

THERMOCHEMISTRY

Introduction

Table I-H-1 lists the parameters of the various geochemical environments modelled in the following section.

Robson's description of the hydrothermal alteration indicates that with the exception of the low temperature (approximately 200°C) Stage 4 fluid which deposited kaolinite the fluids were in equilibrium with sericite in the wall rocks.

Stage 2

An $f\text{S}_2$ versus temperature diagram (Fig. I-H-4) demonstrates that not all of the various minerals grouped in Stage 2 by Robson (Fig. I-H-3) were in equilibrium at the same time. At least two mineral assemblages can be interpreted from Robson's text descriptions: (a) tetrahedrite, famatinite, freibergite, miargyrite and native antimony (Robson, 1979 p177) and (b) pyrite, sphalerite, tetrahedrite, chalcopyrite and galena (Robson, 1979 pp121 - 123). The former is not an equilibrium assemblage because native antimony and famatinite are deposited under very different $f\text{S}_2$ conditions (Fig. I-H-4).

Figure I-H-4: fS_2 versus temperature diagram for various sulphidation reactions relevant to the Whangapoua (Waingaro Stream) mineralisations. The diagram demonstrates that native antimony and famatinite of Robson's (1979) Stage 2 mineralisation were deposited under very different fS_2 conditions. (Methods of construction are given in Appendix V.)

For example, at 280°C (corresponding to 1.8 on the $1000/T^{-1}$ scale in Fig. I-H-4) the famatinitite/tetrahedrite boundary occurs at a $\log fS_2$ value of approximately -7.7, whereas native antimony is stable only at $\log fS_2$ values less than (more negative) -13.0.

The FeS content of Stage 2 sphalerites analysed by Robson indicate $\log fS_2$ values between -9.7 and -9.9 at 280°C. Therefore $\log fS_2$ values between -7.7 and -10 are considered here for Stage 2 mineralisation in the fO_2 versus pH diagram (Fig. I-H-5). The native antimony is regarded as a later phase possibly occurring with arsenopyrite, native arsenic and rutile/anatase of Stage 3.

Two regions of Stage 2 mineralisation are shown in Fig. I-H-5, area A representing the tetrahedrite, famatinitite, freibergite and miargyrite mineralisation and area B the pyrite, sphalerite, tetrahedrite, chalcopyrite and galena mineralisation. The transition from one to the other can be characterised by changes in fO_2 and fS_2 , probably a reduction in values of both parameters so that mineralisation "A" preceded mineralisation "B".

Stage 3

The appearance of Stage 3 mineralisation represents a reduction in fS_2 (with or without a drop in temperature) from Stage 2 particularly if native antimony was deposited in the latter stage (c.f. Fig I-H-4).

Stage 4

The possible range of conditions for stibnite mineralisation at 200°C are shown by the shaded area in Fig. I-H-6.

The pH contours are constructed for a total sulphur in solution concentration of 0.001m ($\log m \leq S = -3$). At values below 0.0005m ($\log m \leq S = -3.3$) Sb_2S_3 is stable rather than stibnite.

Except under conditions of high sulphur fugacity ($\log$

Figure I-H-5: fO_2 versus pH diagram at 280°C and $\leq S=0.01m$ showing the geochemical environments of (A) Stage 2 quartz + tetrahedrite + hematite + freibergite + miargyrite mineralisation and (B) Stage 2 quartz + pyrite + sphalerite + tetrahedrite + chalcopyrite + galena mineralisation in veins of the Waingaro Stream area, Whangapoua. (See Table I-H-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-H-6: fS_2 versus fO_2 diagram at 200°C showing the geochemical environment (line of crosses) for Stage 4 quartz + stibnite + pyrite + kaolinite deposition in veins of the Waingaro Stream area, Whangapoua. (See Table I-H-1 for relevant thermochemical parameters and Appendix V for details of construction.)

$fS_2 > -10.8$) stibnite is deposited from fluids in which dissolved sulphide predominates over sulphate. At $\log fS_2$ values greater than -10.8 concentrations of dissolved sulphate may be equal to or slightly exceed dissolved sulphide, however because Sb_2S_2O is absent highly oxidised fluids are precluded.

GENESIS

Robson (1979) and Moore (1979a) considered that the pattern of hydrothermal alteration zones and stream sediment and rock chip geochemistry in the Whangapoua area was characteristic of a high level exposure of a porphyry copper deposit. Robson (1979) suggested that the postulated porphyry copper mineralisation was related to intrusives emplaced below a developing stratovolcano in the upper Miocene. Regional faulting during the Pliocene provided zones into which the late mineralising solutions migrated and deposited the mineralised quartz veins.

The writer considers that the hydrothermal fluid responsible for the vein mineralisations was deeply circulating meteoric water. The change in fluid chemistry from Stage 2A through Stage 2B (Fig. I-H-5) to Stage 3 is one of progressive reduction of the hydrothermal fluid (increasing proportion of reduced aqueous sulphur species in the fluid) and was probably the principal mechanism of sulphide deposition from chloride complexed metals in solution. During Stage 4 boiling of the hydrothermal fluid with concomitant loss of H_2S caused deposition of stibnite from sulphide complexed antimony in solution. Changes in pH resulting from reactions of the fluid with wall rocks may also have promoted mineralisation, particularly the acidic pH during Stage 4 indicated by the presence of kaolinite associated with the stibnite mineralisation.

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MOORE, C.R.	1979a
ROBSON, R.N.	1979
SCHOFIELD, J.C.	1967
SKINNER, D.N.B.	1976
WILLIAMS, G.J.	1974: see p104

I-I

MANAIAINTRODUCTION

Quartz veins were worked between 1885 and 1901 in two areas of the Manaia Valley, the Golden Hills (or Victoria) Claim and the Jubilee Claim, but yielded a total of only 9,000 grams (296 ounces) of bullion (Downey 1935).

Recently AMOCO Minerals Ltd identified porphyry style mineralisation which was subsequently described by Stevens (1980).

GEOLOGY

The geology of the Manaia area was described by Fraser & Adams (1907), Cornwell (1967) and Stevens (1980). A geological map and cross section based on the latter description are shown in Fig. I-I-1. The major units are as follows:

Manaia Hill Group (Jurassic): greywacke sandstone, argillite, chipwacke and conglomerate.
Coromandel Group (Miocene) : Beesons Island Volcanics; andesite flows and volcanoclastics
Kai-iti Porphyrites: stocks and dikes of hornblende andesite porphyry, hornblende quartz diorite porphyry, hornblende microdiorite porphyry and hornblende microquartz diorite porphyry.

Stevens (1980) inferred age relationships between the intrusives by the presence or absence of hydrothermal alteration and mineralisation and considered that two or three separate periods of intrusive activity occurred.

Stevens also noted the occurrence of an 0.2m wide breccia dike and several pebble dikes (milled breccias) generally less

than 1m in width. They all occur in Manaia Hill Group rocks. He suggested that the dikes were a result of hydrothermal activity; the breccia dike probably being associated with the intrusion and related hydrothermal activity of a hornblende quartz diorite stock but the pebble dikes post dating this period.

HYDROTHERMAL ALTERATION

Stevens classified the hydrothermally altered rocks of the Manaia area into the following four groups, in order of increasing intensity of alteration:

1. Weak propylitic:
 - (a) igneous rocks: chlorite, pyrite, magnetite and calcite.
 - (b) greywacke suite rocks: chlorite and pyrite.
2. Advanced propylitic:
 - (a) igneous rocks: secondary quartz, epidote, clinozoisite, chlorite, calcite, pyrite, magnetite, leucoxene (rutile and anatase), sericite (inter-layered illite-montmorillonite) and very rare tourmaline.
 - (b) greywacke suite rocks: pyrite, chlorite, epidote and sericite (illite type clays).
3. Clay sericite:

igneous rocks only; secondary quartz, pyrite and clay (illite, interlayered illite-montmorillonite, chlorite, interlayered chlorite-montmorillonite and some kaolinite)
4. Quartz sericite:
 - (a) igneous rocks: secondary quartz, sericite (illite and interlayered illite-montmorillonite), pyrite, chlorite and interlayered chlorite-montmorillonite.
 - (b) greywacke suite rocks: pyrite, chlorite, sericite (illite and interlayered illite-montmorillonite) and inter-layered chlorite-montmorillonite.

Figure I-I-1: Geological map and cross-section of the Manaia area (after Stevens, 1980).

Propylitic alteration

Chlorite, calcite, magnetite zone } Advanced propylitic alteration

Epidote zone

Clay-sericite alteration

Quartz-sericite alteration

Alteration associated with late stage hydrothermal activity

Walking Track

Figure I-I-2: Map and cross-section of the hydrothermal alteration zones in the Manaia area (after Stevens, 1980).

MINERAL	PORPHYRY I	PORPHYRY II	EPITHERMAL	SUPERGENE
Pyrite	---	-----		
Ti-oxides	---	-----		
Chalcopyrite		-----		
Molybdenite		-----		
Gold		-----	-----	
Sphalerite		-----		
Galena		-----		
Magnetite	---	-----		
Quartz		-----		
Marcasite			-----	
Pyrrhotite		-----		
Bornite				-----
Chalcocite				-----
Covellite				-----
Limonite/ jarosite				-----
Malachite				-----

Figure I-I-3: Paragenetic sequence of mineralisation in the Manaia area. (From Fig. 4.14 of Stevens, 1980.)

A zonal pattern of hydrothermal alteration occurs around a mineralised (porphyry style) quartz diorite porphyry (Fig. I-I-2) as follows: 1. a central core of advanced propylitic alteration, 2. clay sericite, 3. quartz sericite, 4. advanced propylitic, 5. propylitic, 6. alteration restricted to veins and shears (epithermal alteration), and 7. propylitically altered dikes and small stocks, away from the main area of alteration and post-dating the porphyry mineralisation and alteration.

MINERALISATION

Stevens' paragenesis for the mineralisation in the Manaia area is shown in Fig. I-I-3.

Porphyry style mineralisation consisting predominantly of quartz-pyrite ⁺ chalcopyrite vein stockworks and magnetite-chalcopyrite ⁺ pyrite veins occurs in the pervasively hydrothermally altered rocks. Two stages of porphyry mineralisation and hydrothermal alteration were recognised (Fig. I-I-3). Rocks altered to advanced propylitic assemblages (Stevens' chlorite-calcite-magnetite zone) contain pyrite, magnetite, chalcopyrite, sphalerite, galena and molybdenite (in order of abundance) mineralisation in quartz veins and infilling joints and shears and are grouped as Porphyry I in Fig. I-I-3. Porphyry II mineralisation occurs in the quartz-sericite and clay-sericite altered rocks and consists of pyrite and rare pyrrhotite and chalcopyrite in intrusive host rocks and pyrite and rare chalcopyrite in greywacke suite rocks.

Epithermal mineralisation (Fig. I-I-3) consists of quartz veins with pyrite, marcasite, sometimes kaolinite and presumably rare electrum (e.g. in worked veins of the Golden Hills and Jubilee Claims). Pyrite mineralisation in the breccia dike in Manaia Gorge was also attributed to the epithermal stage.

GENESIS

Stevens' model for the Manaia porphyry mineralisation is illustrated in Fig. I-I-4. He considered that a hydrothermal

Figure I-I-4: Model proposed by Stevens (1980) for the porphyry copper-type deposit at the junction of Kakatarahae Stream and the Manaia River. (From Fig. 5.1 of Stevens, 1980.)

system consisting of meteoric water and late magmatic fluids was initiated by the intrusion of a quartz diorite porphyry and produced a central zone of advanced propylitic alteration (chlorite-calcite-magnetite zone) and Porphyry I mineralisation. This was largely overprinted by continued hydrothermal activity which produced the concentric clay-sericite and quartz-sericite and marginal propylitic zones and Porphyry II mineralisation.

Cessation of pervasive alteration and mineralisation was followed by a resurgence of magmatic activity with the intrusion of dikes. An epithermal mineralisation event followed this, giving rise to quartz reefs, and pebble dikes.

REFERENCES AND BIBLIOGRAPHY

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SCHOFIELD, J.C.	1967
STEVENS, M.R.	1980
WILLIAMS, G.J.	1974: see p104

I-J

KAPOWAIINTRODUCTION

Three small mines in the Kapowai area (Kapowai, Welcome Jack and Big Beetle) produced 192,000 grams (6,153 ounces) of bullion from 5,786 tonnes of quartz between 1899 and 1933.

In the late 1960's ASARCO (reported in Neilson, 1968) investigated the area for possible low grade bulk tonnage prospects but were unable to find any favourable areas. AMOCO are presently investigating the area but results from their work are not available.

GEOLOGY

The rocks of the Kapowai area consist of Whitianga Group rhyolite flows, tuffs and agglomerates (Fig. I-J-1).

HYDROTHERMAL ALTERATION

Neilson (1968) noted that various zones of silicification (Fig. I-J-1) occur in the rhyolite tuffs, whereas the flow rocks are generally unaltered.

MINERALISATION

According to Bell & Fraser (1912) gold mineralisation in the Kapowai Mine was confined to small pipes and segregated veins in an east-west trending, southward dipping, zone of silicified rhyolite tuff. The footwall of the zone is fairly well defined and dips at angles less than 45° but the hanging wall portion merges gradually into unsilicified altered rhyolite tuff. The width of the zone is described only as "wide". The largest pipe, O'Connors, had maximum horizontal dimensions of 15m x 9m and was followed vertically for 21m to near surface where it split into a number of branches.

Bell & Fraser also describe a small easterly dipping pipe with a maximum diameter of 3.7m which was stoped vertically for 17m, and a 75cm wide "cross-reef" which was stoped vertically for 46m. These authors noted that the lensoidal

Figure I-J-1: Geology of the Kapowai area and plan of the Kapowai Mine (after Neilsen, 1968).

pipes were erratic and there was no feature in the surrounding rock to indicate where they might occur.

In the Welcome Jack Mine, gold mineralisation occurred in a 20cm wide quartz vein striking 092° and dipping steeply to the south. The vein is in rhyolite flow rocks and was mined from two levels. The ore shoot was approximately 60m long in the upper level but wedged out with depth and became non-payable approximately midway between the two levels.

GENESIS

The occurrence of gold mineralisation in pipes at the Kapowai Mine suggests that, like some other deposits in rhyolite pyroclastic rocks (e.g. Broken Hills and the Bluffs section of Neavesville), electrum deposition may have been linked with processes of boiling and hydraulic brecciation.

REFERENCES AND BIBLIOGRAPHY

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DOWNEY, J.F.	1935: see pp 192, 193 and 289
NEILSEN, K.I.	1968
SCHOFIELD, J.C.	1967
WILLIAMS, G.J.	1974: see pp 122- 123

I-K

BROKEN HILLSINTRODUCTION

A number of small gold deposits occur in Whitianga Group rhyolite rocks of the Broken Hills area. The bulk of the mining activity was confined to the period 1895 - 1913. Downey (1935) recorded that up to 1935, 1.7 million grams (55,199 ounces) of bullion were recovered from 40,015 tonnes of quartz. The Broken Hills Mine accounted for nearly all of this production: 1.6 million grams (51,012 ounces) compared with 114,000 grams (3,671 ounces) from Golden Hills and 16,000 grams (516 ounces) from various other mines in the area.

The Broken Hills mineralisation was investigated by a Newmont - Minzimp (ICI) joint venture reported by Utting & Adamson (1974) and more recently by a Minzimp - Watties joint venture who drilled a 300m hole to test the continuation of the mineralisation into the andesite underlying the rhyolites. Information on the latter work is not available.

The geology and mineralisation of the Broken Hills area were recently described by Moore (1976, 1979b).

GEOLOGY

The geology of the Broken Hills area is illustrated in Fig. I-K-1. In the vicinity of the Broken Hills Mine flow banded rhyolite (Minden Rhyolite Subgroup) is overlain by rhyolite pyroclastics (Coroglen Subgroup), capped by several sinters. Three breccia pipes occur, two are intersected in the mine and the third is seen in surface exposure only (Moore, 1976). The largest breccia pipe (10m in diameter in 2 level) is represented by "cave" stopes in 2, 3 and 4 levels (Fig. I-K-2) and is believed to commence in the flow banded rhyolite of 4 level (Moore, 1976). A smaller pipe is found in 2 and 3 levels near their eastern portals.

HYDROTHERMAL ALTERATION

The hydrothermal alteration of the pyroclastics is

Figure I-K-1: Geology of the Broken Hills area. (From Fig. 1 of Moore, 1979b.)

Figure I-K-2: Diagrammatic cross-section of the Broken Hills Mine. Detailed mine plans were given by Utting & Adamson (1974) and Moore (1976).

Figure I-K-3: Plan of the veins in low levels of the Broken Hills Mine (after Bell & Fraser, 1912).

generally in the form of silicification although argillic alteration occurs in various pug veins, pumice clasts, and small breccia pipes in and above 2 level (Moore, 1976). In contrast, the predominant alteration type in the flow banded rhyolite is argillic. Moore (1976) described the clay mineralogy of the argillic alteration as sericite (illite and illite-montmorillonite complexes) with minor kaolinite and amorphous clays.

Adularia occurs in the wall rocks adjacent to the veins and may record an early quartz - sericite - adularia stage of alteration which was later overprinted by argillic alteration.

MINERALISATION

A cross section of the Broken Hills mine is illustrated in Fig. I-K-2 and a plan of the veins encountered during mining in the lower levels (e.g. Battery Level) is shown in Fig. I-K-3.

Mineralisation occurred in breccia pipes (described in the geology section), siliceous zones and quartz veins. Only the latter proved economically important and of the various veins mined No. 1, Night, Blucher and Western were the main producers of gold.

The veins strike approximately north-south and dip at high angles to the west. Bell & Fraser (1912) noted that they characteristically contained chalcedonic quartz and wall rock breccia and seldom exceeded a thickness of 2.4m. Slickensided selvages with puggy material and quartzose crusts along the vein-walls were common. The vein ore was mainly confined to shoots occurring in the zone shown in Fig. I-K-3. Within the shoots the richest ore occurred at the intersection of the main reefs with flinty stringers (particularly the one known as Siever's Leader), at marked bends in the reefs themselves, or at the localities where the reefs joined.

Battery Level has collapsed not far from the portal and therefore Moore's study of mineralisation in the underground workings was confined to the upper levels where only the

	Stage 1	Stage 2	Stage 3
Quartz	13950	-----	
Pyrite	13951	-----	
(AuAg) ₁₁ AsSeS ₆	-----		
Cerargyrite	---		
(AuAg) ₁₃ AsSe ₃ S ₅		-----	
Aguilarite	---	-----	
Naumannite/ aquilarite		---	
Electrum	-----	-----	
AuAg ₃ (SeS) ₂		-----	
Native Silver			---
Trechmannite	---		
Acanthite			---
Barite			?-
Amorphous clay		-----	

Figure I-K-4: Paragenetic sequence of minerals determined by Moore (1976, Fig.19) from the large breccia pipe, Broken Hills Mine.

breccia pipes and parts of Bluchers Reef and Siever's Leader are accessible.

Visible mineralisation is rare as the grain size is generally finer than 50 micrometers and often submicroscopic. The paragenetic diagram shown in Fig. I-K-4 is after Fig. 79 of Moore (1976) and represents the mineralisation found in thin quartz and pug veins in and surrounding the large breccia pipe. Pyrite, electrum and a number of gold-silver sulphosalts are present. Blucher's Reef contains electrum and an acanthite-aguilarite intergrowth. The gangue minerals are quartz, barite and clays. The quartz is mostly chalcedonic, however finely crystalline quartz occurs in veins around the breccia pipe and crystals up to 10mm long were collected by the writer from vugs in 2 level (Fig. I-K-5).

FLUID INCLUSIONS

The locations of two samples of vug quartz collected by the writer from 2 level of the Broken Hills Mine are shown in Fig. I-K-5 and their position in Moore's paragenetic scheme is shown in Fig. I-K-4.

Large primary inclusions are common in both samples. Normal, vapour rich and vapour filled (Fig. 6-8) types are present, the latter types indicating that the hydrothermal fluid was boiling at the time of mineral deposition.

Filling temperatures and salinity histograms for apparently normal type inclusions are presented in Fig. I-K-6. Because of a boiling fluid regime no pressure correction is required for the filling temperatures. Allowing for the possibility that some of the higher filling temperatures may result from inclusions which trapped small quantities of vapour, a temperature of 240°C is selected as representative of the depositional temperature.

DEPTH OF MINERALISATION

The presence of sinter or siliceous sediment deposits and the evidence of boiling of the hydrothermal fluid at 2

Figure I-K-5: Plan of 2 level Broken Hills Mine, showing locations of quartz samples studied.

Figure I-K-6: Histograms of filling temperatures and apparent salinities for primary fluid inclusions in samples of quartz from the locations shown in Fig. I-K-5 (the individual measurements are listed in Appendix III). In addition to normal liquid-vapour inclusions, both samples contain vapour rich and vapour filled inclusions (Fig. 6-8) indicating that the hydrothermal fluid was boiling at the time of quartz deposition.

Figure I-K-7: Diagrammatic reconstruction of the depth relations at the Broken Hills Mine at the time of mineralisation. The position of the surface datum is based on the presence of boiling at 2 level, under hydrostatic pressure conditions.

level give some control in the reconstruction of the depth of mineralisation. In the scheme illustrated in Fig. I-K-7, boiling in 2 level is assumed to have been under hydrostatic pressure conditions.

THERMOCHEMISTRY

The geochemical environment of the Broken Hills mineralisation is shown in the fS_2 - fO_2 diagram (Fig. I-K-8). The environment is limited by the presence of pyrite but absence of pyrrhotite, magnetite, hematite and bornite. The latter may not be significant because chalcopyrite is also not present.

Log fS_2 values of -11 and -11.4 were calculated from the mole fraction of silver in electrum from Siever's Leader and the Breccia pipe in 2 level, respectively (the electrum analyses were reported by Moore, 1976). A value of -11 is chosen to represent the mineralisation.

The occurrence of sericite with minor adularia in the wall rocks indicates that the fluid pH was about 6.1 (equivalent to the pH of the sericite/K-feldspar boundary).

Contours of $\log m \leq S$ (Fig. I-K-8) at pH = 6.1 indicate that the concentration of total sulphur in solution was around 0.001m ($\log m \leq S = -3$), limiting $\log fO_2$ between approximately -36 and -38.

An fO_2 versus pH diagram, constructed for a $m \leq S$ of 0.001m, is shown in Fig. I-K-9. The $\log fS_2 = -11$ contour and stability field of barite are also included on the diagram. The mineralisation plots on the oxidised sulphur species/reduced sulphur species boundary as shown by the shaded area in Fig. I-K-9.

GENESIS

Breccia Pipe

Moore (1979b) considered that the large breccia pipe was

Figure I-K-8: f_{S_2} versus f_{O_2} diagram at 240°C showing the geochemical environment (shaded) of gold-silver ($\frac{1}{2}$ barite) mineralisation in quartz veins of the Broken Hills Mine. $\Sigma S = 0.001M$, $pH = 6.1$, log f_{S_2} from electron compositions = -11.0 to -11.4. (Methods of construction are described in Appendix V.)

Figure I-K-9: f_{O_2} versus pH diagram at 240°C and $\pm S=0.001m$ showing the geochemical environment (shaded) of gold-silver ($\pm$ barite) mineralisation in quartz veins of the Broken Hills Mine. $\bar{I} = 0.15$, $mK^+ = 0.023$, $pH \approx 6$, $\log f_{S_2}$ from electrum compositions = -11.0 to -11.4 , mBa^{2+} (estimated) = 0.0001 and $\log f_{CO_2}$ (estimated) = $+1.5$. (See Appendix V for methods of construction.)

formed sometime after the vein system, by either a process of hydraulic brecciation or by a hydrothermal explosion event. He suggested that the gold and silver were transported in the hydrothermal fluid as sulphide complexes. Gold and silver deposition occurred where the complexes became unstable as a result of boiling (with concomitant loss of H_2S) and oxidation (c.f. Fig. I-K-9).

Veins

The presence of barite in some of the accessible veins suggests that precious metal deposition in these locations may have also been a result of oxidation of hydrothermal fluids carrying the metals as sulphide complexes. Samples suitable for fluid inclusion study were unobtainable and therefore it is not known whether the hydrothermal fluid in the veins was boiling, although the occurrence of mineralisation at vein intersections is suggestive of pressure release situations possibly with associated boiling. Moore (1979b) considered that part of the vein system (the ore zone) represents a fault bounded breccia zone which acted as an aquifer for surface waters. Mixing of surface waters with the hydrothermal solution may have promoted oxidation of the metal carrying sulphide complexes (Moore, 1976; 1979b).

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WILLIAMS, G.J.	1974: see p123

TAPU - THAMESINTRODUCTION

Although the mines between Tapu and Thames produced only small quantities of precious metals they are notable for their unique (relative to the other mineralisations in Great Barrier Island and the Coromandel Peninsula) type of mineralisation, characterised by a variety of gold and silver telluride minerals.

The major mines were the Sylvia (3.8 million grams or 123,750 ounces of bullion) and Monowai (1.2 million grams or 38,637 ounces of bullion), together accounting for 77% of the areas bullion production.

The period of intense mining ceased about 1914 although detailed prospecting of the Sylvia Reef including drilling and shafting was carried out between 1935 and 1945 (reported in Williams, 1974). In 1960 South Seas Mining drilled a 230m diamond drillhole on the Sylvia Reef and in the early 1970's Central Pacific Minerals (N.Z.) Ltd drilled several holes on the Monowai Reef. Recently, AMOCO Minerals N.Z. Ltd have identified centres of porphyry mineralisation in the area (Merchant, 1978) and drilled the largest centre in Ohio Creek.

GEOLOGY

The geology of the Tapu - Thames area is shown in Fig. I-L-1. Jurassic greywacke basement rocks (Manāia Hill Group) have limited outcrop on the coast at Rocky Point (north of Tararu) and in Tapu River less than 1km from the coast. They are unconformably overlain by Miocene - Lower Pliocene volcanic rocks of the Coromandel Group.

The oldest rocks of the Coromandel Group in the Tapu - Thames area are a sequence of rhyolite flows and pyroclastics. These are followed by more typical Coromandel Group andesite and dacite flows and pyroclastics.

Hypabyssal quartz diorite and dacite porphyry stocks (Tainui Intrusives) intrude the andesites and dacites and were considered by Merchant to occur associated with circular geomorphic features

	Alluvium	
	Rhyolite pyroclastics of the LOOKOUT ROCKS	WHITIANGA GROUP
	Quartz diorite and dacite porphyries of the TAINUI PLUTONICS	COROMANDEL GROUP
	Andesite and dacite flows, and pyroclastics	
	Greywacke and argillite	MANAIA HILL GROUP
	Quartz vein	
	Pebble dike	
	Fault	
	Mine	

Figure I-L-1: Geology of the Tapu-Thames area (after Merchant, 1978).

interpreted as caldera collapse structures.

The youngest rocks of the area are the Lookout Rocks, a series of rhyolite pyroclastics, which Merchant (1978) correlated with the Whitianga Group. He also noted the occurrence of rhyolite tuffs in Tararu Stream.

K - Ar AGE DATA

Dr C.J.D. Adams, Dr R.J. Merchant and Ms J.E. Gabites (pers. comm.) determined K - Ar ages between 9.5 and 11.9 m.y. for Coromandel Group andesites of the Tapu - Thames area, whereas the K - Ar ages they measured in members of the Tainui Intrusives, with the exception of one age of 19.9 m.y., ranged from 9.3 to 12.6 m.y. The 19.9 m.y. age was determined in a sample of quartz diorite porphyry from Tararu Valley and appears spurious in relation to the other ages because it seems to indicate that the porphyry is much older than the other Coromandel Group rocks that it intrudes. However, an alternative explanation, is that, the ages represent two periods of volcanic-intrusive activity, one at c.a. 20 m.y. and the other at 12-9 m.y. The older volcanic rocks have either not been sampled or have been imprinted with a younger K - Ar age due to hydrothermal alteration.

HYDROTHERMAL ALTERATION

Merchant (1978) classified the hydrothermal alteration in rocks of the Tapu - Thames Coromandel Group and Tainui Intrusives into the following five groups, in order of increasing intensity of alteration:

1. Weak propylitic; chlorite, calcite, epidote, secondary albite, secondary quartz, sericite, pyrite, zeolite and montmorillonite.
2. Advanced propylitic; pyrite, calcite, chlorite, epidote, secondary albite, secondary quartz and sericite.
3. Argillic; sericite, pyrite, quartz, kaolinite and chlorite.
4. Quartz - sericite; quartz, sericite and pyrite.
5. Alkali silicate; biotite, magnetite and secondary albite.

In contrast, hydrothermal alteration of the rhyolite pyroclastics, sediments and breccia pipes of the Lookout Rocks was described as intermediate argillic (dickite, quartz and

TABLE I-L-1: Minerals identified by Merchant (1978) from veins in the Tapu-Thames area. The table was compiled by the writer from Merchant's text description and follows his paragenetic scheme.

Stage	Sylvia Vein	Monowai Vein	Other Veins
Mo	molybdenite anhydrite (tungsten?)		
Cu-Bi	galena, native gold, chalcopryrite, pyrite, rutile, seleniferous tellurobismutite, sphalerite.	seleniferous tetradymite, aikinite, tetrahedrite pyrite, chalcopryrite	chalcopryrite, pyrite sphalerite, argentian tetrahedrite, rutile, pyrrhotite, kobellite, arsenopryrite.
Pb-Zn	galena - sphalerite pyrite, chalcopryrite tellurides: hessite, sylvanite, altaite, nagyrte, tellurobis- mutite gold	galena - sphalerite, tellurides: hessite, stutzite, sylvanite, altaite petzite	galena - sphalerite, tellurides as Monowai except for petzite
Pb-Au	galena, electrum, marcasite	"suspected" but not encountered	galena, electrum, marcasite
Cu-Sb		tetrahedrite, chalcopryrite chalcostibite	
Gold - Pyrargyrite	electrum (pyrargyrite? pyrite?)		Norfolk Mine: electrum, pyrargyrite, polybasite, marcasite, chalcopryrite, pyrite, anatase, stephanite, miargyrite, galena
Stibnite - Barite	carbonates (manganoandolomite, black calcite)	barite	barite or carbonates (occur separately) carbonates: Watchman Mine = calcic rhodochrosite, Paroquet = black calcite, Dunedin = rhodonite and Mn carbonate

pyrite) and advanced argillic (natroalunite - quartz assemblage with specular hematite, barite, kaolinite and rare pyrite, or a pyrophyllite - dickite assemblage).

Some members of the Tainui Intrusives have also been altered to an advanced argillic assemblage (pyrophyllite, dickite, diaspore and quartz).

MINERALISATION

Several quartz veins containing precious and base metal mineralisation occur in the Coromandel Group andesites between Tapu and Thames. These include the Zeehan, Paroquet, Monowai, Colorado (Comstock), Vulcan, Sylvia, Norfolk and Watchman (Fig. I-L-1). Base metals predominate, with pyrite, chalcopyrite, sphalerite and galena being the most common metallic minerals although the area is characterised by the occurrence of gold, silver and bismuth tellurides. In contrast to the gold mines at Thames and Coromandel their Au:Ag ratios are generally low (typically 1:4).

Table I-L-1 lists the minerals described from the Tapu - Thames area by Merchant (1978), grouping them into the various paragenetic stages deduced by him. Merchant's (1978) paragenetic diagram is reproduced in Fig. I-L-2.

Recently, attention has been given to molybdenite mineralisation, originally noted by Allen (1899), and its significance to porphyry style mineralisation. In recent geochemical exploration work, AMOCO Minerals Ltd identified five centres of molybdenite mineralisation; in the Waiomu, Puru, Pohue and Ohio Creek areas (Fig. I-L-3).

The Ohio Creek and Puru mineralisations were described by Merchant (1978). Molybdenite occurs in the quartz diorite porphyry country rocks in the following four settings: (a) as paint on joint faces, (b) with pyrite, magnetite, rutile, hematite, chalcopyrite sphalerite and tetrahedrite in quartz veins up to 30mm thick, (c) in thin quartz veinlets in stockwork patterns and (d) disseminated in the quartz sericite altered rock. The pyrite contains inclusions of rutile, hematite and pyrrhotite. Merchant's paragenesis for this

Figure I-L-2: Paragenetic sequence inferred by Merchant (1978, Fig. 2-12) for vein mineralisation in the Tapu-Thames (and Thames) area.

Figure I-L-3: Location of porphyry copper prospects, in the Tapu-Thames area, at present being investigated by AMOCO Minerals (N.Z.) Ltd. (Compiled from text and figures of Merchant, 1978.)

QUARTZ	_____
SERICITE	_____
MOLYBDENITE	_____
PYRRHOTITE	_____
PYRITE	_____
HEMATITE	_____
RUTILE	_____
CHALCOPYRITE	_____
TETRAHEDRITE	_____
MAGNETITE	_____
SPHALERITE	_____

Figure I-L-4: Paragenetic sequence inferred by Merchant (1978, Fig. 2-11) for quartz-sericite zones of porphyry systems in the Tapu-Thames area.

mineralisation is shown in Fig. I-L-4.

Drilling by AMOCO at Ohio Creek revealed the mineralisation at depth to be pyrite and chalcopyrite with minor gold, but only trace molybdenum, in the geochemical analyses of drill core.

FLUID INCLUSIONS

Merchant (1978) studied fluid inclusions in samples of quartz, sphalerite, barite and ankerite from the Tapu - Thames area. The inclusions are generally normal two phase liquid plus vapour types, but vapour rich and vapour filled types also occur in many samples of the high temperature mineralisation (Cu - Bi stage only?) indicating that the inclusions were trapped from boiling fluid.

Merchant determined fluid inclusion filling temperatures ranging from 95°C (barite, Zeehan Reef) to 435°C (quartz, Kaiser Reef)*. He grouped his analyses on several histograms and correlated their various peaks with individual stages in his assigned paragenesis as follows:

Cu - Bi; 360 - 410°C (periods of boiling)
 Pb - Zn; 230 - 320°C
 Pb - Au; 282 - 315°C

The minimum temperature of gold - pyrrargyrite mineralisation was considered to be indicated by a sample of quartz from the Norfolk Reef (Tararu) containing fluid inclusions with filling temperatures between 190 and 200°C. Temperature ranges for predominant gold-pyrrargyrite and stibnite - barite mineralisation were defined as 215 - 238°C and 200 - 260°C respectively by filling temperatures of inclusions in barite from the Thames area, discussed in a later section (I-M).

Merchant investigated the freezing temperatures of some fluid inclusions and presented his results graphically. It

FOOTNOTE: * Merchant records temperatures as 105 - 445°C in his Tables 4-1 and 4-3 but these have an additional 10°C pressure correction.

TABLE I-L-2: $\delta^{34}\text{S}$ values of minerals and temperatures calculated from the fractionation of sphalerite - galena pairs in samples from the Tapu - Thames area. All values are of unpublished analyses by Dr. B.W. Robinson.

I.N.S. Sample number	Location	Mineral				Chalco- pyrite	Galena	Δ Sp-gn	Sp-gn Temperature °C
		Barite	Pyrite	Sphalerite					
5549/1a-d	Sylvia Mine 3L		+1.7	+1.4	+0.8	-0.6	2.0	315	
5513/10 a-b	Sylvia Mine 3L			+2.0		-1.3	3.3	190	
5549/2a-d	Sylvia Mine 4L		+1.6	+0.8	+1.1	-1.3	2.1	305	
5549/3A	Stokes 1 L dump		+2.9	+2.0	+1.9				
5549/3B	"		+1.5	+1.7					
5549/3C	"		+1.9	+1.4		-0.8	2.2	290	
5513/9a-c	"			+1.8	+1.4	+0.3	1.5	410	
5549/5A	Stokes Reef 2L		+1.9	+1.5	+1.7				
5549/5B	"		+1.8	+1.7	+1.7				
5549/10A	" 3L		+2.1	+1.4	+1.7	-0.5	1.9	335	
5513/5b-d	"			+1.1	+1.2	+0.3	0.8	> 500	
5549/4A,B	Kaiser Mine Top L dump		+3.6		+3.0				
5549/11	"		+2.1						
5549/20	"		+1.0						
5513/12a-b	Kaiser Reef		+3.0		+2.3				
5549/6A	Zeehan Mine 5L			+1.9	+2.6	-0.1	2.0	315	
5549/6B	"			+1.6		+0.3	1.6	390	
5549/7A	" Pohue		+3.1	+1.8	+2.0	+0.3	1.5	410	
5549/8	"			+2.5	+2.7				
5549/9A,B	" dump		+0.8	+1.4	+2.1	+0.2	1.4	430	
5549/12	Monowai 3L		+2.3		+1.9				
5513/2	"	+24.7							
5513/11ab	"			+2.0		+0.9	1.1	> 500	

is apparent from his Fig. 4-6 that inclusions in samples from the Sylvia, Monowai and Kaiser veins had freezing temperatures in the range -0.9°C to -2.2°C corresponding to salinities of 1.6 to 3.7 eq. wt. % NaCl (for consistency with this thesis conversion data of Potter *et al* [1978] were used), whereas material from the biotite alteration zone in Ohio Creek range from -2.7 to -3.4°C corresponding to salinities of 4.5 to 5.5 eq. wt. % NaCl.

Merchant analysed the fluid inclusions in samples of quartz and barite by crushing the samples, leaching them with water and analysing the leachates by AAS and colorimetric methods. He combined the compositional data of some of the leaches with apparent salinity data from fluid inclusion freezing temperature studies to derive the chemical composition of the fluid inclusion waters.

The resulting analyses are dominated by Na^+ , Ca^{2+} , Cl^- and occasionally Li^+ . The concentration of Ca^{2+} exceeds that of K^+ in many analyses and is also higher than Na^+ in a few analyses. Li^+ concentrations are very high and in some analyses predominate over all other ions. Most Na/K ratios are around 2 although they average 3.0, with a range of 0.8 to 11 (33 samples).

The problems of contamination encountered in fluid inclusion analyses during this study (see Chapter 7) indicate that Merchant's analyses are probably also contaminated to varying degrees. His high Ca^{2+} and Li^+ concentrations are believed to be caused by contamination as are some of his high K^+ concentrations relative to Na^+ .

SULPHUR ISOTOPES

Unpublished sulphur isotope analyses by Dr B.W. Robinson of sulphides and barite from the Tapu - Thames area are listed in Table I-L-2. $\delta^{34}\text{S}$ values of the sulphides range from -3.1 per mil (pyrite) to +3.6 per mil (pyrite and sphalerite), whereas barite from Monowai 3 level has a $\delta^{34}\text{S}$ value of +24.7 per mil.

TABLE I-L-3: General thermochemical parameters for the depositional environments of Merchant's (1978) Cu-Bi and Pb-Zn associations in the quartz veins between Tapu and Thames (mainly the Sylvia and Monowai veins).

	Stage		Reference
	Cu-Bi	Pb-Zn	
Temperature °C	400 (fluid boiling)	280	Table V-1
True ionic strength	0.07	0.39	"
Salinity (m NaCl eq.)	0.34	0.55	"
mK^+	0.094	0.095	"
pH	5.0	5.0	See text
pH of kaolinite/sericite boundary	4.2	4.1	Table V-1
pH of sericite/K-feldspar boundary	5.6	5.6	"
Total S ($\log m\pm S$)	-1.3to-2.0	-2.0	See text
$\log fS_2$ (sphalerite comp.)	-4.4to-4.6	-7.3to-9.8	Table V-4B
$\log fO_2$	-24to-28 (Fig.I-L-5)	-33.3to-35.5 (Fig.I-L-7)	Figures cited
$\log fCO_2$	+1.5	+1.5	Table V-1

Temperatures calculated by fractionation between cogenetic pairs of sphalerite and galena range from 170 to 500°C (sample R5513/5c-d with $\Delta_{\text{sp-gn}} = 0.8$ per mil disregarded). The average fractionation of 1.8 per mil is equivalent to a depositional temperature of 350°C.

THERMOCHEMISTRY

Porphyry Mineralisation

Merchant observed a zonation (time, temperature or both) of pyrrhotite - pyrite (earliest or highest temperature), magnetite - pyrite and hematite - pyrite in the porphyry mineralisation. He considered that the changing mineralogy could be explained simply by deposition at decreasing temperatures from a fluid with constant $f\text{O}_2$ and $f\text{S}_2$. Alternatively $f\text{O}_2$ and $f\text{S}_2$ may have changed making the situation more complex.

His suggested parameters for the porphyry mineralisation, at a temperature of 350°C, were $\log m \leq S = -1$ to -2 , $\text{pH} = 3.2$ to 5.2 , $\log f\text{O}_2 = -25.4$ and $\log f\text{S}_2 = -5.8$.

Vein Mineralisations

$f\text{S}_2$ versus $f\text{O}_2$ and $f\text{O}_2$ versus pH diagrams were not calculated by Merchant (1978) for the vein type mineralisations and therefore two of his mineral associations, Cu - Bi and Pb - Zn, are modelled here. Additionally the gold - pyrrargyrite association is modelled in the Thames section (I-M). These particular associations were chosen because both temperatures (from fluid inclusions and sulphur isotopes) and sulphur fugacities (from sphalerite and electrum compositions) are known, whereas one or both are unknown for the other mineral associations.

Table I-L-3 lists various parameters for the geochemical environments of the Cu - Bi and Pb - Zn mineralisations. $f\text{S}_2$ values, derived from wt % Fe in sphalerites, presented in Table I-L-3 differ from those given by Merchant because of the different method of calculation and also because only specific temperatures are considered here, whereas Merchant listed values for ranges of temperatures.

Figure I-L-5: fS_2 versus fO_2 diagram at 400°C showing the geochemical environment (shaded) proposed here for Cu-Bi mineralisation described by Merchant (1978) from the veins in the Tapu-Thames (and Thames) area. Most assemblages of this stage contain pyrite, chalcopyrite and sphalerite and plot near the upper end (high fS_2) of the shaded area, however pyrrhotite and arsenopyrite are present in some assemblages indicating that the latter were deposited in an environment represented by the lower end (low fS_2) of the shaded area. (See Table I-L-3 for relevant thermochemical parameters and Appendix V for details of construction.)

Cu - Bi Mineralisation

An fS_2 versus fO_2 diagram, constructed for a temperature of 400°C to represent Cu - Bi mineralisation, is presented in Fig. I-L-5.

A comparison with other high temperature mineralisations suggests that the concentration of total sulphur in solution during mineralisation was probably around $0.01m$ but may have been as high as $0.05m$ ($\log m \leq S$ values of -2 to -1.3 respectively). Contours of $\log m H_2S$, approximately equivalent to $\log m \leq S$ in the pyrrhotite and pyrite plus chalcopyrite fields, are plotted in Fig. I-L-5.

On the basis of the textures observed in a sample from the Dunedin Reef, Tararu Valley, Merchant (1978) considered that the earliest mineralisation of the Cu - Bi association was pyrrhotite followed by arsenopyrite and then later pyrite + chalcopyrite + tetrahedrite + various other minerals of the association. Sphalerites in the latter indicate $\log fS_2$ values of -4.4 to -4.6 , at 400°C , whereas $\log fS_2$ must be lower than -6.5 for arsenopyrite stability and lower than -7.2 for pyrrhotite to be stable. Therefore, as Merchant suggested, the depositional sequence pyrrhotite, arsenopyrite, pyrite plus chalcopyrite at constant or slightly decreasing temperature indicates increasing fS_2 . The resulting range of Cu - Bi mineralisation in Fig. I-L-5 is shown by the shaded area. If the increase in fS_2 is achieved within the ranges of $\log m \leq S$ values suggested previously, a range in $\log fO_2$ of approximately -28 to -24 is indicated.

In conclusion it is suggested that because the early pyrrhotite and subsequent arsenopyrite mineralisations are rare the more typical conditions of deposition of Cu - Bi mineralisation are characterised by $\log fS_2$ values around -4.5 and $\log fO_2$ values around -24 .

Pb - Zn Mineralisation

The stability of the Pb - Zn mineralisation of the Thames - Tapu deposits is limited on the fS_2 versus fO_2 diagram (Fig.

Figure I-L-6: fS_2 versus fO_2 diagram at 280°C showing broad limits of stability (before consideration of the concentration of total sulphur in solution) proposed here for Pb-Zn mineralisation identified by Merchant (1978) from veins in the Tapu-Thames (and Thames) area. (See Table I-L-3 for relevant thermochemical parameters and Appendix V for methods of construction.)

I-L-6) by the presence of pyrite and chalcopyrite but absence of pyrrhotite, magnetite, hematite and bornite. Merchant's sphalerite analyses indicate $\log fS_2$ values ranging from -7.3 to -9.8.

A $\log fO_2$ versus pH diagram constructed for a total sulphur in solution concentration of 0.01m ($\log m \leq S = -2$) is presented in Fig. I-L-7.

Merchant considered that sericite commonly accompanies Pb - Zn mineralisation, whereas kaolinite and K-feldspar are absent. Therefore a pH of 4.9 is considered representative.

The field of probable mineral deposition is shown by the shaded area in Fig. I-L-7. Deposition was from a fluid containing sulphur predominantly or almost exclusively as H_2S . Deposition from a fluid with sulphur predominantly as SO_4^{2-} , at a pH of around 4.9, is precluded by the sphalerite compositions.

$\log fO_2$ values ranging from approximately -35.5 to -33.3 are indicated and CO_2 concentrations up to $\log fCO_2 = +1.5$ are possible with the absence of graphite.

The Tapu - Thames Pb - Zn mineralisation is defined on the fTe_2 versus fS_2 (Fig. I-L-8) and fO_2 versus $m \leq Te$ (Fig. 11-4) diagrams by the presence of hessite and altaite. Relatively high values of fTe_2 and $m \leq Te$ are indicated.

GENESIS

Merchant (1978) considered that the porphyry style and base metal vein type mineralisations between Tapu and Thames were "manifestations of a high level porphyry molybdenum deposit which formed at a depth of approximately 2 km in a greywacke dacite - andesite pile" (Merchant, 1978 p2). He suggested the following sequence of events:

1. Greywacke basement rocks intruded by quartz diorite pluton(s?) with associated subaerial andesite volcanism	}	Lower to Mid Miocene

Figure I-L-7: f_{O_2} versus pH diagram at 280°C and $a_S = 0.01m$ showing the geochemical environment (shaded) of Pb-Zn mineralisation in the Tapu-Thames (and Thames) veins. (See Table I-L-3 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-L-8: f_{Te_2} versus f_{S_2} diagram at 280°C showing the geochemical environment (shaded) of Tapu-Thames Pb-Zn assemblages containing hessite. Some assemblages also contain altaite (+ electrum?) and were formed either at lower values of f_{S_2} than indicated by the sphalerite compositions or at high values of f_{Te_2} . Because calaverite is apparently absent from these assemblages (although reported in float by Randohr, 1980) the electrum/calaverite boundary must occur at higher f_{Te_2} than the gold/calaverite boundary shown, to allow altaite precipitation without calaverite at log f_{S_2} values around -9.6.

2. Emplacement of molybdenum ore shells at shallow depths (2km)

3. Formation of distal pyrite - magnetite and pyrite - hematite haloes

4. Deposition of base metals and quartz in fissures above the ore shell in the order of Cu - Bi mineralisation followed by Pb - Zn - tellurides mineralisation at depths of 1.5km and 1.5km or less respectively.

Mid to Upper
Miocene

The existence of Merchant's porphyry molybdenum deposits is disputed here. Recent drilling by AMOCO failed to locate more than trace Mo at depth although Cu and Au occur in cores. Also the tectonic environment is not favourable for the occurrence of a porphyry molybdenum deposit of the Colorado type (c.f. Westra & Keith, 1981). Instead the porphyry mineralisation is considered to be of the porphyry copper type.

Merchant recognised several circular features in the andesites of the Tapu - Thames area which were interpreted as caldera structures. Such structures may be unwelcome features for porphyry copper exploration if Sillitoe's (1980) hypothesis, that cauldron subsidence may promote vein mineralisation but inhibit porphyry copper formation, is correct. However, this theory would be consistent with the apparent absence of economic copper mineralisation at depth in the Tapu - Thames porphyry deposits.

The $\delta^{34}\text{S}$ value of barite from Monowai 3 level indicates that $\delta^{34}\text{S}_{\text{S}}$ in solution was approximately 0 per mil (Chapter 9) and therefore the sulphur in the vein deposits may have originated from a magmatic source.

Merchant (1978) suggested that some of the vein deposits may represent peripheral mineralisations to the porphyry copper deposits. His view is supported by the very high temperatures of the early Cu - Bi mineralisation. This stage may have been deposited by a hydrothermal fluid, partly magmatic, emanating from the porphyry environment. Dilution by deeply circulating meteoric water probably reduced the magmatic water component to an insignificant quantity by the time of Pb - Zn deposition.

From Merchant's description the Cu - Bi stage appears to have been characterised by boiling fluids and this factor may have been an important mechanism for mineral deposition. Merchant found no evidence for boiling during Pb - Zn mineralisation, however, a wide range in fS_2 is indicated by the compositions of sphalerites and may be a clue to the reasons for mineralisation. One possible mechanism might be fluctuations in H_2S concentrations caused by periodic influxes and condensations of H_2S vapour evolved from lower (Cu - Bi) boiling horizons. If such a mechanism operated, deposition of sulphides would occur from chloride complexed metals in solution during influxes of H_2S . Alternatively, or during other periods, fluid - wall rock reactions may have been the main causes of mineral deposition.

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I-M

THAMESTHAMES SPECIAL AREA

Fraser's (1910) "Thames Special Area" roughly consists of a triangular shaped area of land with the Lookout Rocks as the apex, the Thames foreshore the base and Tararu Creek and part of Hape Creek, the northern and southern sides respectively (Fig. I-M-1). However, because the Sylvia, Day Dawn, Norfolk and Watchman Mines have mineralisations different to other mines of the Thames Special Area but similar to mines north of this area they are excluded from this section and discussed in the Tapu - Thames section. Therefore the northern boundary of the Thames area considered here is placed immediately north of the Waitangi Mine and Shellback Creek, rather than Tararu Creek (Fig. I-M-1).

INTRODUCTION

The Thames area, although only the third largest gold producing centre in the Coromandel Peninsula (69 million grams or 2.2 million ounces of Au and Ag bullion) is famous for its rich near surface bonanza deposits. Most of the gold and silver came from within 150m of the surface in a 80 hectare block.

Pockets of extremely gold rich ore, called bonanzas, were encountered in five localities:

Shotover (3.2 million grams or 102,000 ounces of bullion), Moanataiari (4.6 million grams or 148,000 ounces of bullion), Caledonian (8.6 million grams or 277,000 ounces of bullion), Cambria (1.8 million grams or 59,000 ounces of bullion) and Waiotahi (2.2 million grams or 70,000 ounces of bullion) One 2 tonne stope block from the Caledonian assayed approximately 56% gold, 16% silver and 28% quartz.

GEOLOGY

The geology of the Thames area is illustrated in Figs. I-M-2, I-M-3 and I-M-4. The rocks are predominantly andesites

- Shaft
- Y Adit
- Kuranui-Caledonian drill hole site
- ⊙ Victoria Companies drill hole site
- Boundary of Thames Area

Figure I-M-1: Location of some mines worked in the Thames area during the late 1800's. See Fig. I-L-1 for the relation between the Thames and Tapu-Thames areas as described here. (Map compiled from Fraser, 1910; Merchant, 1978.)

	Alluvium	
	Rhyolite pyroclastics of the LOOKOUT ROCKS	WHITIANGA GROUP
	Young andesite and dacite flows and pyroclastics.	
	Quartz diorite and dacite porphyries of the TAINUI PLUTONICS	
	Andesite flows of the PREMIER ANDESITE	COROMANDEL GROUP
	Andesite, dacite and minor rhyolite; flows and pyroclastics	
	Greywacke and argillite of the MANAIA HILL GROUP	
	Quartz vein	
	Fault	
	Line of Cross-section shown in Fig. I-M-3A	
	Line of Cross-section shown in Fig. I-M-3B	

Figure I-M-2: Geology of the Thames area. (Compiled from Fraser, 1910; Merchant, 1978.)

Figure I-M-3: NW-SE and SW-NE cross sections of the Thames area (see Fig. I-M-2 for locations). Note that different scales have been used. (Modified from Fraser, 1910; Merchant, 1978.)

Figure I-M-4: Drillhole log of the 1904 Kuranui-Caledonia drillhole (see Fig. I-M-1 for location). (From Fig. 1-2 of Merchant, 1978.)

of the Coromandel Group. Fraser (1910) distinguished two lithostratigraphic units; (a) a complex series of alternating andesite and dacite flows and breccias and associated dikes, hereafter termed the Tararu Andesite, and (b) a relatively uniform non-brecciated pyroxene andesite flow unit, which because it was host to approximately 90% of the gold and silver mineralisation, was named the Premier Andesite.

The 1904 Kuranui - Caledonian drillhole (located near the entrance to the Moanataiari Tunnel) provides the only detailed stratigraphic section through the field). Fraser (1910) described the down hole sequence as follows (bottom of hole depth 448m scaled off Fig. 1-2 of Merchant, 1978):

0 - 46m (-24m below m.s.l.) Premier Andesite	} (Coromandel Group)
46 - 378m (24 - 356m b.m.s.l.) Tararu Andesite	
378 - 470m (356 - 448?m b.m.s.l.) greywacke	(Manaia Hill Group)

Merchant (1978) investigated the drill core and compiled the column reproduced in Fig. I-M-4.

Two major north-west striking faults, the Moanataiari Fault and the Beach Slide, divide the Thames area into three blocks; the Back Block, Middle Block and Seaward Block (Fig. I-M-3). The Moanataiari Fault has a prominent surface expression for a considerable distance, and was located in several underground workings. It dips 45° to the west and has a vertical displacement progressively increasing southwards, estimated at 183m in Moanataiari Stream and 305m at Una Hill (Fraser, 1910).

The Victoria Companies drillhole, located 262m west of the "Old Big Pump Shaft", was drilled 341m into alluvium of the seaward block but failed to intersect hard rock, indicating a considerable throw on the Beach Slide.

HYDROTHERMAL ALTERATION

The andesites are hydrothermally altered to propylitic (chlorite, carbonate, sericite, epidote and pyrite) and argillic (sericite, pyrite, quartz, kaolinite and chlorite) assemblages.

The miners termed the weakly chloritically altered rock "hard bars", because of their greater resistance relative to the clay pyrite areas.

MINERALISATION

Mineralisation of the bonanza type generally occurred in stringers and stockworks associated with north-west trending cross reefs termed "flinties" (so called because of their fine grained siliceous nature) and at the intersection of these veins with older north-east trending crystalline quartz and chalcedonic reefs. The Hague-Smith and Moanataiari Cross Lode were notable exceptions to the NW and NE trends.

Dips on the veins were a minimum 45° and generally to the north, but at Una Hill dip direction is variable, and south of the Saxon Shaft in the Middle Block, dips to the south are common.

The quartz veins pinch and swell, varying in width from a few centimetres to "blows" of 9m, although the average width was approximately 1m.

Massive white chalcedonic quartz characterised the veins, but banded, crustiform, comby and vuggy textures also occurred. Veins were usually well defined and bounded by "puggy" clay. In some areas, generally in proximity to the major faults, hard bars and present land surface, the major veins bifurcated or branched considerably.

Mineralisation was predominantly pyrite, pyrargyrite and electrum although sphalerite, stibnite, arsenopyrite, chalcopryite, marcasite, enargite and cinnabar were also noted by Fraser (1910). In addition to this list, Merchant (1978) identified galena, several telluride minerals (hessite, sylvanite, stutzite, altaite, petzite and coloradoite), kobellite, tetrahedrite and bournonite from some of the mines. The major gangue minerals were quartz and barite although rare carbonates (identified as ankerite and dolomite by Merchant) were noted. The paragenesis is similar to the northern mines (Tapu - Thames c.f. Fig. I-L-2), however the relative abundance

of the stages is different with the gold - pyrrargyrite and barite - stibnite stages being almost overwhelmingly dominant in the Thames area.

FLUID INCLUSIONS

Merchant (1978) studied fluid inclusions in quartz, sphalerite and barite from several of the mineralisations in the Thames area. They are generally two phase liquid plus vapour normal types, but vapour rich and vapour filled types also occur in many samples from the high temperature mineralisations, indicating that the inclusions were trapped from a boiling fluid. Liquid CO_2 was identified in a few vapour rich inclusions in quartz from the Garbo Mine, Karaka Creek and individual samples of quartz from the Lucky Hit and Magnet Mines each contained a single inclusion with a spindle - shaped daughter mineral (these dissolved at the filling temperature and therefore differ from included minerals described in this thesis from other areas, see Chapter 6).

Merchant's (1978) visual estimate of the relative volumes of water, liquid CO_2 and vapour in the fluid inclusions from the Garbo Mine, when corrected for relative density, are used here to indicate a CO_2 concentration of around 20 mole %.

Merchant determined fluid inclusion filling temperatures ranging from 120°C (quartz, Halcyon low level) to 400°C (quartz, Halcyon low level and Atlantic 2 level) *. Filling temperatures of inclusions in barite from the Moanataiari Cross Lode ranged from $215 - 238^\circ\text{C}$ and were considered to represent gold - pyrrargyrite stage mineralisation, whereas inclusions in barite coexisting with stibnite in the Magnet Mine, representing stibnite - barite mineralisation, ranged from $200 - 260^\circ\text{C}$. Various samples from Thames, together with samples from the mines in the Tapu - Thames area, indicated temperature ranges of $360 - 410^\circ\text{C}$ and $230 - 320^\circ\text{C}$ for Cu - Bi and Pb - Zn stages respectively.

FOOTNOTE: * Merchant records temperatures of $130-410^\circ\text{C}$ in his Table 4-1 but these have an additional 10°C correction for pressure.

TABLE I-M-1: $\delta^{34}\text{S}$ values of minerals from the Thames area. All values are of unpublished analyses by Dr B.W. Robinson.

I.N.S. Sample Number	Location	Mineral				Stibnite
		Barite	Pyrite	Sphalerite	Chalcopyrite	
5513/4a,b	Kurānui Mine	+19.1				+2.6
5513/7b	Reuben Parr					+2.8
5513/8a,b	Moanataiari 3L	+17.2				+2.3
5513/3 & 13	Halcyon Mine	+19.7	-2.6			
5513/15a,b	Log Drive Creek		+2.8	+0.1		
5513/14a,b	Climax Creek		+2.8		+1.7	
5513/14-2	Climax Creek					
5513/16a-c	Wood Creek		+2.2		+2.3	
5513/1	Magnet Mine	+21.3	+1.0	+3.6		

Freezing temperatures of fluid inclusions in samples representing Pb - Zn mineralisation of the Shellback, Atlantic, Waiotahi - Cambria and Lucky Hit veins range from approximately -1.1 to -1.8°C (read off Merchants Fig. 4-6) corresponding to a salinity range of 1.9 to 3.0 eq. wt. % NaCl (using the conversion data of Potter et al, 1978).

Merchant (1978) analysed the fluid inclusions in samples of quartz, barite and calcite by crushing the samples, leaching them with water and analysing the leaches by AAS and colorimetric methods. He combined the compositional data of some of the leaches with apparent salinity data from the fluid inclusion freezing temperature studies to derive the chemical composition of the fluid inclusion waters.

Like the analyses of material from the Tapu - Thames area the resulting analyses were dominated by Na^+ , Ca^{2+} , Cl^- and Li^+ . Most Na/K ratios were around 2 although they averaged 4.4 and range from 1.3 to 37 (23 analyses). The concentration of sulphate in some analyses was equal to chloride but Merchant acknowledges that some contamination may have occurred from sulphide minerals.

The writer considers that the high concentrations of several elements in Merchant's analyses, particularly Ca^{2+} , and Li^+ are also due to contamination (c.f. Chapter 7). This may account for the generally low Na/K ratios exhibited by Merchant's analyses.

SULPHUR ISOTOPES

Unpublished sulphur isotope analyses by B.W. Robinson of sulphides and barite from the Thames area are listed in Table I-M-1.

$\delta^{34}\text{S}$ values of the sulphides range from -2.6 per mil (pyrite) to $+2.8$ per mil (pyrite and stibnite), whereas the barites range from $+17.2$ per mil to $+21.3$ per mil.

Although the absence of galena analyses limits the application of sulphur isotope geothermometry, fractionation between a pyrite - chalcopyrite pair from Climax Creek (sample

Figure I-M-5: fS_2 versus fO_2 diagram at 230°C showing the stability relations of some minerals deposited during Merchant's (1978) gold-pyrargyrite stage of the Thames vein deposits. The predominant assemblage appears to be pyrite + electrum + pyrrhotite, represented by the star, however, some assemblages also contain stibnite and were deposited at lower values of fO_2 (and higher values of mS), to the left of the stibnite/kermesite boundary, whereas others contain arsenopyrite and were deposited at lower values of fS_2 , below the arsenopyrite/pyrite + arsenic boundary. $\Sigma S \approx 0.001m$, $pH=4.4$ and log fS_2 from electrum compositions ≈ -11.0 . (See Appendix V for methods of construction.)

R5513/14a,b) indicates a depositional temperature of 370°C . Because of problems experienced with py - cp pair temperatures from other areas (c.f. Chapter 9) this figure probably represents only a maximum temperature.

DEPTH OF MINERALISATION

Boiling of the early high temperature fluid and the presence of liquid CO_2 in inclusions in a sample from the Garbo Mine indicate a pressure of around 300 bars (c.f. Merchant, 1978) corresponding to depths between approximately 1km (lithostatic pressure) and 3km (hydrostatic pressure). Bonanza gold (gold - pyrargrite) mineralisation occurred at much shallower depths, i.e. 300 - 500m, if boiling occurred at temperatures between 200 and 240°C (Merchant, 1978 p278).

THERMOCHEMISTRY

The geochemical environment of gold - pyrargrite mineralisation is limited on the $f\text{S}_2$ versus $f\text{O}_2$ diagram (Fig. I-M-5) by the absence of magnetite, hematite, pyrrhotite and bornite and presence of pyrite and in some instances barite, chalcopyrite, arsenopyrite and stibnite. Log $f\text{S}_2$ values around -11 are indicated by Merchant's electrum analyses but values lower than -13.3 are required for the stability of arsenopyrite. The presence of pyrite but absence of hematite indicates that log $f\text{O}_2$ was lower than -33.0.

The general value of +1.5 for log $f\text{CO}_2$ does not seem applicable here; lower CO_2 fugacities are indicated for the stability of some sulphides in the absence of graphite (viz. log $f\text{CO}_2 < +1.0$ for electrum + stibnite and log $f\text{CO}_2 < -1.5$ for stibnite + arsenopyrite; Fig. I-M-5).

Merchant (1978) noted that although kaolinite is the common clay mineral associated with the gold - pyrargrite ore, sericite was also present. Therefore a pH of 4.4 (pH of the kaolinite/sericite boundary) is indicated.

Contours of total sulphur in solution at a pH of 4.4 indicate that log m_{S} must be greater than -4 for arsenopyrite stability and possibly as much as -2 for deposition of stibnite.

Figure I-M-6: f_{O_2} versus pH diagram at 230°C and $\Sigma S = 0.001m$ showing the geochemical environments of various Thames gold-pyrargyrite assemblages: (A), electrum + pyrargyrite + pyrite; (B), electrum + pyrargyrite + pyrite + arsenopyrite; (C) and (D) alternatives for electrum + pyrargyrite + pyrite + barite. $\bar{I} = 0.35$, $mK^+ = 0.056$, $pH \approx 4.4$, $\text{log } f_{S_2}$ from electrum compositions ≈ -11.0 , and $\text{log } f_{CO_2}$ (estimated) = $+1.5$. (Methods of construction are described in Appendix V.)

An intermediate $\log m \leq S$ value of -3 ($m \leq S = 0.001m$), similar to other mineralisations around this temperature, is used to construct the fO_2 versus pH diagram (Fig. I-M-6)

Contours of $\log fS_2$ plotted in Fig. I-M-6 indicate that low sulphur fugacities (below $\log fS_2 = -11$), without the presence of hematite, are only possible in the H_2S predominant field.

The deposition of the various mineral associations, electrum + pyrargyrite + pyrite $\pm$ arsenopyrite $\pm$ stibnite $\pm$ barite, can be modelled by variations of fO_2 , fS_2 and $m \leq S$ at constant temperature and pH (although in reality the latter parameters must have also varied). For example, assume that electrum + pyrargyrite + pyrite mineralisation was formed predominantly at $\log fS_2 = -11$ and $\log m \leq S = -3$ (Field A of Fig. I-M-6). An assemblage of electrum + pyrargyrite + pyrite + arsenopyrite may be formed by a decrease in $\log fS_2$ to -13.5 , accompanied by either a decrease in fO_2 (field B of Fig. I-M-6) or $m \leq S$ (c.f. Fig. I-M-5); electrum + pyrargyrite + pyrite + stibnite is formed by an increase in $\log m \leq S$, accompanied by a decrease in fO_2 (c.f. Fig. I-M-5), whereas electrum + pyrargyrite + pyrite + barite may be precipitated by an increase in fO_2 (field C of Fig. I-M-6). Alternatively the latter assemblage may be formed by a decrease in pH (field D of Fig. I-M-6).

Merchant's proposed boiling fluid environment for the deposition of the Thames bonanzas offers a mechanism for varying the concentration of dissolved sulphur, fO_2 and pH by loss of H_2S (and other acidic gases in the case of pH) during periods of boiling.

GENESIS

Merchant (1978) considered that the electrum - pyrargyrite mineralisation at Thames was deposited above a boiling zone in a fossil geothermal system during the Mid to Upper Pliocene. Merchant's evidence for boiling is mainly inferential but convincing. Bonanza mineralisations are related to structural features where pressure release and mixing of waters probably occurred.

Boiling off of H_2S from the fluid would cause instability of gold and silver sulphide complexes in solution and the acidic environment indicated by the alteration mineral assemblage in the wall rocks would also help promote deposition.

Below the boiling zone, mineralisation characterised by tetrahedrite and several sulphosalts was deposited presumably from chloride complexed metals in solution.

$\delta^{34}S$ values of barite indicate a sedimentary source (greywacke suite rocks) for the sulphur and sulphate minerals. The hydrothermal fluid was probably recirculated meteoric water.

The alunited rhyolite rocks of the Lookout Rocks area, described in the previous section (I-L, Tapu - Thames), probably represent the near surface acid sulphate water environment of the Thames hydrothermal system. If so, then the Thames mineralisation must have occurred during the period of regional rhyolite volcanism (i.e. during deposition of the Whitianga Group) in the Pliocene as suggested by Merchant (1978).

REFERENCES AND BIBLIOGRAPHY

DOWNEY, J.F.	1935:	see pp 68 - 144, 157 - 162 and 270 - 283
FRASER, C.	1910	
MERCHANT, R.J.	1978	
SCHOFIELD, J.C.	1967	
WILLIAMS, G.J.	1974:	see pp 104 - 107

NEAVESVILLEINTRODUCTION

Although the deposits of the Neavesville area produced only small quantities of gold and silver the area is particularly interesting because it is on the boundary between Miocene Coromandel Group andesites and Pliocene Whitianga Group rhyolites, with mineralisation occurring in both rock types.

The main workings occur in two groups geographically; a northern group consisting of the Golden Belt (Ajax Reef), Birds, Golden Arrow and Graces and a southern group consisting of the Champion Workings. Mining began in 1875 and continued intermittently until 1938 producing 910,000 grams (29,282 ounces) of bullion from 21,256 tonnes of quartz. The Ajax Reef was the major producer accounting for approximately 80% of the fields production (720,000 grams or 23,160 ounces).

ASARCO (Neilsen, 1968) investigated the area in the late 1960's with a program of geological mapping and geochemical sampling. Torckler (1978) studied the geology and mineralisation, and further geological information gained from recent diamond drilling by AMOCO was reported by Barker et al (1980).

GEOLOGY

The geology of the Neavesville area is summarised in Figs I-N-1 and I-N-2. Coromandel Group andesites, consisting predominantly of lavas with minor breccias and lapilli tuffs are overlain by Whitianga Group pyroclastic rocks. The latter consist of a sequence of tuffs and breccias, initially andesitic to dacitic, but later rhyolitic in composition, interrupted by a carbonaceous shale and interlayered rhyolitic tuff unit. The carbonaceous shale unit contains coal fragments and a beech pollen microflora and is considered by Torckler to have been deposited in a lake, 2 to 3km in diameter, containing a number of thermal springs. The individual shale units vary in thickness from 10m to a few centimeters, being composed of alternating quartz and carbonaceous laminae and

Figure I-N-2: Cross-section A-B located in Figure I-N-1. (From Fig.2 of Barker et al., 1980.)

Figure I-N-3: Classification of hydrothermally altered rocks at Neaveville.
(From Fig.3 of Barker, et al, 1980.)

containing 5 - 30% syngenetic pyrite and marcasite mineralisation. The other Whitianga Group pyroclastic units were considered by Barker et al (1980) to have been deposited subaerially as non-welded pyroclastic flows and air-fall tuffs.

HYDROTHERMAL ALTERATION

Torckler (1978) noted that hydrothermal alteration of the andesites at Neavesville is propylitic (calcite, chlorite, zeolites, epidote and quartz) increasing in intensity towards quartz veins, whereas potassium silicate assemblages, consisting mainly of quartz and adularia with minor sericite and plagioclase, occur in the rhyolites.

Barker et al (1980) classified the altered rocks into three alteration rank classes; low, medium and high (Fig. I-N-3) which they considered to approximately correspond to propylitic, argillic and phyllic alteration types. The alteration assemblages are very similar to those of modern geothermal fields at Broadlands and Wairakei.

MINERALISATION

Mineralisation in Andesite

Mineralisation in andesitic host rocks is mainly confined to a lenticular quartz vein known as the Ajax Reef. Torckler (1978), working with samples from mine dumps, found rare fine grained chalcopyrite, galena, sphalerite, hessite and pyrite in a gangue assemblage of quartz, adularia, sericite and brookite. The quartz is commonly coarsely crystalline; large vug crystals up to 40mm are abundantly present on dumps of 1 and 2 levels. Torckler considered that the occurrence of the sulphide mineralisation in brecciated quartz zones indicated that it was deposited late in the vein sequence.

Barker et al (1980) noted that material from 1 level dump contained grains of electrum, 0.03 - 0.05mm in length, included in large (0.4mm) pyrite grains in wall rocks adjacent to vein quartz.

Adams (1915) reported the mining of approximately 200kg of massive molybdenite from footwall and hanging wall zones of the Ajax Reef (No. 1 level?) in 1915. Barker et al (1980) described an unlocated sample from the Golden Belt workings, in the Geological Survey Collection, containing fine grained molybdenite as a thin crust on vein quartz.

Mineralisation in Rhyolite

Graces and the "Bluffs"

Several zones of post depositional brecciation occur in the rhyolitic tuff and these are considered by Barker et al (1980) to have been formed by hydraulic fracturing. The breccias have been silicified and infilled with interconnecting networks of quartz veinlets containing minor pyrite and electrum mineralisation.

The strongest mineralisation (assay values up to 175 g/t Au and 88g/t Ag for quartz vein samples) occurs in Graces workings (Fig. I-N-1) where silicified tuffs contact the pyritised carbonaceous shales. Quartz veins 0.5 to 300mm in width, containing vugs up to 30mm in diameter, occur in the contact zone. Two phases of electrum deposition occurred; the first forming concentrations at the quartz vein - shale interface with partial replacement of syngenetic marcasite and pyrite contained in the shale, whereas the second is concentrated near the centre of the quartz veinlets, often on vug quartz crystals (Torckler, 1978). The electrum occurs as anhedral masses varying in size from less than 0.005mm up to 2mm long.

Birds and Golden Arrow open cuts have been excavated in localised areas of brecciation and intense quartz veining in a NNW trending zone of intense silicification along the "Bluffs". Networks of quartz veinlets and vugs (with quartz crystals up to 20mm long) cement the breccia and in Birds Open Cut electrum occurs as scattered grains 0.03 - 0.08mm in size, in the late stage vein quartz (Barker et al, 1980).

Neilsen (1968) recorded typical Au assay values of

Figure I-N-4: Histograms of primary fluid inclusion filling temperatures and apparent salinities determined in samples of quartz from the Neavesville area (the individual measurements are listed in Appendix III). Samples 13942 through to 13946 contain vapour rich (Fig. 6-6) and vapour filled (Fig. 6-7) fluid inclusions, in addition to normal liquid-vapour types, indicating that the hydrothermal fluid from which they grew was boiling.

4.8ppm in Graces open cut, 2ppm in Birds and 6ppm in Golden Arrow with an overall range of 0.5 to 15.1ppm.

Champion

Nine adits have been excavated in rhyolitic tuff of the Champion area to intercept a 15m wide zone of intense silicification. Downey (1935) recorded that the venture generally proved unprofitable and ASARCO's assays showed that the zone was generally unmineralised except for a few patches containing up to 4ppm Au (Neilsen, 1968).

FLUID INCLUSIONS

Torckler determined filling temperatures of fluid inclusions in vug quartz samples from Graces and Birds open cuts. Histograms of his results (Fig. 5.2 of Torckler, 1978) have well defined modes of approximately 210°C and 230°C respectively.

Seven samples were investigated by the writer, one of which (13944) was Torckler's sample from Graces open cut. The location of the various samples is shown in Fig. I-N-1.

All samples contain 2 phase liquid plus vapour normal type fluid inclusions but samples 13942, 13943, 13944, 13945 and 13946 also contain many vapour rich (Fig 6-6) and vapour filled (Fig. 6-7) inclusions indicating that the hydrothermal fluid was boiling at the time of their entrapment.

Filling temperature and salinity histograms are presented in Fig. I-N-4. Filling temperatures for Torckler's sample (sample 13944) presented here were determined by the writer and the results differ slightly from those given by Torckler (Fig. 5.2 of Torckler, 1978) partly because more measurements are presented here and also because in some cases different inclusions may have been measured.

Pressure - salinity corrections are not required for the filling temperatures of the samples formed in a boiling environment and are less than 5°C for the two other samples

Figure I-N-5: Diagrammatic representation of the depth relations, at the time of mineralisation, for the Golden Belt area, Neavesville. The model assumes that boiling of the hydrothermal fluid occurred in Ajax 1 level (and above) under hydrostatic conditions.

(13940 and 13941). Therefore the filling temperatures are believed to indicate depositional temperatures of 260 - 230°C for base metal mineralisation of the Ajax Reef, 230 - 190°C for gold-silver mineralisation of the Bluffs section (Birds and Golden Arrow) and Graces workings and 220 - 210°C for gold-silver mineralisation of the Champion area.

Salinities are low, being less than 1 eq. wt. % NaCl, possibly reflecting a low concentration of CO₂ due to boiling off.

A partial chemical analysis of fluid inclusions in quartz from Ajax 2 level (sample 13941), determined by crushing and leaching experiments (Chapter 7) indicates the presence of 740ppm Na⁺, 630ppm K⁺, 31ppm Li⁺, 1220ppm Cl⁻ and approximately 0.14 moles/Kg of CO₂. Quartz from Ajax 1 level (sample 13938) was also analysed but because the water content is not known only the Na/K ratio of 2.6 can be reported.

HYDROGEN ISOTOPES

Fluid inclusions in quartz from Ajax 2 level (sample 13941) contain water with a δ D value of -38.3, indicating a probable origin from meteoric waters.

SULPHUR ISOTOPES

Samples of pyrite collected by the writer from Graces adit have $\delta^{34}\text{S}$ values of -0.3 per mil (sample 13904) and -0.4 per mil (sample 13905).

DEPTH OF MINERALISATION

A reconstruction of the depth regime at the time of mineralisation is illustrated in Fig. I-N-5 using a paleo-surface datum 200m above the highest peak in the area, Pakirarahi (787m a.s.l.). This model assumes that boiling occurred in Ajax 1 level (and above) under conditions of hydrostatic pressure.

TABLE I-N-1: General thermochemical parameters for epithermal mineralisations in the Ajax vein and Bluffs section of Neavesville.

	Ajax	Bluffs Section	References
Host rocks	andesite	rhyolite	
Temperature °C	250	220 (fluid boiling)	Table V-1
True ionic strength	0.04	0.10	"
Salinity (m NaCl eq)	0.11	0.10	"
mK^+	0.016	0.012	"
pH	6.1	6.5	See text
pH of kaolinite/sericite boundary	4.7	5.0	Table V-1
pH of sericite/K-feldspar boundary	6.1	6.4	"
Total S ($\log m\pm S$)	-2.0	-2.0	See text
Log fS_2 (electrum comp.) estimated	-10to-12.4 (Fig.I-N-6)	-11.3	Table V-6B
Log fO_2	-35.5to-38.0 (Fig.I-N-7)	-38.0to-40.0 (Fig.I-N-9)	Figures cited
Log fCO_2	+1.1	+1.2	Table V-1

THERMOCHEMISTRY

Introduction

Two mineralisations are modelled for the Neavesville area: (a) quartz, adularia, sericite, brookite, chalcopyrite, galena, sphalerite, hessite, pyrite and electrum mineralisation of the Ajax Reef in andesite host rocks and (b) the lower temperature quartz, pyrite and electrum mineralisation in the overlying rhyolites (Graces, Birds and Golden Arrow workings). Table I-N-1 lists some parameters of the geochemical environments of these mineralisations.

Ajax Reef

The geochemical environment of the Ajax Reef is limited on an fS_2 versus fO_2 diagram (Fig. I-N-6) by the presence of pyrite, chalcopyrite and galena but absence of pyrrhotite, bornite, magnetite, hematite and graphite. A pH of 6.1, calculated for the K-feldspar - sericite boundary using the concentration of K^+ measured from fluid inclusion analyses, is assigned to the hydrothermal fluids because both K-feldspar and sericite are vein constituents.

Contours of $\log m \pm S$ plotted at pH 6.1 in Fig. I-N-6 indicate that concentrations of total sulphur in solution between 0.1 and 0.001 m are possible ($\log m \pm S = -1$ to -3). Comparisons with other mineralisations suggest that a value around 0.01 m might be appropriate (shaded in Fig. I-N-6) and therefore this value was used to calculate the fO_2 versus pH diagram shown in Fig. I-N-7. The shaded area in Fig. I-N-7 represents the Ajax Reef fluids.

Graces, Birds and Golden Arrow

The quartz, pyrite and electrum mineralisation in the rhyolite host rocks (Graces, Birds and Golden Arrow workings) is modelled in Figs I-N-8 and I-N-9 at 220°C. Analyses of electrum from Graces open cut reported by Torckler (1978) are used here to define a $\log fS_2$ value of -11.3.

Torckler described secondary quartz and K-feldspar

Figure I-N-6: fS_2 versus fO_2 diagram at 250°C showing the geochemical environment (line of crosses) of quartz + adularia + chalcocopyrite + galena + sphalerite + hessite + pyrite + electrum mineralisation in the Ajax Vein, Neavesville. (See Table I-N-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-N-7: fO_2 versus pH diagram at 250°C and $\Sigma S=0.01M$ showing the geochemical environment (shaded) of quartz + adularia + chalcocopyrite + galena + sphalerite + hessite + pyrite + electrum mineralisation in the Ajax Vein, Neavesville. (See Table I-N-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-N-8: fS_2 versus fO_2 diagram at 220°C for electrum mineralisation in the Bluffs section, Neavesville. The composition of electrum (reported by Torckler, 1978) indicates a log fS_2 value of -11.3. The absence of graphite and hematite limit log fO_2 between -40.6 and -35.8 respectively. Finally the intersections of log mS contours with the log $fS_2 = -11.3$ line suggest that log mS was approximately -2.0 and therefore that the chemical environment of deposition was near the intersections of the log $mS = -2$ contour, and dissolved sulphide = dissolved sulphate boundary, with the log $fS_2 = -11.3$ line. (See Appendix V for methods of construction.)

Figure I-N-9: fO_2 versus pH diagram at 220°C and $\Sigma S = 0.01$ showing the geochemical environment (shaded) of electrum mineralisation in the Bluffs Section, Neavesville. (See Table I-N-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

alteration in the wall rocks and therefore the pH of the fluid is considered to be around 6.4 (equivalent to the sericite/K-feldspar boundary). Contours of $\log m \leq S$, plotted in Fig. I-N-8, indicate that the concentration of total sulphur in solution was around 0.01m ($\log m \leq S = 2.0$). Therefore this value was used to construct the fO_2 versus pH diagram (Fig. I-N-9). The probable region of mineral deposition in this figure is shown by the shaded area. A fluid with approximately equal concentrations of sulphate and sulphide is indicated.

Discussion

Comparison of the two sets of diagrams for the different mineralisation temperatures (Figs. I-N-6 and I-N-7 at 250°C and Figs. I-N-8 and I-N-9 at 220°C) shows that the two fluids occupy similar fields of stability. The differences in fO_2 , fS_2 and $m \leq S$ values are mainly a function of the different temperatures. Therefore it is probable that the different mineralisations were concurrent and their plumbing systems interconnected. The mineralisation in the rhyolite host rocks was formed at a high level, slightly lower temperature and from more evolved fluids than that of the Ajax Reef. The slightly higher pH indicated for the lower temperature mineralisation was probably caused by boiling (as evidenced by vapour rich fluid inclusions) and loss of CO_2 .

GENESIS

The Bluffs section and Ajax vein are considered to represent different levels of a single fossil geothermal system. The hydrothermal solution was hot recirculated meteoric water.

Mineralisation in the Ajax vein was probably in response to an increase in pH of the hydrothermal fluid caused by reactions with the wall rocks and resulting in deposition of metals from chloride complexes.

At a higher level in the hydrothermal system, boiling occurred and gold (electrum) was deposited at various sites

along the Bluffs section from sulphide complexes as a result of the loss of H_2S from the fluid. Oxidation (by mixing with near surface waters) is indicated by the stability relations in Fig. I-N-9 (and possibly also Fig. I-N-7) and may have also been an important factor.

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MARATOTOINTRODUCTION

Bell & Fraser (1912) noted that the history of mining in the Maratoto area had been one of repeated failures because of the difficulty in treating the low grade argentiferous ore and the decreasing ore grade with depth. Recent attempts at mining some of the deposits by Consolidated Silver Mining Company proved no exception and in 1973 they abandoned their operations on the Camoola and Silver Queen Reefs.

680,000 grams (21,930 ounces) of bullion were produced from 12,830 tonnes of quartz up until 1935 (Downey, 1935), whereas Consolidated Silver Mining Company produced 3 million grams (95,000 ounces) of silver and 23,000 grams (730 ounces) of gold between 1968 and 1973 (Mines Division records).

The geology and mineralisation of the deposits were described by Bell & Fraser (1912) and Main (1971, 1979), while Robinson & Christie (1980) investigated the stable isotopes and fluid inclusions of the Camoola and Silver Queen veins.

During the writers study only 3 level was readily accessible, the levels below being flooded. Rapid deterioration in the state of the workings was noted between visits, the last in early 1978.

GEOLOGY

A geological map of the area is presented in Fig. I-0-1. The veins occur in Coromandel Group andesites and dacite flows, breccias, tuffs and intercalated sediments (conglomerates, sands and silts).

HYDROTHERMAL ALTERATION

Main (1971) noted that the hydrothermal alteration of the andesite and dacite flow and breccia rocks in the Maratoto area occurred in a concentric zonal pattern around the quartz

Figure I-0-1: Geology of the Maratoto-Golden Cross-Komata-Waitekauri area.
(Compiled from Bell & Fraser, 1912; Rabone, 1975; Main, 1979.)

veins. The sequence was described, in order of increasing intensity of alteration, as follows:

- Zone 1 unaltered rocks
- Zone 2 mildly altered rocks: alteration of pyroxene to chlorite and carbonates.
- Zone 3 moderately altered rocks: pyroxene completely replaced, whereas feldspars and opaques show varying degrees of replacement. The alteration produces chlorite, epidote, carbonate, sericite, secondary quartz, adularia, zeolite (heulandite), pyrite and minor clay.
- Zone 4 highly altered rocks: an assemblage of quartz, clay (kaolinite and mixed layer chlorite - montmorillonite identified in one specimen from the Camoola vein) and pyrite is produced.

MINERALISATION

Introduction

17 veins were mined in the Maratoto area, the most important being the Payrock, Maratoto, Silver Queen and Camoola (Fig. I-0-2). The Payrock and Maratoto are the largest veins, traceable for 3 and 2.8km respectively. Most of the veins average less than 3m thick but the Camoola averages 6.1m and attains a maximum thickness of 24.4m (Main 1979).

The mineralisation is fine grained and occurs in quartz, quartz pseudomorphs after calcite and calcite gangue. Table I-0-1 lists the metallic minerals reported from some of the veins by Bell & Fraser (1912) and Main (1971) and additional minerals identified here. Au:Ag ratios are generally less than 1:100. Silver occurs as acanthite (argentite), hessite and native silver: electrum is extremely rare. Main (1971) and Main et al (1972) also recorded aguilarite (Ag_4SeS) but this could not be confirmed by the writer even after examination of Main's specimens M18185 and M18186. The latter contained silver and selenium as seleniferous acanthite. Chalcopyrite, sphalerite and galena, although absent (oxidised?) from the upper levels, are the

Figure I-0-2: The veins of the Maratoto area (after Robinson & Christie, 1980 Fig.2). Detailed plans of the Maratoto Mine were given by Main (1971).

TABLE I-O-1: Checklist of primary metallic minerals in some of the veins of the Maratoto area. Identifications by:
 1 = Bell & Fraser (1912), 2 = Main (1971), 3 = Main (1979),
 4 = this study. (? = uncertain identification)

Mineral	Acanthite	Agallite	Chalcocopyrite	Electrum	Galena	Hessite	Marcasite	Pyrite	Sphalerite
Vein									
St. Hippo							2	2	
Camoola	4	?2	2	3	2	4		2	2
Silver Queen	1		2	4	2	1	?3	2	2
Julia	1			1		1		2	
Corbetts	1							2	
Royal								2	
Gordens (Welcome Jack)	1					1			
Golden Spur	3			3	?2	3		2	?2
Maratoto	1		3	3	2	1		2	2
Payrock	1				2	1

Figure I-O-3: Generalised plan and longitudinal section of the Maratoto veins, after Main (1979 Fig.7). Main (1979) concluded that silver mineralisation at Maratoto occurred in fan shaped zones (longitudinal section) widening upwards. These zones were associated with the widest parts of the veins and a variance of vein strike direction.

predominant mineralisation in the lower levels of the veins in which they were recorded (e.g. Camoola and Silver Queen).

Following a detailed appraisal of the structure and production records of four veins (Silver Queen, Camoola, Maratoto and Golden Spur) Main (1979) concluded that the silver mineralisation occurred in fan shaped zones widening upwards (Fig. I-0-3). These zones were associated with the widest parts of the veins and a variance of vein strike direction.

Camoola Vein

The paragenesis of the Camoola vein is illustrated in Fig. I-0-4.

Stage 1. The Camoola vein is dominated by breccias containing blocks (up to 1.5m) of country rock, calcite or both, cemented by calcite, quartz and pyrite. These are followed by calcite deposition in an open vein producing a band of blocky calcite.

Stage 2. A series of alternating quartz and calcite bands (Stage 2a) precede the sulphide mineralisation (Stage 2b). Bands of rhodochrosite (Mn carbonate) are also deposited at this stage and later during initial sulphide mineralisation, whereas siderite occurs at various times throughout mineralisation and after it.

In hand specimen the mineralisation (Stage 2b) occurs as a single or paired narrow (up to 40mm, e.g. sample 285/37/8) black band of fine grained sulphides in quartz and calcite (Fig. 4-5).

In polished sections (13937, 13967, 285/37/7 and 285/37/8) sphalerite, galena, pyrite, chalcopryrite, acanthite, electrum and hessite (in order of abundance) occur as individual grains or aggregates scattered in quartz and calcite gangue (Figs. 4-32 and 4-33). The various metallic minerals generally make up only 5 to 20% of the band but in some parts they are up to 50% (285/37/7). The mineralisation is generally fine grained averaging 0.3mm (e.g. 285/37/7 and 285/37/8) but

Figure I-0-4: Paragenetic sequence of minerals in the Camoola Vein, Maratoto.

considerably finer grained mineralisation, averaging 0.05mm occurs in some specimens (13937 and 13967).

The sulphides occur as regular grains in quartz, the latter generally exerting euhedral grain boundaries on the sulphides, especially galena, whereas in calcite gangue the sulphides are irregular, generally finer grained (especially in 13937 and 13967) and often scattered in a "peppered" texture (Fig. 4-32). In the latter, grains of sulphide may be surrounded by large numbers of minute blebs of sulphide often oriented in "streaky" textures. Acanthite also occurs as thin ribbons along the margins of euhedral quartz grains in all specimens. In calcite it commonly occurs as atolls. Generally, when contacting, the sulphides have mutual boundaries (Fig. 4-33).

Stage 2 ends with a period of barren quartz deposition (Stage 2c).

Stage 3. Stage 3 consists of vug quartz coated with later carbonate and pyrite. Quartz crystals up to 40mm occur. In one sample collected by the writer the euhedral quartz crystals are assymmetrically coated by later minerals. However, because this feature was not observed in situ in the mine and the original orientation of the specimen is not known, the flow direction of the hydrothermal fluid cannot be determined.

Although supergene minerals were absent from Camoola Vein material studied by Main (1979), chalcocite and rare covellite occur in samples 13937 and 285/37/7 replacing chalcopyrite and a few grains of galena.

Silver Queen Vein

The paragenesis of the Silver Queen vein is illustrated in Fig. I-0-5. Three depositional stages are recognised from observations in the mine and of hand specimens and polished sections.

Stage 1. Brecciation of the country rock with subsequent

Figure I-0-5: Paragenetic sequence of minerals in the Silver Queen Vein, Maratoto.

deposition of quartz and calcite has produced a number of bands of quartz, quartz cemented wall rock breccia and quartz pseudomorphs after calcite which make up the bulk of the vein. Pyrite was deposited at various times during this stage.

Stage 2. An initial period of barren quartz deposition (Stage 2a) is followed by quartz with scattered fine grained composite grains of galena and hessite (early Stage 2b). Fine grained sphalerite and pyrite appear later (late Stage 2b) accompanied by quartz and galena - hessite. These early periods of mineralisation were recognised in only a single specimen (285/37/6). The sulphides occur as individual grains (galena - hessite composite) scattered in quartz, the latter making up 60 to 70% of this material. The galena - hessite grains occur as T, X, and Y shapes filling spaces between euhedral quartz crystals (Fig. 4-17).

Stage 2c contains an assemblage of fine grained sphalerite galena - hessite (composite grains), chalcopryite and pyrite (in order of abundance) and is the predominant form of mineralisation with various combinations of these minerals occurring in all polished sections (13920, 13925, 13931, 13932, 13945, 13946, 285/37/2 and 285/37/6).

Stage 2c minerals generally occur as individual grains or aggregates of two or three grains scattered in quartz, the proportion of mineralisation to gangue varying from one sample to another (quartz averages 80%). The sulphides generally fill spaces between euhedral quartz grains, a texture most marked in the case of galena - hessite (Fig. I-0-6) and chalcopryite. When contacting, the different sulphide minerals appear to have mutual boundary relations although some pyrite may be replaced by later minerals.

Stage 2c silver mineralisation is interrupted by a 2 to 5mm band of fine to medium grained chalcopryite, sphalerite and quartz (13931 and 285/37/6). In one hand specimen the chalcopryite and sphalerite occur interlayered with the silver mineralisation (Fig. I-0-7). In contrast to earlier quartz dominant mineralisation, quartz makes up only 10 to 40% of the chalcopryite and sphalerite mineralisation. Chalcopryite

Figure I-0-6: Galena-hessite composite grains (white) surrounded by subhedral -
euhedral quartz (grey), Stage 2c, Silver Queen Vein. Sample 13936. X100.

Figure I-0-7: Cut surface of a hand specimen from the Silver Queen vein showing alternating bands of Stage 2c silver (black) and chalcopyrite - sphalerite (yellow) mineralisation. Photo courtesy of Mr E. Coppard.

Figure I-O-8: Medium grained Stage 2c sphalerite (grey), chalcopyrite (white) and quartz (dark grey-black) from the Silver Queen Vein, Maratoto (sample 285/37/6). The sphalerite exhibits a graphic-poikilitic intergrowth with quartz. The pale grey circular spots in chalcopyrite are tarnish, whereas the black areas are pits. X100.

predominates and has mutual boundary relations with adjoining sphalerite. The latter displays a graphic to poikilitic intergrowth with quartz (Fig. I-0-8).

Stage 2 ends with barren quartz deposition (Stage 2d).

Stage 3. Late quartz occurs in vugs and is coated with later carbonates and pyrite (Fig. 4-8). Quartz crystals up to 70mm long occur (e.g. sample 13922).

Supergene covellite and chalcocite occur rimming and veining the sulphides in some specimens. Main noted rare occurrences of bornite and although he initially considered them to be hypogene (c.f. Fig. 52, p124 of Main 1971,) he later assigned them to the supergene assemblage (Main, 1979 p44).

FLUID INCLUSIONS

Fluid inclusions in quartz, calcite and sphalerite are generally two phase, liquid plus vapour, normal types although some inclusions contain a fibrous solid phase (samples 13916, 13921, 13922, 13923, 13926, 13927, 13928 and 13945; see Chapter 6) and samples 13919, 13922, 13925 and 13945 have vapour rich and vapour filled (Fig. 6-1) inclusions in addition to normal types.

Large vug quartz crystals (samples 13919 and 13922) contain zones of orientated regularly shaped (generally elongate - cylindric) inclusions (Figs. 6-9 and 6-10). Most of the inclusions are normal types but a few vapour rich and vapour filled types also occur (see Chapter 6).

Filling temperature and salinity measurements are listed in Appendix III and presented as histograms in Figs. I-0-9A (Camoola) and I-0-9B (Silver Queen). Filling temperatures of samples 13918, 13922, 13925 and 13945 require no pressure - salinity correction but approximately 10°C must be added to filling temperatures of other samples to obtain depositional temperatures.

Fig. I-O-9A

Figure I-O-9: Histograms of primary fluid inclusion filling temperatures and apparent salinities for quartz and calcite (see Appendix IX for differentiation) samples from the Camoola Vein (Fig. I-O-9A) and the Silver Queen Vein (Fig. I-O-9B) Maratoto. The individual measurements are listed in Appendix III. Samples 13919, 13922, 13925 and 13945 have vapour rich and vapour filled (Fig. 6-1) inclusions in addition to normal liquid-vapour types, indicating that the hydrothermal fluid was boiling at the time of their growth.

Fig. I-O-9B

TABLE I-0-2: Isotopic composition of sulphide minerals from the Maratoto Mine, after Robinson & Christie (1980). Some sample numbers have been changed to conform with those used in this thesis and the silver mineral listed as agularite by Robinson & Christie (1980) was identified here as seleniferous acanthite.

Sample	Location	Stage	Description	Mineral	$\delta^{34}\text{S}_{\text{CDT}}$ (‰)
13929	Camoola 3 Level	1	Blocky calcite with minor	Pyrite	+3.0
13929	South Stope	2b	Fine-grained silver minerals and sulfides	Acanthite	+1.6
13929	"	2b	" " "	Pyrite	+3.6
		"	" " "	Chalcopyrite	+2.2
13916	Camoola 3 Level North Stope	2b	Silver mineralization and sulfides	Acanthite	+0.7
13916	"	"	" " "	Chalcopyrite	+1.6
285/37/2	Silver Queen 3 level	2b-c	" " "	Pyrite	+3.1
13932	"	"	" " "	Chalcopyrite	+2.6
13920	"	5	2c Fine-grained silver mineralization	Chalcopyrite	+1.6
13920	"	"	" Coarse sulfide band	Sphalerite	+2.6
13920	"	"	" " "	Chalcopyrite	+2.1
285/37/6	"	3	" " "	Sphalerite	+1.0
285/37/6	"	"	" " "	Chalcopyrite	+1.4
13922	"	5	3 Post late calcite	Pyrite	+16.9
13922	"	"	" " "	Pyrite	+16.0

13920 is the only sample studied representing sulphide mineralisation: all other samples occur either earlier or later in the vein paragenesis. Nevertheless fairly constant temperatures, as indicated by the modes of the filling temperature histograms (Fig. I-0-9), occurred throughout the various stages of the Silver Queen and Camoola veins. Sulphide mineralisation probably occurred in a temperature range of 270-300°C. A temperature of 280°C is considered representative.

Salinities were also fairly similar throughout the various vein stages although considerable variability is displayed by individual samples.

Table 7-7 lists partial chemical analyses of fluid inclusions in quartz samples 13919 and 13926, determined by crushing and leaching experiments. The Na^+ and Cl^- values of the two analyses are very similar, whereas 13919 has a higher proportion of K^+ and much less CO_2 (Table 7-9) than 13926. The Na/K ratio derived from 12926 is approximately the same as that predicted by the Na/K geothermometer at a temperature of deposition around 280°C, whereas the Na/K ratio of 13919 is much lower than predicted theoretically, 3.4 instead of around 7 at 230°C.

SULPHUR ISOTOPES

Robinson & Christie (1980)* investigated the sulphur isotopes of sulphide minerals from the Camoola and Silver Queen veins. Their results are reproduced in Table I-0-2.

$\delta^{34}\text{S}$ values of Stage 2 sulphides range from +0.7 per mil to +3.6 per mil, whereas two samples of Stage 3 pyrite have unusually high $\delta^{34}\text{S}$ values of +16.0 and +16.9 per mil. Because of difficulties experienced in separating the very fine grained sulphides only two cogenetic mineral pairs could be measured, their fractionations indicating temperatures of 290 $\pm$ 60°C (12929, py-cp) and 275 $\pm$ 100°C (12920, sp-cp) in agreement with the fluid inclusion filling temperatures.

FOOTNOTE: * The writer was involved in only a few of these analyses.

Figure I-0-10: A plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ for vein carbonates from the Camoola and Silver Queen veins, Maratoto, (after Robinson & Christie, 1980 Fig.4). The temperature scale, defined for a value of $\delta^{18}\text{O}_{\text{fluid}} = -4$ per mil, indicates a decreasing temperature regime down to 60°C for late overgrowths of calcite on Stage 3 quartz. The position of the samples relative to the $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3}$ contours (dashed lines) suggests a value of -7 per mil for this parameter (also $\approx \delta^{13}\text{C}_{\text{EC}}$).

CARBON AND OXYGEN ISOTOPES

Robinson & Christie (1980)* analysed the carbon and oxygen isotopes of several vein carbonates. $\delta^{18}\text{O}$ values ranged from +0.7 per mil to +17.5 per mil, whereas $\delta^{13}\text{C}$ values ranged from -0.7 to -9.2 per mil. When plotted on a $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ diagram (Fig. I-0-10) these analyses can be used to indicate depositional temperatures for a specific value of $\delta^{18}\text{O}$ in the hydrothermal fluid. A value of -4 per mil was used and defined a decreasing temperature regime down to 60°C for late overgrowths of calcite on Stage 3 vug quartz. A few discrepancies with fluid inclusion filling temperature evidence were reconciled by considering variations of the $\delta^{18}\text{O}$ value of the hydrothermal fluid. The carbon isotopes were believed to relate to a $\delta^{13}\text{C}$ value of -7 per mil for H_2CO_3 in solution (the carbon fluid species fractionating against the precipitating carbonates).

HYDROGEN ISOTOPES

Fluid inclusions in samples 13926 and 13928 contain water with δD values of -48.5 and -42.4 per mil respectively. If the water was originally meteoric it must have been formed in a cooler climate than present. Alternatively, if the meteoric water had a similar δD to present day waters the measured δD values of the fluid inclusion waters could be formed by a mixture of meteoric and magmatic waters.

DEPTH OF MINERALISATION

The depth of mineralisation is constrained by the occurrence of boiling, at a minimum temperature of approximately 260°C, in 5 level during Stage 3. Depending on the concentrations of dissolved salts and CO_2 in the fluid, boiling could occur at 260°C under hydrostatic pressure conditions at maximum depths between 540m and slightly greater than 1km (c.f. Haas, 1971; Merchant, 1978). A depth of 800m was used for this factor in the construction of the depth model illustrated in Fig. I-0-11.

FOOTNOTE: * All carbon and oxygen isotopic analyses and interpretation by B.W. Robinson and staff of I.N.S.

Figure I-O-11: Diagrammatic reconstruction of the depth of mineralisation at the Maratoto Mine. The position of the surface datum is limited by the occurrence of boiling at 5 level during Stage 3.

THERMOCHEMISTRY

The geochemical environment of mineral deposition for both the Camoola and Silver Queen veins is limited on the fS_2 versus fO_2 diagram (Fig. I-0-12) by the presence of pyrite and chalcopyrite but absence of pyrrhotite, magnetite, hematite and bornite.

Values of $\log fS_2$ between -8.8 and -11 are indicated by the sphalerite and electrum compositions, whereas $\log fO_2$ is limited between -36.1 and -32.5 by the absence of graphite and the presence of calcite but not anhydrite, respectively. A further limitation on fO_2 in the Camoola vein is provided by the presence of rhodochrosite but absence of alabandite (MnS).

Intermittent periods of siderite deposition occurred during Stage 2 mineralisation in the Camoola Vein. The approximate (see Appendix V) position of the siderite stability field at $\log fCO_2 = +1.2$ is shown in Fig. I-0-13 together with the probable field of sulphide mineralisation (the shaded area transferred from Fig. I-0-12) and indicates that the transition from pyrite to siderite deposition was probably caused by a decrease in fS_2 or an increase in fO_2 (or both).

An fO_2 versus pH diagram, constructed for a total sulphur in solution concentration of $0.01m$ ($\log m \leq S = -2$), is presented in Fig. I-0-14. The shaded area "A" represents the possible range of mineralisation for the Camoola vein and indicates deposition from a fluid containing approximately equal concentrations of dissolved sulphate and sulphide and at a pH around 6.2, in equilibrium with K-feldspar and sericite in the wall rocks. The absence of rhodochrosite and alabandite in the Silver Queen vein allows a greater possible range of fluid compositions (fields A + B in Fig. I-0-14) extending well into the reduced sulphur species predominant field, as far as the calcite soluble/insoluble boundary at pH 5.5.

The stability field of siderite shown in Fig. I-0-13 demonstrates that the magnetite field of Fig. I-0-14 may in fact be occupied by siderite. Therefore periods of siderite deposition in the Camoola Vein (e.g. at $\log fO_2 = -32.0$ to -33.0 in the "magnetite" field of Fig. I-0-14) probably re-

Figure I-0-12: fS_2 versus fO_2 diagram at 280°C showing the chemical environment (shaded) of Stage 2 quartz + calcite + sphalerite + galena + pyrite + chalcopryrite + acanthite + hessite + electrum mineralisation in the Maratoto veins. $\log fS_2$ from sphalerite compositions = -8.8 to -9.7, $\log fS_2$ from electrum compositions (Camoola vein only) = -10.7 to -11.0, and $\log fCO_2$ from fluid inclusion analyses = +1.2. (Construction methods are described in Appendix V.)

Figure I-0-13: fS_2 versus fO_2 diagram at 280°C , including the siderite stability field at $\log fCO_2 = +1.2$, for Stage 2 mineralisation in the Camoola Vein. Intermittent periods of siderite deposition were probably caused by a decrease in fS_2 and/or an increase in fO_2 relative to the more common pyrite + chalcopryrite (+sphalerite + galena + acanthite + electrum) depositional environment.

Figure I-0-14: f_{O_2} versus pH diagram at 280°C and $a_S = 0.01m$ showing possible chemical environments for Stage 2 quartz + calcite + sphalerite + galena + pyrite + chalcopryrite + acanthite + electrum + rhodochrosite mineralisation in the Camoola Vein (shaded area A) and Stage 2 quartz + calcite + sphalerite + galena + pyrite + chalcopryrite + hessite mineralisation in the Silver Queen Vein (shaded area B + upper part of A). $\bar{I} = 0.09$, $mK^+ = 0.019$, $pH \approx 6$, $\log f_{S_2}$ from sphalerite compositions = -8.8 to -9.7, $\log f_{S_2}$ from electrum compositions (Camoola Vein only) = -10.7 to -11.0, and $\log f_{CO_2}$ from fluid inclusion analyses = +1.2. (Methods of construction are described in Appendix V.)

sulted from increases in fO_2 and the dissolved sulphate/dissolved sulphide ratio.

Kaolinite in the wall rocks and veins was not in equilibrium with Stage 2 fluids and was probably deposited at a later stage at lower temperatures. The Stage 2 fluids are however considered to be in equilibrium with Main's Zone 3 moderately altered rocks containing sericite and K-feldspar.

The fTe_2 versus fS_2 diagram (Fig. I-0-15) demonstrates that fTe_2 was higher in the Silver Queen Vein, where silver was deposited as hessite, than in the Camoola Vein, where silver occurs as acanthite. This may be a reflection of the concentration of total Te in solution (c.f. Fig. 11-4).

GENESIS

Robinson & Christie (1980) considered that $\delta^{34}S_{\text{S}}$ of the Maratoto fluid was represented by the $\delta^{34}S$ value of Stage 3 pyrite (+16.0 and +16.9 per mil) and assigned a value of +16 per mil for this parameter. They suggested that the probable source of sulphur with this $\delta^{34}S$ value was Jurassic sea water sulphate leached from the greywacke basement rocks.

The source of carbon, however, was postulated as magmatic CO_2 because of the -7 per mil $\delta^{13}C$ value derived for the H_2CO_3 in solution.

The water was considered to be meteoric water precipitated during a cooler climate or onto a higher altitude location than at present. The water was deeply circulated through the volcanic and basement rocks in an area of high geothermal gradient. It exchanged oxygen isotopes with the wall rocks and became enriched in various elements.

Deposition of Stage 2 sulphide minerals with $\delta^{34}S$ values between +0.7 and +3.6 per mil must have occurred from a fluid containing approximately equal proportions of dissolved sulphate and dissolved sulphide (Fig. I-0-16) if $\delta^{34}S_{\text{S}}$ was around +16 per mil. Therefore both the Camoola and Silver Queen Stage 2 environments must plot in field A of Fig. I-0-14.

Figure I-O-15: $f\text{Te}_2$ versus $f\text{S}_2$ diagram at 280°C showing the different stability regions relative to $f\text{Te}_2$, of the hessite-bearing mineralisation of the Silver Queen Vein (stippled area) and the acanthite (argentite) - bearing mineralisation of the Camoola Vein (diagonally ruled pattern). (Methods of construction are described in Appendix V.)

Figure I-0-16: fO_2 versus pH diagram at $280^\circ C$ and $\Sigma S = 0.01M$ with contours of $\delta^{34}S_{H_2S}$ for $\delta^{34}S_{\Sigma S} = +16$ per mil. Precipitation of Stage 2 sulphide minerals with $\delta^{34}S$ values between +0.7 and +3.6 per mil must have occurred near or on the oxidised = reduced aqueous sulphur species boundary (i.e. the SO_4^{2-}/HS^- boundary in the diagram). This information, together with that presented in Fig. I-0-14, suggests that Stage 2 mineralisation in both the Camoola and Silver Queen veins was formed in an environment represented by the shaded area in the diagram above.

Robinson & Christie (1980) considered that the ratio of oxidised:reduced sulphur species in the fluid decreased progressively in time so that during late Stage 3 the fluid contained sulphur almost exclusively in reduced form. Sulphate reduction was considered to have resulted from reactions with wall rock minerals (e.g. pyrite) or by reaction with hydrogen in the fluid. Stage 2 mineral deposition was considered to result from changes in fluid pH, also due to reactions with wall rocks.

The mixing model suggested by Henley & Seward (in prep) for epithermal deposits offers an alternative mechanism for Stage 2 mineralisation. In their model a hydrothermal fluid containing sulphur predominantly in reduced form mixes with near surface waters causing dilution, oxidation a decrease in temperature and therefore mineralisation. However, this model is difficult to reconcile with the apparent regression to a reduced fluid during Stage 3.

Boiling occurred during Stage 3 and was possibly the predominant mechanism of mineral deposition during this stage.

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and 429

GOLDEN CROSSINTRODUCTION

Discovered in 1892, the Golden Cross Mine was worked from 1895 to 1917 producing 12 million grams (386,331 ounces) of bullion from 157,667 tonnes of quartz mined (Downey, 1935). The veins were mined from shafts which have since collapsed making the mine inaccessible.

No geological investigations have been made on the deposit since Bell & Fraser (1912).

GEOLOGY

Bell & Fraser (1912) mapped the area around the Golden Cross mine as pyroxene dacite (c.f. Fig. I-0-1).

HYDROTHERMAL ALTERATION

Bell & Fraser (1912) described the hydrothermal alteration as propylitic.

MINERALISATION

Three semi-parallel veins; Empire, Realm and Golden Cross, occur in the mine, however the Golden Cross proved to be the only one with sufficient gold for profitable mining.

In the Golden Cross vein gold and silver occurred in a single ore shoot as very fine grained electrum in a gangue of quartz and quartz pseudomorphs after calcite. Acanthite, pyrite and other sulphides occurred in the lower levels.

The ore shoot was bounded at both ends by barren primary calcite. It was longest near the surface and was gradually pinched out by the calcite with depth. At the lowest level of mining, No. 7 level (approximately 210m below surface), the vein consisted of "numerous parallel joints, narrow fissures and pug-filled shattered zones, in which little or no calcite or quartz has been deposited" (Bell & Fraser, 1912 p111). Three diamond drill holes were put down from 7 level,

the longest going down a further 247m, but no ore was intersected.

Bell & Fraser (1912) noted that large caverns (up to 60m long) were found in the ore shoot during mining and were attributed to the dissolution of original calcite.

GENESIS

The association of ore with zones of leached calcite suggests that the physiocochemical conditions causing hydrothermal leaching may have been conducive to precious metal deposition. The solubility of calcite in hydrothermal solutions generally increases with decreasing temperature and pH (from neutral) and increasing $f\text{CO}_2$. These factors may have been responsible for ore deposition at Golden Cross.

REFERENCES AND BIBLIOGRAPHY

BELL, J.M.; FRASER, C.	1912: see pp 108 - 112
DOWNEY, J.F.	1935: see pp 212-215 and 287
SCHOFIELD, J.C.	1967
WILLIAMS, G.J.	1974: see p 108

I-Q

KOMATAINTRODUCTION

The Komata Reefs were mined from 1891 until the 1930's producing 16.6 million grams (534,852 ounces) of bullion from 206,040 tonnes of quartz (Downey, 1935). The mine ranks fourth in gold production compared with other mining centres of the Hauraki Gold - Silver Province. It consisted of eight adit levels. The ore was passed down a shaft to 8 level from higher levels and taken to the battery by tramway.

Recently 8 level was reopened by Handley & Anderson for extraction of andesite to be crushed and used on roof tiles.

No geological investigations of the mine have been reported since Bell & Fraser (1912).

GEOLOGY

The Komata Reefs occur in dacite flows and, less commonly, breccias (Bell & Fraser, 1912) of the Coromandel Group (c.f. Fig. I-Q-1).

HYDROTHERMAL ALTERATION

Bell & Fraser (1912) described the hydrothermal alteration as propylitic.

MINERALISATION

Most of the ore from the Komata Mine came from a pair of parallel veins known as No. 1 and No. 2, shown in longitudinal section in Fig. I-Q-1. These veins tend to converge with depth, being approximately 40m apart at the surface but only 10m apart in the lowest workings (Bell & Fraser, 1912). Both veins are lenticular in longitudinal and vertical section and split into stringers at their northern extensions. The widths of the veins and ore grade varied with the hardness of the country rock, with maximum width of 3m (although No. 2 Reef had local bulges up to 6m wide) and good ore grade occurring in hard rock.

Figure I-Q-1: Longitudinal sections of workings on No.1 and No.2 Reefs of the Komata Mine. (From Figs. 25 and 26 of Downey, 1935.)

Three ore shoots were found. Two occurred "back to back", one in No. 1 and the other in No. 2, in the northern part of the mine, whereas the third occurred only in No. 1 Reef. The two former shoots attained maximum length at 4 level and were found to be patchy and generally not profitable below 5 level. The third ore shoot apparently became unprofitable at 7 level. The richest ore found in the third shoot occurred where a generally barren vein, Lavingtons, joined No. 1. Both No. 1 and Lavingtons were strongly mineralised in the vicinity of their junction.

The veins consisted of a wall rock breccia (fragments up to 1m) cemented by quartz and calcite (Bell & Fraser, 1912). Quartz pseudomorphs after calcite were common in the leached parts of the veins. The mineralisation, consisting of pyrite, electrum and acanthite, occurred mainly in banded quartz but also in the breccia fragments.

Several veins are exposed in the workings presently accessible on 8 level (Fig. I-Q-2). They contain quartz and calcite, but no visible mineralisation, although the wall rocks are pyritised. Vugs are common and contain euhedral quartz crystals up to 25mm long. The stoped veins are very leached and contain abundant platy quartz, typical of quartz pseudomorphs after calcite.

FLUID INCLUSIONS

Fluid inclusions were investigated in samples of quartz and calcite from the locations shown in Fig. I-Q-2. The fluid inclusions are two phase liquid plus vapour normal types, with the exception of sample 13947 quartz in which vapour rich (Fig. 6-5) and vapour filled inclusions also occur, indicating that this later sample was formed in a boiling environment.

Filling temperature and salinity measurements are presented as histograms in Fig. I-Q-3. Pressure - salinity corrections of approximately 5°C must be added to the filling temperatures, except those of sample 13947 quartz. The corrected filling temperatures indicate depositional temperatures predominantly in the range 270 - 240°C. The filling temperature histogram

Figure I-Q-2: Plan of the accessible sections of 8 level, Komata Mine, showing the location of samples studied.

Figure I-Q-3: Histograms of primary fluid inclusion filling temperatures and apparent salinities for samples of quartz and calcite from 8 level of the Komata Mine (Fig. I-O-2). The individual measurements are listed in Appendix III. Sample 13947 contains vapour rich (Fig. 6-5) and vapour filled inclusion, in addition to normal liquid-vapour types indicating that the hydrothermal fluid was boiling during its growth. Sample 13949 is quartz.

Figure I-Q-4: Diagrammatic reconstruction of the depth of mineralisation at the Komata Mine assuming that boiling of the hydrothermal fluid at 8 level occurred under hydrostatic pressure conditions.

of sample 13947 quartz may indicate a lower temperature of around 210°C but because of its complicated shape such an interpretation is not made with much confidence. The initiation of boiling indicated by this sample probably resulted from a reduction in pressure (e.g. further opening of the fissure). Boiling may have in turn caused a drop in temperature.

The apparent salinities are quite high considering the type of mineralisation and may result from high concentrations of CO_2 .

SULPHUR ISOTOPES

Pyrite in a sample of vein material (13906) taken off the mullock heap outside 8 level has a $\delta^{34}\text{S}$ value of +2.8 per mil.

DEPTH OF MINERALISATION

The fluid inclusions in sample 13947 quartz indicate that the hydrothermal fluid was boiling at a depth now represented by 8 level of the Komata Mine. Boiling probably occurred at a temperature around 220°C under hydrostatic pressure conditions, indicating depths between 250 and 800m (depending on the concentration of dissolved CO_2 in the fluid, c.f. data of Haas [1971] and Fig. 5-6 of Merchant [1978]). A depth of 600m was assigned to 8 level to construct the model illustrated in Fig. I-Q-4.

GENESIS

The Komata Reefs are characterised by the apparent absence of base metal mineralisation. This factor, together with the fluid inclusion evidence for boiling at 8 level, suggest a near surface environment of mineralisation. Mixture of the hydrothermal fluid with near surface oxygenated waters, resulting in dilution, cooling and oxidation, together with boiling are therefore suggested as possible mechanisms for ore deposition.

REFERENCES AND BIBLIOGRAPHY

- BELL, J.M.; FRASER, C. 1912: see pp 105 - 108
DOWNEY, J.F. 1935: see pp 222 - 227 and 287
SCHOFIELD, J.C. 1967
WILLIAMS, G.J. 1974: see p 110

WAITEKAURIINTRODUCTION

The Waitekauri area supported several small gold mines which collectively produced 1.4 million grams (44,038 ounces) of bullion from 35,848 tonnes of quartz between 1875 and the 1930's (Downey, 1935). One of these mines, the Jubilee, was re-investigated by Consolidated Silver Mining Co. in the early 1970's. They reopened the Jubilee Low Level but discovered that on this level the Waitekauri vein contained minor base metal sulphide mineralisation but practically no precious metals. In conjunction with this work Rabone (1971, 1975) studied the geology of the Waitekauri area and the accessible mineralisations.

GEOLOGY

The geology of the Waitekauri area (Fig. I-R-1) consists of Coromandel Group andesite flows (Puketawa Andesite and Jubilee Andesite) and sediments, Whitianga Group dacite flows and pyroclastics capped by ignimbrite (Owharoa Ignimbrite Formation).

HYDROTHERMAL ALTERATION

Rabone (1975) classified the hydrothermally altered rocks of the Waitekauri area into four zones as summarised in Fig. I-R-2. Zones I to III are regarded here as propylitic alteration, whereas zone IV is intermediate argillic alteration (andesites) and potassium silicate alteration (dacites).

Two types of Zone III alteration occur: where carbonate activity was relatively high, carbonates, clay minerals, minor sericite, rare epidote and rare secondary biotite occur, whereas in non-carbonate alteration, assemblages of pistacitic epidote, secondary plagioclase (albite - oligoclase), prehnite and apatite occur.

Intense alteration (Zone IV) developed assemblages of

Figure I-R-1: Geology of the Waitekauri area and location of the Jubilee Low Level (after Rabone, 1975).

ZONE:	I	II	III	IV
ALTERATION:	fresh rock to weak	weak to moderate	moderate to strong	Intense
Chlorite				
Carbonate		—		
Clay Minerals			—	—
Sericite			—	
Epidote			—	
Secondary plagioclase			—	
Secondary biotite			—	
Secondary quartz			—	—
Prehnite			—	
Pyrite			—	
K-feldspar				—
Hematite				—

Figure I-R-2: Hydrothermal alteration minerals in andesites and dacites of the Waitekauri area and their relation to alteration intensity. K-feldspar and hematite occur only in the dacites. (Compiled from descriptions in Rabone 1971; 1975.)

Minerals \ Stages	1		2			3	4
			a	b	c		
Quartz	Faulting and brecciation
Calcite
Sphalerite				Faulting and brecciation			
Chalcopyrite
Galena
Pyrite
Adularia			---?---	?	---?---		
Kaolinite
Chalcocite
Covellite

Figure I-R-3: Paragenetic sequence of minerals in the Waitēkauri Vein, Jubilee Low Level.

quartz, clay (chlorite, with minor kaolinite and illite) and pyrite although in the dacites this zone is represented by assemblages of quartz, K-feldspar (adularia) and hematite.

MINERALISATION

Quartz veins occur in both the andesites and dacites of the Waitekauri area although in the latter they tend to be small and grouped as vein systems, due to their less competent host rocks.

The main veins are Durbar, Grace Darling, Huanui, Waitekauri (Jubilee), Scotia and Maoriland (Fig. I-0-1). The Waitekauri vein is the largest of the group, being approximately 1km long and commonly up to 2.5m wide although a maximum width of 10m was recorded.

The mineralisation in the various veins consisted of very fine grained electrum widely dispersed in quartz and quartz pseudomorphs after calcite gangue. Primary calcite was rare or absent in the veins. In the low levels of the Jubilee mine the Waitekauri vein contains pyrite, chalcopyrite, sphalerite and galena, but electrum is generally absent. The Scotia vein also contained sulphides, including acanthite, but only in small patches and very fine grained (Bell & Fraser, 1912).

Rabone (1971a, 1975) investigated the mineralisation of the Waitekauri vein in the Jubilee low level (Fig. I-R-1) after it was reopened by Consilver in the early 1970's. The vein varies in width from 0.6 to 3m. Quartz and calcite are the main constituents but adularia, kaolinite, pyrite, sphalerite, galena and chalcopyrite also occur.

The paragenesis, illustrated in Fig. I-R-3, was compiled from Rabone's descriptions and the writers observations of samples donated by Rabone.

Several periods of fault movement and brecciation occurred during Stage 1 which is represented by bands of quartz and calcite and wall rock breccia cemented by quartz and calcite. A large proportion of the calcite has been subsequently leached

Figure I-R-4: Stage 2b galena (pale grey-white) replacing Stage 2a sphalerite (grey, upper right) around the rims of grains. The galena is in turn replaced by supergene covellite. Stage 2b subhedral pyrite (white, center-left and bottom left) contains abundant inclusions of galena (pale grey, high relief) and a few inclusions of chalcopyrite (pale grey, no relief) probably replacing the pyrite. The dark grey-black background is quartz and the black spots are pits. Sample 14020. X200.

out leaving quartz pseudomorphs after calcite. Stage 1 material makes up most of the vein.

Stage 2 mineralisation, consisting of fine to coarse grained quartz, sphalerite, galena, chalcopryrite and pyrite, occurs in a 20mm to 0.3m wide (averaging 0.1m) band near the hanging wall. Early mineralisation (Stage 2a) consisting of medium to coarse grained sphalerite, chalcopryrite, galena and pyrite (in order of abundance) occurs in quartz veinlets and also as replacement mineralisation in wall rock breccia. The ratio of sulphide to gangue is high in coarse grained mineralisation but low in fine grained mineralisation. Mutual boundary relations between sphalerite, chalcopryrite and galena and rare subgraphic intergrowths of galena and sphalerite noted by Rabone (1971a, 1975) indicate that these minerals precipitated together. Pyrite is a minor phase and generally euhedral.

A period of minor brecciation is followed by Stage 2b mineralisation consisting of fine to medium grained quartz, galena and pyrite. Galena occurs as replacement rims on earlier sphalerite (Fig. I-R-4) and intergrown with quartz in a "fishnet" texture (Fig. 4-16), whereas pyrite occurs as solitary subhedral grains in quartz. The pyrite contains abundant inclusions of galena possibly formed by replacement. (Fig. I-R-4).

Further brecciation is followed by quartz with minor pyrite and chalcopryrite deposition (Stage 2c). Small quartz crystals (up to 5mm long) are developed in vugs. Pyrite and chalcopryrite fill cracks in Stage 2a sphalerite and also occur as solitary sulphide grains on vug quartz crystals.

Stage 3 is marked by vug quartz crystal deposition and later filling of vugs and shears by kaolinite.

Supergene covellite and chalcocite replace Stage 2 chalcopryrite, sphalerite and galena along cracks and around rims.

Figure I-R-5: Histograms of primary fluid inclusions filling temperatures and apparent salinities for samples of quartz from the Waitekauri area. The individual measurements are listed in Appendix III.

FLUID INCLUSIONS

Fluid inclusions in quartz samples from the Jubilee and Maoriland workings are generally two phase, liquid plus vapour, normal types, although a fibrous solid phase also occurs in some fluid inclusions of samples 14010 and 14014 (Fig. 6-13).

Filling temperature and salinity measurements are presented as histograms in Fig. I-R-5. A pressure - salinity correction of approximately 10°C must be added to the filling temperatures. Corrected filling temperatures indicate depositional temperatures between 260 and 280°C for quartz samples bracketing the sulphide mineralisation in the Waitekauri vein and quartz deposition in the Maoriland vein.

SULPHUR ISOTOPES

$\delta^{34}\text{S}$ values of sulphide minerals from the Jubilee Mine are listed in Table 9-1. They range from $+0.3$ per mil (galena) to $+3.8$ per mil (sphalerite). Because galena is not common in the sulphide mineralisation and is generally fine grained, sufficient galena for isotopic analysis could be separated from only two samples: 14010 (Wk 1b) and 14020 (Wk 13). Fractionation between galena and sphalerite indicates depositional temperatures of $355 - 390^{\circ}\text{C}$ (two different sp-gn pairs of sample 14010) and 280°C respectively. Other mineral pairs are generally not in isotopic equilibrium.

THERMOCHEMISTRY

The geochemical environment of Stage 2 mineralisation is limited on the $f\text{S}_2$ versus $f\text{O}_2$ diagram (Fig. I-R-6) by the presence of pyrite and chalcopyrite but absence of pyrrhotite, magnetite, hematite and bornite. The iron content of sphalerites indicate $\log f\text{S}_2$ values between -9.7 and -10.4 , whereas $\log f\text{O}_2$ is limited between -32.0 and -36.0 by the presence of calcite but absence of graphite, anhydrite and magnetite.

A value of $0.01m$ was used for the concentration of total sulphur in solution ($\log m \leq S = -2$) in the construction of the $f\text{O}_2$ versus pH diagram shown in Fig. I-R-7.

Figure I-R-6: fS_2 versus fO_2 diagram at 280°C showing the geochemical environment (shaded) of Stage 2 quartz + pyrite + chalcopyrite + sphalerite + galena mineralisation in the Waitekauri Vein. Log fS_2 from sphalerite compositions = -9.7 to -10.4, and log fCO_2 = +1.5 (estimated). (Methods of construction are described in Appendix V.)

Figure I-R-7: fO_2 versus pH diagram at 280°C and $\Sigma S = 0.01m$ showing the chemical environment (shaded) of Stage 2 quartz + pyrite + chalcopyrite + sphalerite + galena mineralisation in the Waitekauri Vein. $\bar{I} = 0.15$, $mK^+ = 0.040$, $\text{pH} \approx 5.8$, $\text{log } fS_2$ from sphalerite compositions = -9.7 to -10.4 , and $\text{log } fCO_2$ (estimated) = $+1.5$. (Methods of construction are described in Appendix V.)

K-feldspar occurs as a vein mineral, whereas the wall rock alteration is characterised by the occurrence of sericite (secondary hematite and kaolinite in some intensely altered rocks of the Waitekauri area are considered to result from post Stage 2 fluids). The hydrothermal fluid is therefore considered to have had a pH near that of the sericite/K-feldspar boundary (5.8) and is represented by the shaded area in Fig. I-R-7. Sulphur was present in solution predominantly in reduced form.

GENESIS

Deposition of Stage 2 mineralisation at Waitekauri probably occurred because of changes in fluid chemistry (e.g. pH) as a result of fluid - wall rock reactions.

$\delta^{34}\text{S}_{\text{S}}$ of the hydrothermal fluid was probably around +4 per mil, similar to the $\delta^{34}\text{S}$ values of the sulphide minerals, because sulphur was present in solution predominantly in reduced form. Therefore the sulphur was probably of magmatic origin.

REFERENCES AND BIBLIOGRAPHY

BELL, J.M.; FRASER, C.	1912: see pp 113 - 117
DOWNNEY, J.F.	1935: see pp211-213, 215-222 and 287
RABONE, S.D.C.	1971a
	1975
SCHOFIELD, J.C.	1967
WILLIAMS, G.J.	1974: see pp 107 - 109

WAIHIINTRODUCTION

The mines at Waihi comprised the largest and most successful long term gold mining venture in New Zealand. Between 1878 and 1952 1.1 billion grams (35,523,768 ounces) of bullion were produced from 12 million tonnes of quartz (Williams, 1974). The ore was taken from 14 levels and an opencut representing a total vertical range of 500m.

The veins in the Waihi area occur in two geographically separate groups (Fig. I-S-1), one under Martha Hill and the town of Waihi (Martha, Empire, Royal and associated veins) termed here the Martha vein system, and the other under Rosemont Hill (Union, Mascotte, Amaranth, Silverton and Gladstone veins), termed here the Rosemont Hill veins.

The Martha vein system produced approximately 200 million grams (6.5 million ounces) of gold, whereas the Rosemont Hill veins produced less than one million grams (30,000 ounces).

Several companies operated in the area in the late 1800's but by the turn of the century were mostly amalgamated into three; the Waihi Gold Mining Co. (W.G.M.Co.), Grand Junction Co. (G.J.Co.) and the Waihi Extended Co. (W.E.Co.). The areas of operation of these companies are shown in Fig. I-S-1. The literature describing their operations is confusing because although the mines were adjacent and generally operating on the same major veins, they were worked from different levels, so that levels with the same number occurred at markedly different depths in the different mines (Fig. I-S-2).

The W.E.Co. was taken over by the G.J.Co. around 1918 and the latter companies operations were taken over by the W.G.M.Co. in 1925. During its continued production until 1952 the operation was generally known as the Waihi or Martha Mine. The latter term is used here.

Figure I-S-1: Map of the veins, and areas of operation of the major mining companies in Waihi during the late 1800's and early 1900's. The veins occur in two geographically separate groups termed here the Martha Vein system (Martha Empire, Royal and associated veins) and the Rosemont Hill veins (Union, Mascotte, Amaranth, Silverton and Gladstone veins).

Figure I-S-2: Depth relations of the different mining levels used by the three companies that worked the Martha vein system during the late 1800's and early 1900's. In most cases, levels with the same number in the different mines were worked at markedly different depths. The numbers in brackets are depths in metres below surface (shaft collar).

Figure I-S-3: Geology of the Waihi area. (Modified from Morgan, 1924; Modriniak & Marsden, 1938.)

At present the AMAX - Mineral Resources - Green & McCahill consortium are evaluating the possibility of reopening the Martha Mine. Mineral Resources - Green & McCahill tested the upper levels with a large open cut prospecting operation (Fig. 1-6) reported by Hancock (1979), whereas AMAX are presently carrying out an extensive diamond drilling program. They had drilled 28 holes (averaging 200m) up to November 1981 and planned to drill a further 24 up to the end of 1982.

The geology of the Waihi mines was described by Bell & Fraser (1912) and Morgan (1924). Brathwaite (1980) described the thin sections of Waihi rocks in the Geological Survey's collection and is presently studying AMAX's drill core. The mining history was described by Downey (1935) and McAra (1978).

Modriniak & Marsden (1938) carried out a comprehensive geophysical survey on the surface, using seismic refraction, magnetic and electrical resistivity methods. From their results they interpreted rock type (andesite or rhyolite) and zones of hydrothermal alteration at depth, in addition to mapping several new faults and determining extensions of some previously known faults and veins.

At the time of the writers investigation some of the upper levels were opened by Mineral Resources Ltd and limited access was gained to the Martha Vein and a parallel vein termed Martha Branch.

GEOLOGY

The geology of the Waihi area is illustrated in Fig. I-S-3.

Bell & Fraser (1912) and Morgan (1924) distinguished two units of andesites and dacites (Table I-S-1): (1) an early series of predominantly flow rocks identified as dacites by Bell & Fraser but termed quartz andesites by Morgan, and (2) a later series of flows and minor pyroclastics (the latter mainly in the G.J.Co section) of pyroxene andesites and lesser dacites.

Brathwaite (1980) confirmed Morgan's description of the

TABLE I-S-1: Stratigraphy of the rocks in the Waihi area showing the divisions of Bell & Fraser (1912), Morgan (1924) and the scheme adopted here.

Bell & Fraser (1912)	Morgan 1924	Compilation (Scheme adopted here)	
Tridymite Bearing Rhyolite	Tridymite Rhyolite	Tridymite Rhyolite	WHITIANGA GROUP
Wilsonite	Rhyolitic tuffs	Owharoa Ignimbrite Formation	
Spherulitic rhyolite	Spherulitic Rhyolite	Undifferentiated (spherulitic rhyolite)	
		Minden Rhyolite Subgroup	
Andesites (Second Period Volcanics)	Beesons Island Series	Omahia Andesite (late pyroxene andesites)	CORONANDEL GROUP
Dacites (First Period Volcanics)	Kapanga Series	(intermediate pyroxene andesite, Rosemont Hill) (early quartz pyroxene andesite, Martha Hill)	

lower unit as predominantly quartz andesite rather than dacite but considered that the rocks of Rosemont Hill were pyroxene andesites rather than the dacites and quartz andesites of Bell & Fraser (1912) and Morgan (1924) respectively.

In addition to compositional differences (presence or absence of phenocrystic quartz) the distinction between the two units described by Bell & Fraser and Morgan was also marked by the occurrence of the quartz veins and moderate to strong hydrothermal alteration in the quartz andesite unit, whereas the upper pyroxene andesite unit was not penetrated by the veins and was only weakly altered. Bell & Fraser (1912) considered that the boundary between the two units was irregular and postulated that a period of erosion and weathering occurred between their respective deposition, producing a very dissected landscape on the lower unit.

Bell & Fraser (1912) postulated that the major portion of the producing field was contained within a large intrusive dacite boss. This hypothesis was not substantiated in later work by Morgan (1924) and Brathwaite (1980) who considered that most rocks from this section were volcanic quartz andesites. However, the latter author did identify two rocks (from the W.G.M.Co. section) in thin section as dacite porphyry intrusives indicating that small intrusive bodies do occur in the volcanic sequence.

Thin beds of pyroclastics interstratified with the andesite flows were identified by Brathwaite (1980) as dacite and rhyolitic crystal and lithic tuff and fine grained siliceous tuff. Morgan (1924) considered that some pyroclastic beds were in fact sediments (volcanic epiclastites) and he also noted the occurrence of various carbonaceous bands.

The andesites of Black Hill (Fig. I-S-3) were considered by Bell & Fraser and by Morgan to be intrusive and were mapped by Schofield (1967) as Omaha Andesite as shown in Fig. I-S-3.

A series of conglomerate beds were identified between the andesites and overlying rhyolites by Bell & Fraser and were considered by these authors to be fluvial and indicate a

period of erosion between the andesite and rhyolite volcanism.

In summary the Coromandel Group sequence at Waihi consists of at least four andesites as follows (in order of decreasing age): (1) quartz pyroxene andesite (comprising Martha Hill and host to the Martha vein system), (2) pyroxene andesite (comprising Rosemont Hill and host to the Rosemont Hill veins), (3) pyroxene andesite (barren of mineralisation) and (4) an intrusive hornblende andesite (Omahia Andesite) comprising Black Hill.

The Whitianga Group sequence consists of spherulitic rhyolite (Minden Rhyolite Subgroup) overlain by a series of welded and non-welded pyroclastics of the Coroglen Subgroup (classified as the Owharoa Ignimbrite Formation and the Tridymite Rhyolite).

HYDROTHERMAL ALTERATION

Bell & Fraser (1912) and Morgan (1924) described the hydrothermal alteration of the andesites and dacites in the Martha Mine in a general sequence as chloritic, propylitic and silicic with increasing proximity to the veins: These authors noted the following trends:

- (1) feldspars were altered to sericite, carbonates, adularia (valencianite in the early literature), secondary quartz and apatite.
- (2) ferromagnesians were altered to chlorite, serpentinous material, secondary quartz, leucoxene, pyrite and carbonate.
- (2) magnetite and ilmenite were altered to leucoxene and pyrite.

The carbonate was mainly calcite although Morgan suggested that dolomite also occurred and Bell & Fraser considered that much of the leucoxene was siderite but this was refuted by Morgan.

The zeolites stilbite and laumontite were noted in some altered andesites of the W.E.Co. section by Morgan (1924 p89).

The intensity of hydrothermal alteration was considered to be primarily a function of the proximity to veins although some exceptions were noted by Bell & Fraser.

Brathwaite (1980) classified the hydrothermal alteration of the andesites in his thin section study as follows:

Weakly altered andesites: these contain hydrothermal assemblages of carbonate, chlorite and traces of sericite (illite). Hypersthene is completely replaced by chlorite, augite is fresh or partly altered to chlorite and carbonate, whereas plagioclase is unaltered.

Moderately altered andesites: these contain hydrothermal assemblages of carbonate, chlorite, sericite (illite), adularia, sphene, pyrite and one rare occurrence of epidote (as a plagioclase alteration product). Augite is replaced by carbonate and chlorite, plagioclase is variably altered to carbonate plus sericite (illite), or adularia, or adularia plus albite, whereas primary magnetite is destroyed and is indirectly replaced by sphene and pyrite.

Strongly altered andesites: these contain hydrothermal assemblages of secondary quartz (in groundmass and veins), sericite (illite), adularia, chlorite (less than in moderately altered rocks), carbonates, pyrite (3 - 25% of rock), sphene (ubiquitous) and apatite. Plagioclase is completely replaced by adularia, sericite (illite) and carbonate, and sericite (illite) in turn replaces adularia.

Brathwaite (1980) noted that there were no obvious trends in increasing or decreasing alteration along strike or with depth (both strongly altered and weakly altered rocks occurred around the 1000 foot level).

The unmineralised pyroxene andesites (Second Period Volcanics of Bell & Fraser and Beesons Island Series of Morgan) were generally only weakly altered and the mineralised pyroxene andesites of the Rosemont Hill area were unusual in that they contained no carbonate (Brathwaite, 1980). Brathwaite considered that the latter may be related to the intense silicification of the samples.

In summary, the hydrothermal alteration of wall rocks in the Martha Mine is characterised by the development of adularia

Figure I-S-4: Cross sections of the Martha vein system. (From Williams 1974; after Morgan, 1924.)

and sericite (illite) and the intensity of alteration is related to the proximity to quartz veins.

MINERALISATION

Martha Vein System

Economic mineralisation occurred in a number of veins in the Martha vein system, the most important being the three semi-parallel veins known as the Martha, Empire and Royal (Fig. I-S-1). These veins were found to converge with depth (Fig. I-S-4). Only the Martha outcrops at the surface.

Gold occurred in the Martha Mine as very fine grained electrum (not visible to the naked eye) although visible 'leafy' gold was reported from Smithy Level (Morgan, 1924 p93) and occurring "on joint - surfaces not far below the outcrop" of the Martha Reef (Morgan, 1924 p105 and 148). The electrum had an average fineness of about 650 (Bell & Fraser, 1912 p58; Morgan, 1924 p93).

Silver, in addition to that in electrum, occurred predominantly as acanthite although native silver, in the form of scales and wire was found on various levels in the Martha vein and 11 level of the Empire Lode (p 93 of Morgan) and pyrargyrite (Ag_3SbS_3) and proustite (Ag_3AsS_3) occurred in cleavages and vugs at several locations between 2 level G.J.Co. (493') and 11 level W.G.M.Co. (1301'). Hessite was not recorded and no trace of Te was detected in the assays of ore although these contained small quantities of Se which Bell & Fraser (1912) suggested was held in acanthite. Analyses of acanthite by the writer confirm this hypothesis.

The overall Au:Ag ratio of the ore was quite variable with the following figures quoted:

- (1) 1:6 to 1:7; average for the W.G.M.Co. section (the Martha Mine at this time consisted of the W.G.M.Co. and the G.J.Co. sections), estimated from production figures up to 1922(?) by Morgan (1924 p163).
- (2) 1:4; average for the G.J.Co. section, estimated from production figures up to 1922 by Morgan (1924 p163).

- (3) 1:3 to 1:4; oxidised ore (Bell & Fraser, 1912 p139).
- (4) 1:4.5; Martha open cut.
- (5) 1:30 in sulphide ore at its upper limit on 2 level (Bell & Fraser p141 quoting earlier work by Morgan).
- (6) 1:9; average for all ore mined by the W.G.M.Co. during 1910. (Bell & Fraser, 1912 p137).
- (7) 1:0.5 to 1:5; 5 level of Jelicoe Lode (Morgan, 1924 p152).
- (8) 1:2; No. 2 Lode W.E.Co. (Morgan, 1924 p168).

Assays of AMAX's drill core average approximately 1:9 (Mr M. Baker, AMAX, pers. comm. 1980).

The bullion production (35,523,768 ounces) up to 1952 and its value (28,496,011 pounds sterling) quoted by Williams (1974) indicates an average Au:Ag ratio of approximately 1:6 for the entire mine.

Pyrite occurred throughout the mine and was often host to the electrum.

Sphalerite, galena and chalcopyrite were found in the intermediate and lower levels. Sphalerite was the most abundant of these sulphides. Galena occurred on 3 level (W.G.M.Co. section) and deeper levels. Chalcopyrite, from its initial appearance in the upper levels, increased in quantity to a maximum in the intermediate levels but decreased towards the lower levels.

Molybdenite was reported by Morgan (1924 p171) from the W.E.Co. Mine. It occurred as spots and irregular streaks in a quartz vein intersected (in a shaft?) 23m above 7 level and similarly in a small vein on 7 level. The former vein assayed 0.13 - 0.45% Mo but contained only traces of Au and Ag. Brathwaite (1980 p25) described a sample (P 7915) of a quartz vein from 7 level of the W.E. Co. section containing fine grained (0.3mm) molybdenite, pyrite, adularia, sericite and carbonate. Molybdenite was not recorded from any other locations in the Martha Mine.

The gangue minerals in approximate order of abundance were quartz, calcite, adularia, kaolinite, sericite (illite)

and chlorite.

Quartz was generally chalcedonic but fine grained quartz with comb structure was found in intermediate and deep levels: coarse grained quartz and vug quartz were rare. Amethystine quartz was quite common in the Martha Mine, frequently lining cavities (Morgan 1924). AMAX have found concentrations of amethystine quartz on the footwall side of the Martha vein and consider it to be a late stage vein mineral (Mr M. Baker pers. comm.). Morgan (1924 p95) attributed its colour to Mn.

Quartz pseudomorphs after calcite were quite common in so called "oxidised ore" from 2 level down, however in the Martha Vein primary calcite did not appear until 5 level, was most abundant at 8 level, and was absent below 9 level (although quartz pseudomorphs after calcite occurred in the lower levels). Much of the calcite was manganiiferous and rhodochrosite occurred in several parts of the mine (Morgan, 1924 c.f. p95).

Adularia (valencianite in the early literature) also first occurred at 5 level and persisted into the deeper levels. It was a common constituent of the samples studied by Brathwaite (1980).

Kaolinite was found mainly in the upper levels. Bell & Fraser (1912 p57) report an analyses of kaolinite from 6 level W.G.M.Co. section which Morgan considered a mixture of kaolinite and sericite.

Sericite (illite) was a fairly persistent although minor constituent in samples originating from 5, 6, 7 and 9 levels of the W.G.M.Co. section studied by Brathwaite (1980). Morgan (1924 p89) noted that it occurred as fine white or pale - brown fibres included in vein quartz.

Chlorite occurred as soft greenish scales and masses in several veins and was particularly abundant in the Royal Lode. Morgan (1924 p89) noted that in the upper and middle levels of the Martha Mine chlorite was an indicator of ore but this relationship did not always hold in the lower levels. Brathwaite (1980) identified chlorite in only one vein specimen

(P18543 Martha Lode 5 Level W.G.M.Co. section) during his study.

Bell & Fraser (1912) divided the paragenesis into three stages: (1) calcite vein filling, (2) brecciation with subsequent ore deposition and (3) later gold - silver bearing sulphide stage, cross-cutting Stage 2. Morgan (1924), however claimed that Bell & Fraser's early calcite stage did not exist.

It is apparent from the early descriptions of the main ore stage that it was characterised by wall rock breccia with replacement mineralisation occurring in the breccia fragments and fissure filling banded mineralisation between the fragments. The banded mineralisation is most commonly alternating veinlets of quartz and quartz with pyrite, acanthite and electrum in the upper levels but galena, sphalerite and chalcopryrite also occurred in the intermediate and lower levels.

Several adits in Martha Hill are accessible to workings on the Martha Vein and a vein known as Martha Branch. In these, the veins consist of banded chalcedonic quartz. A few vugs are found and contain quartz crystals up to 6mm long. The veins contain gold and silver, as indicated by assays, but it is extremely fine grained (in the order of 5 micrometres, Mr E. Coppard pers. comm.) and was not observed by the writer.

In contrast samples of mineralisation obtained from institutional collections contain abundant sulphide mineralisation and a few also contain microscopically visible gold. Of the dozen sulphide samples originating from the Martha vein only three are located to specific levels; 14047 (Wh44) from 7 level and 14050 (Wh47) and 14052 (Wh50) from 10 level. Presumably the remainder are also from deep levels. Because the time and spatial relationships between the specimens is unknown and they differ widely in content a detailed account of the petrography of individual specimens is not given here but may be found in Appendix VI. The following description summarises the most important characteristics of the suite of samples.

Most samples contain sphalerite, galena, chalcopryrite and pyrite, some contain acanthite and/or electrum (14032,

14043, 14046, 14047, 14048 and 14052), two contain pyrrhotite (13978 and 14040) and one contains tetrahedrite (14052). Most are banded with individual bands containing sphalerite, galena, pyrite and chalcopyrite in various quantities, or associations of sphalerite and galena, or pyrite and chalcopyrite. A period of chalcopyrite enclosing euhedral pyrite occurs in 14047 (Wh44; 7 level) and 14050 (Wh47; 10 level). Sphalerite and galena bands generally have sphalerite predominating and some (13978, 14040 and 14046) contain complex orientated intergrowths. In 14046 (Wh43) "streaks" of galena occur in sphalerite and in 13978 (Wh27) and 14040 (Wh29) "streaks" of galena in various combinations with one or more of pyrite, chalcopyrite and pyrrhotite occur in sphalerite (Fig. 4-25). Also in these specimens some sphalerite grains contain inclusions of these minerals in a poikilitic texture (Fig. 4-26) which is interpreted as being cross-sections of the "streaky" texture. Samples 14049 (Wh42) and 14052 (Wh50; 10 level) exhibit a lamellar texture of sphalerite in quartz.

Electrum occurs as blebs (5 micrometres) in galena, solitary in quartz or as grains intergrown with galena (av. 0.01, max. 0.02mm) in 14047 (Wh44; 7 level) but generally in pyrite in 14046 (Wh43).

Rosemont Hill Veins

The mineralisation in the Rosemont Hill area occurred in four north-west trending (parallel to the major Martha vein system) veins known as the Union, Mascotte, Amaranth and Gladstone, and the NNW trending Silverton Vein (Fig. I-S-1). Most of the fields production came from the Union Vein. Several unmineralised "quartz blows" (massive lenticular bodies of chalcedonic quartz) also occurred outcropping in the area (Fig. I-S-3) and were interpreted as sinters by Bell & Fraser (1912).

Only scant information is available concerning the mineralisation of the veins because the early writers were unable to enter the mines and observed only surface exposures, dump material, mine plans and mine records. However, the following description is gleaned from Bell & Fraser (1912) and Morgan (1924).

Figure I-S-5: Histograms of primary fluid inclusion filling temperatures and apparent salinities for samples of quartz and calcite from Waihi. The individual measurements are listed in Appendix III. Samples 14045, 14051 and 74/7/10 contain vapour rich and vapour filled inclusions, in addition to liquid-vapour normal types, indicating that periods of boiling occurred during mineral deposition.

The economic mineralisation occurred near the surface below poorly mineralised outcrop. Fine grained electrum (up to 30 micrometres, Mr E. Coppard pers. comm.) and acanthite occurred in quartz and quartz pseudomorphs after calcite gangue. Primary calcite was apparently absent. The ore was considered to be oxidised, being stained with iron and manganese oxides and containing "remnants" of pyrite and chalcopyrite (galena and sphalerite were suspected to have occurred in the original vein material). Mustard gold was found in some specimens and was attributed to secondary enrichment.

Te, Se and Sb were detected in analyses of ore (Bell & Fraser, 1912; Morgan, 1924). The former was attributed to hessite, identified in some material, whereas the latter was believed by Morgan to indicate the presence of pyrargyrite.

Morgan listed several assays of ore from the different veins in which the Au:Ag ratio is typically around 1:6 with a range of 1:1 to 1:100. In another section (Morgan, 1924 p132) he suggested that the Au:Ag ratio was approximately 1:1 but quotes a value of 1:2.5 suggested by Griffiths for the Silverton Lode.

FLUID INCLUSIONS

Primary fluid inclusions in samples of quartz and calcite from the Martha Mine are rare and of small size. They are generally two phase, liquid plus vapour normal types but samples 14045 (Wh41; Empire Vein 12 level) and possibly also samples 14051 and 74/7/10 (Wh49 and Wh46 respectively; both unlocated) contain vapour rich and vapour filled inclusions indicating that the hydrothermal fluid was boiling at the time of their entrapment.

Results of filling temperature and salinity (calculated from freezing temperatures) determinations are presented as histograms in Fig. I-S-5. Because of their small size only a few inclusions were suitable for freezing temperature measurements and hence the small number of salinity results.

Pressure - salinity corrections required for filling temperatures of samples other than 14045 (Wh41), 14051 (Wh49)

Figure I-S-6: Composite primary fluid inclusion filling temperature histogram for samples of quartz from the upper levels of the Martha Mine (samples 13913, 14035, 14036 and 14037). The mode of the histogram is between 190 and 200°C, similar to the average value of approximately 200°C.

and 74/7/10 (Wh46) are less than 15°C . A value of 10°C is suggested for all unlocated samples, whereas the corrections for 14044 (Wh40; 5 level) is less than 5°C and those for samples 14036 (Wh8), 14037 (Wh10) and 14038 (Wh15) are negligible (probably only 2 or 3°C).

Samples 13913 (Wh24), 14035 (Wh4), 14036 (Wh8) and 14037 (Wh10), consisting of small quartz crystals collected from rare vugs in otherwise banded chalcedonic or finely crystalline quartz in the upper levels, have filling temperatures ranging from 150 to 290°C . When grouped together (Fig. I-S-6) they occur predominantly between 190 and 230°C . The mode of the histogram (Fig. I-S-6) is around 190 - 200°C and the measurements average approximately 200°C . Although visible mineralisation is not present assays of the banded quartz by Mineral Resources Ltd indicate that gold and silver are present. Therefore an average temperature of 200°C is deduced for shallow level gold - silver mineralisation.

Vug quartz crystals growing on earlier quartz plus sulphide banded vein mineralisation (sample 14051) indicate temperatures of 260 to 290°C following sulphide deposition in intermediate or deep levels (the sample is unlocated).

Amethystine quartz from Empire 12 level (sample 14045) was deposited between approximately 260 and 290°C , whereas unlocated amethystine quartz of samples 14042 and 77/7/10 indicate depositional temperatures in the 210 to 250°C range.

The three samples of calcite appear to have been deposited during different phases at different temperatures: sample 14030 (GJ1) around 250°C , 14031 (GJ2) 230 - 190°C and 14044 (Wh40; 5 level) 210 - 180°C .

SULPHUR ISOTOPES

$\delta^{34}\text{S}$ values of sulphide minerals from samples 14039 (Wh28), 14041 (Wh30) and 14051 (Wh49) are listed in Table 9-1. Fine banding and complex intergrowth textures (e.g. Figs. 4-25 and 4-26) precluded separation of cogenetic sulphide minerals from other Waihi samples.

The measured $\delta^{34}\text{S}$ values range from -1.0 per mil

Figure I-S-7: Depth of mineralisation in the Martha Vein system, based on evidence of boiling at 12 level and Brathwaite's (1980) comparison of the hydrothermal alteration mineral assemblages with those of modern geothermal systems. The depth ranges shown for some minerals are based on their occurrence in the mined ore, as noted by Bell & Fraser (1912) and Morgan (1924).

(galena) to +2.1 per mil (pyrite). Fractionation between sphalerite - galena pairs indicate depositional temperatures of 315° (sample 14041), 335°C (sample 14039) and 370°C (sample 14051). All samples come from institutional collections and were described as originating from the "Martha Mine". Presumably they were collected from one of the deep levels on the Martha Vein where sulphide ore was common.

HYDROGEN ISOTOPES

Fluid inclusions in sample 14035 (Wh4) contain water with a δD value of -44.5 per mil. Several different origins are possible: meteoric water precipitated during a cooler climate than at present, modified magmatic water, mixed magmatic - meteoric waters and lastly formation (connate) water. An origin from meteoric water is favoured here.

DEPTH OF MINERALISATION

A scale of depth below the surface at the time of mineralisation is shown in Fig. I-S-7 for the Martha vein system. The surface datum is considered to be now represented by a level 200m above Martha Trig. The evidence for choosing this particular datum is the near surface style mineralisation in the upper levels and the pressure - depth constraints of the hydrothermal fluid boiling on 12 level.

The reconstruction is consistent with the depth of mineralisation indicated by the hydrothermal alteration assemblages; 425 - 600m (Brathwaite 1980).

THERMOCHEMISTRY

Introduction

Three mineralisations of the Waihi Mine are modelled as follows:

(a) deep level quartz, calcite, K-feldspar, sericite, pyrite, chalcopryite, sphalerite, galena, acanthite, electrum, ⁺ pyrrhotite at 325°C.

(b) intermediate level quartz, calcite, sericite, K-feldspar, pyrite, acanthite, electrum, ⁺ chalcopryite, ⁺ sphalerite, ⁺ galena at 280°C.

TABLE I-S-2: General thermochemical parameters for three different environments of mineral deposition in the Martha Vein System, Waihi.

	Environment			Reference
	Low Levels	Intermediate Levels	Upper Levels	
Temperature °C	325	280	220	Table V-1
True ionic strength	0.20	0.23	0.30	"
Salinity (m NaCl eq.)	0.33	0.33	0.33	"
mK^+	0.070	0.057	0.039	"
pH	5.5	5.5	5.6	See text
pH of kaolinite/sericite boundary	4.1	4.2	4.6	Table V-1
pH of sericite/K-feldspar boundary	5.5	5.7	6.0	"
Total S ($\log mS$)	-2.0	-2.0	-3.0	See text
Log fS_2 (sphalerite comp.)	-8.0to-10.1			Table V-4A
(electrum comp.)		-9.7to-10.3	-11.1	Table V-6A
Log fO_2	-30.5to-32.2 (Fig. I-S-9)	-34.2to-36.0 (Fig. I-S-10)	-39.0to -39.5 (Fig I-S-12)	figures cited
Log fCO_2	+1.7	+1.9	+2.0	Table V-1

(c) shallow level quartz, sericite, K-feldspar, pyrite, acanthite, electrum at 220°C.

Table I-S-2 lists some of the parameters for these different mineralisations.

Deep level mineralisation

The geochemical environment of the deep level mineralisation is limited on the fS_2 versus fO_2 diagram (Fig. I-S-8) by the presence of pyrite and chalcopryrite but absence of hematite, magnetite and bornite. Pyrrhotite is present with pyrite and chalcopryrite as inclusions in sphalerite in only two samples studied.

The FeS content of sphalerites indicate a range in $\log fS_2$ values from -8.0 to -12.1, whereas the graphite/ CO_2 and calcite/anhydrite boundaries, defined by the $\log fCO_2$ value of +1.7 (extrapolated from the fluid inclusion analyses of late stage quartz samples) limit fO_2 between -32.7 and -29.2.

The mineralisation plots in the reduced sulphur species region of the fO_2 versus pH diagram (shaded area of Fig. I-S-9) and indicates a fluid containing sulphur in solution predominantly as HS^- .

Intermediate level mineralisation

Intermediate level quartz, calcite, sericite, K-feldspar, pyrite, acanthite, electrum $\pm$ chalcopryrite, $\pm$ sphalerite and $\pm$ galena mineralisation is represented by the shaded area in the fO_2 versus pH diagram (Fig. I-S-10). The mole fraction of silver in electrum indicates $\log fS_2$ values between -9.7 and -10.3 at 280°C. The absence of magnetite and hematite restricts the mineralisation to the reduced sulphur species field.

The $\log fS_2$ values stated, are possible at $\log fCO_2 = +1.9$ only when the graphite free mineralisation is in equilibrium with K-feldspar. Assemblages containing sericite must have been deposited at lower CO_2 fugacities.

Figure I-S-8: fS_2 versus fO_2 diagram at 325°C showing the geochemical environment (shaded) of quartz (+ calcite) + pyrite + chalcopyrite + sphalerite + galena + acanthite + electrum + tetrahedrite + pyrrhotite vein mineralisation in the low levels of the Martha vein system, Waihi. (See Table I-S-2 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-S-9: fO_2 versus pH diagram at 325°C and $a_S = 0.01$ showing the geochemical environment (shaded) of quartz (+ calcite) + pyrite + chalcopyrite + sphalerite + galena + acanthite + electrum + tetrahedrite + pyrrhotite vein mineralisation in the low levels of the Martha Vein system, Waihi. pH of the calcite soluble/insoluble boundary = 5.9. (See Table I-S-2 for other relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-S-10: fO_2 versus pH diagram at $280^\circ C$ and $a_S = 0.01m$ showing the geochemical environment (shaded) of quartz (+ calcite) + pyrite + acanthite + electrum + chalcopyrite + sphalerite + galena vein mineralisation in the intermediate levels of the Martha Vein system, Waihi. (See Table I-S-2 for relevant thermochemical parameters and Appendix V for methods of construction.)

$f\text{Te}_2$ and $m\pm\text{Te}$ in solution were probably higher in the Rosemont Hill veins than in the Martha Vein System as indicated by the occurrence of hessite in the former but acanthite in the latter (c.f. Figs. 11-4 and 11-5).

Shallow level mineralisation

The geochemical environment of the shall level mineralisation is shown as shaded areas in Figs. I-S-11 and I-S-12.

Samples strictly of the mineralisation modelled here were not available for study but the mole fraction of silver in electrum in sample 14032 (GJ3) (low temperature pyrite, acanthite, sphalerite, galena and electrum mineralisation) is used here to calculate an approximate value for sulphur fugacity of the low temperature mineralisation. A $\log f\text{S}_2$ value of -11.1 is indicated.

$\log f\text{O}_2$ is limited between -39.8 (graphite/ CO_2 boundary) and -36.6 (calcite/anhydrite boundary) at $\log f\text{S}_2 = -11.1$ by the presence of calcite but absence of graphite and anhydrite (Fig. I-S-11).

A total sulphur in solution concentration of 0.001M was used for the construction of the $f\text{O}_2$ versus pH diagram

Figure I-S-11: fS_2 versus fO_2 diagram at 220°C showing the geochemical environment (line of crosses) of quartz (+ calcite) + pyrite + acanthite + electrum vein mineralisation in the upper levels of the Martha Vein system. (See Table I-S-2 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-S-12: fO_2 versus pH diagram at $220^\circ C$ and $a_S = 0.001$ showing the geochemical environment (shaded) of quartz (+ calcite) + pyrite + acanthite + electrum vein mineralisation in the upper levels of the Martha Vein system, Waihi. The pH of the calcite soluble/insoluble boundary = 4.9. (See Table I-S-2 for other relevant thermochemical parameters and Appendix V for methods of construction.)

complexes predominantly from this source. The fluid ascended via the various fault fissures depositing some of its constituents along the way.

The vertical metal zonation in the veins at Waihi is attributed to changing physicochemical conditions with depth resulting from fluid - wall rock reactions, boiling horizons and mixing of the hydrothermal fluid with oxygenated waters near the surface. Variations in $f\text{CO}_2$ are considered to have also had a marked effect on mineral deposition (and wall rock alteration) and may have been important in causing hydrothermal leaching of calcite. Extrapolation of the $f\text{CO}_2$ values suggested for the intermediate and shallow level late stage fluid (fluid inclusion analyses) to the deep level environment indicates that calcite was stable at only high values of pH. Therefore, although large quantities of calcite were deposited, especially during the early stages of vein filling, periods of deposition may have alternated with episodes of hydrothermal leaching. This alternating deposition - solution process was probably caused by fluctuations in temperature, pH and $f\text{CO}_2$, possibly as a result of boiling, reactions with wall rocks or variations in the temperature and composition of the fluid supplied to the system (source variations).

The large size of the Waihi deposits suggest that the hydrothermal system and the various mechanism of deposition were active over a long period of time. Suitable structural environments for vein formation must have been continually produced during this period. In fact the structural aspects may be the most important factors that determined the size of the Waihi deposit and may give a clue to its genesis.

The Martha Vein System comprises a group of veins with three predominant trends: NW (Martha, Welcome and north-eastern sections of the Empire and Royal Lodes), NNW (Edward and Albert Lodes) and WNW (south-western sections of the Empire and Royal Lodes) forming an overall loop vein pattern. The north-eastern extension is cut by a dextral transcurrent fault striking 005° (Wellman, 1954). The veins converge with depth (Fig. I-S-4), generally onto the Martha Lode, and the displacements of country rock form a series of collapsed

Figure I-S-13: Block diagram showing the vein pattern and relative displacements of country rock in the Martha vein system (Fig. I-S-13A). The system appears to comprise a series of collapsed inverted elliptical cones, one inside the other and resembles the structures that Koide & Bhattacharji (1975) and Koide (in part VII-2 of Imai, 1978) consider occur above some magmatic intrusions (Fig. I-S-13B).

inverted elliptical cones, one inside the other, produced by tension in NW - SE directions. Work by Koide & Bhattacharji (1975) and Koide (in Part VII-2 of Imai, 1978) indicates that such a pattern could be produced above a magmatic intrusion (Fig. I-S-13). However, this interpretation requires that the upper pyroxene andesite be present prior to vein formation (magmatic intrusion) which may not be compatible with the apparent absence of significant hydrothermal alteration in this unit (c.f. Bell & Fraser, 1912; Morgan, 1924).

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KARANGAHAKEINTRODUCTION

The mines in the Karangahake area produced 125 million grams (4,011,741 ounces) from 1.14 million tonnes of quartz between 1875 and the 1930's. Although a large number of small companies were active in the early years of the fields development, the high cost of mining and ore treatment due to the steep and rugged terrain, and low recovery of gold from the ore, allowed two companies, Talisman and Crown, to eventually take over the rest.

The Talisman was the second largest mine in the province, after Waihi, and the third largest in New Zealand.

The Karangahake mining area is also notable for the first application of the cyanide treatment process for extraction of gold from the crushed ore, introduced by the Crown Mines in 1899.

The investigation by Henderson & Bartrum (1913) is the most recent published original geological description of the deposits. They have since been reviewed by Downey (1935) and Williams (1965, 1974).

In the early 1970's Southern Cross Minerals reopened 7 and 8 levels for Au and Ag mining but after spending most of their money on plant and machinery found insufficient gold in the veins for continued work. Around 1972 they diamond drilled from just above river level (corresponding to 11 level in the mine) down several hundred feet to intersect the major quartz veins. The results of this activity are held on closed file at the Mines Department. Recently Southern Cross have renewed activity in association with an overseas company.

Dr. R.L. Brathwaite of the Geological Survey is presently investigating the geology, hydrothermal alteration and mineralisation of the Karangahake area.

GEOLOGY

The country rocks in the Karangahake area are mostly Coromandel Group andesite flows and pyroclastics, however Whitianga Group spherulitic rhyolite caps Mt. Karangahake.

Henderson & Bartrum (1913) described the succession of rocks in the Talisman Mine, in ascending order, as follows: (a) andesite, (b) breccia with argillite fragments, (c) andesitic tuff, (d) breccia with andesitic fragments only, (e) augite - hypersthene andesite and (f) spherulitic dacite (regarded here as spherulitic rhyolite). They noted (Henderson & Bartrum, 1913 p55) that basement argillite (Manaia Hill Group) was reported to have been reached at the bottom (335m below sea level) of a drill hole sunk by the Woodstock Company. The lowest level of workings in the mine, 16 level, was approximately (scaled off Fig. 23 of Downey, 1935) 160m below sea level.

HYDROTHERMAL ALTERATION

The hydrothermal alteration of the andesites was described by Henderson & Bartrum (1913) as propylitic. They observed the following sequence:

1. The first stages of alteration are marked by the conversion of hypersthene and feldspars to chlorite, some sericite and two unidentified minerals, one described as "serpentinous material" and the other as "resembling uralite".
2. Further alteration involves the breakdown of augite to chlorite, epidote, calcite and secondary quartz and the conversion of the "serpentinous material" to chlorite.
3. Feldspars are altered to sericite, calcite and quartz. Epidote is converted to chlorite, calcite and quartz. Siderite and sometimes leucoxene are produced from the breakdown of iron oxides.
4. Intense alteration adjacent to the veins produces a rock consisting of a fine whitish mixture of quartz, sericite, calcite and pyrite.

In another section of their bulletin, Henderson & Bartrum mention that adularia was present in some rocks. Dr. R.L. Brathwaite (pers. comm.) considers that adularia is more

Figure I-T-1: Mine workings and veins of the Karangahake area (from Williams, 1974; after Henderson & Bartrum, 1913.)

common than implied by Henderson & Bartrum's description and is a major alteration product in the wall rocks adjacent to the veins.

The Whitianga Group rhyolite rocks capping Mt. Karangahake are also hydrothermally altered (Brathwaite, pers. comm.), however the specific types of alteration have not been described.

K - Ar AGE DATA

Hydrothermally altered andesites from Karangahake have been K-Ar dated at 4.8 m.y. (2 samples), whereas samples of unaltered andesite gave ages of 4.9 and 5.2 m.y. (Dr C.J.D. Adams and Dr A. Wodzicki pers. comm.).

MINERALISATION

Mineralisation occurs in three major veins (Fig. I-T-1); the Crown, Welcome (both Crown Mines) and Maria (Talisman and Woodstock Mines). All Karangahake samples studied here are from the Maria Vein.

Crown Vein

The Crown vein was the smallest producer of gold of the three major veins. It strikes north-north-east and dips westward at a high angle. From the cross-section (Fig. I-T-2) the Crown vein appears to be a "footwall dropper" from the Welcome, although no junction was ever found. Little geological information is recorded although Henderson & Bartrum (1913) noted that the lode was best developed on 3 level.

Welcome Vein

The Welcome vein was traced for 1.2km and found to strike north-north-east and dip 50° to the west. It is displaced by a number of faults dividing it into blocks but no definite ore shoots were recognised. "Oxidised" ore occurred in all levels with the exception of a small quantity of sulphide ore in the deepest level. The gold to silver ratio in oxidised ore was 1:1. The vein was mined from 12 levels (six adit and six shaft) and Henderson & Bartrum (1913) noted that levels 1 to 3 contained little gold.

Figure I-T-2: Cross section of the veins in Karangahake Mountain (from Henderson & Bartrum, 1913.)

Maria Vein

The Maria vein was traced for 2.0km and, in contrast to the general north east strike of most of the other veins, was found to have a composite strike being, from north to south: north-east, north-west, north-east and north (Fig. I-T-1). In the lower levels of the north striking section numerous small stringers, striking north-east, join the hanging wall but do not leave the footwall.

The Maria proved to be the most profitable vein at Karangahake producing approximately ten times as much gold and silver as the Welcome and Crown Veins together. South of the Waitawheta River it contained four ore shoots known as the Woodstock, Talisman, Bonanza and Dubbo (Fig. I-T-3). Practically all the rich ore came from the Talisman and Bonanza shoots which were worked from 14 levels and several intermediate levels, eleven of which were adit levels, the remaining being from an underground shaft.

The Bonanza section of the Maria Reef is the only vein section in the Karangahake area where the geology was recorded in any detail. Henderson & Bartrum (1913) noted changes in vein content with depth and these are summarised in Fig. I-T-4. In the upper and intermediate levels, the vein consists of quartz and quartz pseudomorphs after calcite and contains marcasite, electrum and acanthite, whereas in the lower levels quartz and calcite contain pyrite, sphalerite, chalcopryite, galena, acanthite and electrum. In addition the presence of hessite was suspected by Henderson & Bartrum (Te was detected in some ore assays) and Merchant (1978) noted its occurrence in a sample from an unstated location in the Maria Lode. The gold to silver ratio varies systematically towards the lowest value in 11 level (1:15) and reaches the highest recorded value in the intermediate level between 14 and 15 levels, where gold predominates over silver. In the low levels, barren portions of the vein are marked by the presence of abundant calcite.

Southern Cross Minerals Exploration Ltd reopened 7 and 8 levels in the late 1960's - early 1970's but found insufficient

Figure I-T-3: Longitudinal section of the Talisman Mine (mostly the Maria Vein), Karangahake showing the stoped blocks (shaded) and ore shoots (Woodstock, Talisman, Bonanza and Dubbo). (From Fig. 23 of Downey, 1935.)

Figure I-T-4: Some mineralogical changes with depth in the Bonanza section of the Maria Vein (compiled from descriptions by Henderson & Bartrum, 1913). The hypothetical depth of mineralisation scale given down the left hand side of the diagram uses a surface datum 200m above Mt. Karangahake.

gold values for profitable extraction. The present caretakers have opened 8 level to beyond the Talisman shaft. The Maria vein is exposed in a cross cut and here consists of mainly chalcedonic quartz but many vugs containing small euhedral quartz crystals occur. No visible mineralisation is present.

No. 11 level is also presently accessible but only to the beginning of the Woodstock section. A few quartz veins and a stope were found but no visible mineralisation other than pyrite.

A few samples of sulphide mineralisation were obtained from institutional collections. The petrography of the individual specimens is described in Appendix VII and therefore only a brief account is given here.

A sample of a crustified vein from 14 level consists of banded quartz and calcite with sphalerite, galena, chalcopryite, pyrite and electrum (Fig. 4-6). Sphalerite and galena occur in complex intergrowths (e.g. Figs. 4-27 and 4-28) and in a few bands sphalerite contains inclusions of galena [†] chalcopryite [†] electrum in poikilitic (Fig. 4-29), dendritic - "streaky" (Fig. 4-30) and myrmekitic textures. Electrum also occurs as inclusions in chalcopryite and, at a later stage, with quartz invading the earlier sulphides (Fig. 4-31).

Other samples contain bands of fine grained sulphides, and in one case rare electrum, in which the metallic minerals generally occur as individual grains scattered in quartz. The ratio of sulphides to gangue is approximately 1:3 in the sulphide bands but much less when the whole specimen is considered. Silver minerals apart from electrum were not identified in the specimens and their absence may account for the high Au:Ag ratios reported from the lowest levels by Henderson & Bartrum (1913).

FLUID INCLUSIONS

Primary fluid inclusions in quartz from 11 level (sample 14022) and 8 level (sample 14021) of the Talisman mine and outcrop of the Marmion Extended Lode (sample 14029) are rare

Figure I-T-5: Histograms of primary fluid inclusion filling temperatures and apparent salinities for samples of quartz from the Talisman Mine, Karangahake: 14021, 11 level; 14022, 8 level; 14029, Marmion Extended Lode. The individual measurements are listed in Appendix III.

and of small size. They are two phase, liquid plus vapour, normal types.

Filling temperatures and salinities are shown as histograms in Fig. I-T-5. Pressure-salinity corrections in the order of 5 - 10°C must be added to the filling temperatures. Corrected filling temperatures indicate depositional temperatures around 230°C for the 8 level sample and 260°C for the others.

Only a few inclusions in the Talisman samples were suitable for freezing temperature measurements and these indicate fluid compositions of relatively high salinity, around 2.5 eq. wt. % NaCl.

SULPHUR ISOTOPES

Complicated intergrowths of sulphide minerals (e.g. Figs. 4-27 to 4-30) precluded separation of cogenetic sulphide minerals in all samples from Karangahake except sample 14023 (TL 17). $\delta^{34}\text{S}$ values of this sample are; chalcopyrite +3.0 per mil, sphalerite +2.9 per mil and galena +0.7 per mil. The fractionation between sphalerite and galena indicates a depositional temperature of 290°C.

The original location of sample 14023 (TL 17) within the Talisman Mine is not known but because it contains abundant medium grained sulphides, and sulphides were reported by Henderson & Bartrum (1913) to be common only below 11 level, it presumably came from this lower region.

DEPTH OF MINERALISATION

A scale of depth below the surface at the time of mineralisation is shown in Fig. I-T-4. Assuming that mineralisation occurred around the time of rhyolite volcanism and allowing for some rhyolite cover, the original surface is considered to have been approximately 200m above the trig on top of Mt Karangahake.

THERMOCHEMISTRY

The geochemical environment of the quartz, calcite, pyrite,

Figure I-T-6: fO_2 versus pH diagram at $300^\circ C$ and $a_S = 0.01m$ showing the geochemical environment of (A) quartz (+ calcite) + pyrite + chalcopyrite + sphalerite + galena and (B) quartz + electrum mineralisations of the Maria Vein in the low levels of the Talisman Mine, Karangahake. $\bar{I} = 0.27$, $mK^+ = 0.075$, $pH = 5 - 5.5$, $\log fS_2$ from sphalerite compositions = -9.4 to -9.9 (A), $\log fS_2$ from electrum compositions = -8.6 to -8.7 (B), and $\log fCO_2$ (estimated) = $+1.5$. (Methods of construction are described in Appendix V.)

sphalerite, galena, chalcopyrite and electrum mineralisation in the low levels is modelled in the fO_2 versus pH diagram (Fig. I-T-6) at a temperature of 300°C and a total sulphur in solution concentration of 0.01M.

Fraser & Adams (1907) description of the hydrothermal alteration and unpublished work by Brathwaite (pers. comm.) indicate that the fluids were in equilibrium with sericite and adularia in the wall rocks, restricting pH to values near the sericite/K-feldspar boundary (5 to 5.5).

Log fS_2 values between -9.4 and -9.9 are indicated by the iron content of sphalerites, whereas values between -8.6 and -8.7 are indicated by the mole fraction of silver in slightly later electrum. Therefore two fields of mineralisation, A; base metal and B; electrum, are shown in Fig. I-T-6. Both mineralisations plot in the reduced sulphur species predominant field of the diagram. Values of log fCO_2 up to the general value of +1.5 are possible in the absence of graphite.

GENESIS

Based on the values of $\delta^{34}\text{S}$ for the sulphide minerals and the apparent presence of sulphur in solution predominantly in reduced form, a value of +5 per mil is assigned to $\delta^{34}\text{S}_{\text{S}}$ (i.e. $\delta^{34}\text{S}_{\text{sulphide minerals}} \approx \delta^{34}\text{S}_{\text{H}_2\text{S}} \approx \delta^{34}\text{S}_{\text{S}}$). The most likely source of sulphur with this $\delta^{34}\text{S}$ value is magmatic sulphur.

The short interval between the deposition of the andesite rocks at Karangahake and their subsequent hydrothermal alteration, as indicated by the K-Ar ages, suggests that the early stages of vein formation and mineralisation may have been associated with the waning of andesitic volcanism. Hydrothermal activity continued during rhyolite volcanism as evidenced by the presence of hydrothermal alteration in the rhyolite rocks capping Mt. Karangahake.

Favourable structure allowed the development of a large geothermal system in the Karangahake area with upward migration

of the hydrothermal fluid (predominantly meteoric water?) via the various fault fissures. A vertically zoned mineral sequence was deposited in the veins as a result of the changing physicochemical conditions with decreasing depth. Base metal with minor precious metal mineralisation was deposited at depth with quartz calcite and adularia, as a response to fluid - wall rock reactions and varying $f\text{CO}_2$. Mixing of the hydrothermal fluid with oxygenated near surface waters and decreasing temperature and pH were the probable causes of precious metal deposition in the shallow levels.

The large size of the Karangahake deposits implies that a large quantity of hydrothermal fluid circulated through the system and that it was active for a long time.

REFERENCES AND BIBLIOGRAPHY

DOWNNEY, J.F.	1935: see pp 199-211 and 287
HENDERSON, J.; BARTRUM, J.A.	1913: see pp 84-87, 89-101 and 110 to 116
SCHOFIELD, J.C.	1967
WILLIAMS, G.J.	1974: see pp 114-117

TUI MINEINTRODUCTION

Tui Mine, under management of Norpac Mining Co., produced copper, lead and zinc concentrates for export to Japan between 1967 and 1974. Total production for this period was 7,291 tonnes Zn, 4,424 tonnes Pb, 404 tonnes Cu, 2.49 million grams (80,000 ounces) Ag and 60,000 grams (1,952 ounces) Au. (All figures for pure metals, Mines Division records).

During this period of operation the deposit was studied by Auckland University students (Cochrane, 1969; Weigel, 1978) and several members of the DSIR (Weissberg & Wodzicki, 1970; Wodzicki & Weissberg, 1970; Adams et al., 1974; Robinson, 1974; Ansin, 1975).

Before closure of the mine the Mines Department funded the drilling of two holes to test the mineralisation below Champion 5 level (Fig. I-U-1). Both holes were drilled from the same location in 5 level but at different angles: 45° and 70°. The results are reported by Ker & Wodzicki (in press).

GEOLOGY

Tui Mine is located on Mt Te Aroha, a 952m high peak composed of andesites of the Coromandel Group. Cochrane (1969) collectively named them Te Aroha Andesites and subdivided them as follows:

1. Tui Andesite; a massive, quartz free two pyroxene andesite, occurring on the surface below an elevation of 488m.
2. Ruakaka Quartz Andesite; a quartz andesite with massive breccia and tuffaceous phases, occurring on the surface between elevations of 488m and 914m.
3. Summit Andesite; a massive andesite, identical with the Tui Andesite, forming a hard cap on the summit of Mt Te Aroha.

Figure I-U-1: Geology and workings in the Tui Mine. (From Wodzicki & Weissberg, 1970.)

The geology within the mine is shown in Fig. I-U-1 reproduced from Wodzicki & Weissberg (1970). The predominant rock type, pyroxene andesite, is equivalent to Cochrane's Tui Andesite, whereas all the other units noted belong to Cochrane's Ruakaka Quartz Andesite. The sequence of rocks in 5 level cross cut in Fig. I-U-1 is similar to Cochrane's cross section (Fig. 14 of Cochrane, 1969).

HYDROTHERMAL ALTERATION

Hydrothermal alteration in the Tui Mine area is propylitic with various assemblages of chlorite, pyrite, epidote, adularia, sericite, calcite, quartz, montmorillonite and kaolinite. Weissberg & Wodzicki (1970) classified these assemblages into four groups (Fig. I-U-2) with the progression from Groups I to IV representing increasing intensity of alteration. The most altered rocks (Group IV) occur in narrow zones adjacent to and in between the two major veins, the Champion and Ruakaka Lodes.

Wodzicki & Weissberg (1970) considered that at a given location, adularia formed before sericite and that montmorillonite, interlayered illite-montmorillonite (sericite) and kaolinite were formed by late stage low temperature fluids.

K - Ar AGE DATA

Adams *et al* (1974) determined whole-rock K-Ar ages on nine samples of andesite, displaying various degrees of hydrothermal alteration, from Tui Mine. The rocks yielded a spread of ages from 16.2 my to 2.6 my. Adams *et al* (1974) concluded that the maximum age of 16.2 my (the least altered andesite) was a close approximation to the eruptive age of the andesites, whereas hydrothermal alteration occurred at least 2.6 my, but less than 7 my ago.

MINERALISATION

Zinc, - lead - copper mineralisation occurs in two quartz veins, the Champion and Ruakaka Lodes, formed in fissures of normal faults dipping between 50°-80° north-west, and 50°-85° south respectively. Several stages of fault movement, brecciation of country rock and

Figure I-U-2: Changes in mineralogy with increasing intensity of hydrothermal alteration (Group I weakly altered through to Group IV strongly altered).
(From Wodzicki & Weissberg, 1970.)

earlier vein material, and mineral deposition occurred ultimately forming quartz veins up to 2m (Champion) and 8m (Ruakaka) thick. The paragenetic diagram (Fig. I-U-3) and following description are compiled from several complimentary published descriptions of the mineralisation (Cochrane, 1969; Wodzicki & Weissberg, 1970; Robinson, 1974; Ansin, 1975; Ker & Wodzicki, in press) and the writers observations of Stage 1 material.

The major vein constituents are quartz, sphalerite, galena, pyrite, kaolinite and chalcopryrite. Minor amounts of carbonate, adularia, epidote, wairakite, tetrahedrite, marcasite, cinnabar, barite, hematite, gold and prehnite are also found. Recently bornite, wolframite and bismuth tellurides were reported (Merchant, 1978; Weigel, 1979). Bismuthinite and tetradymite were identified during this study.

Stage 1. The first stage of mineralisation is characterised by a milky quartz cemented wall rock breccia 1 to 5m in width. Pyrite occurs disseminated in the wall rocks and in the milky quartz. On Champion 4 and 5 levels, between 425 and 700m N.E. of the 5 level access cross cut, significant quantities of chalcopryrite, sphalerite and galena in addition to quartz, pyrite and minor hematite occur (Ker & Wodzicki, in press). Chalcopryrite preceeds galena and sphalerite. The sulphides are generally medium grained (less than 2mm) and the lode, commonly wider than 1m, has poorly defined walls.

Samples of Stage 1 material from M Stope, 5 level Champion, contain chalcopryrite, pyrite, hematite, bismuthinite, gold and tetradymite. The following sequence, deduced from the specimens shown in Fig. I-U-4, is tentatively assigned:

1. massive chalcopryrite with rare marcasite balls (now represented by pyrite) infilling wall rock and quartz breccia (fragments up to 10mm).
2. quartz plus bismuthinite, gold and tetradymite (Figs. 4-10 and 4-11).
3. quartz plus pyrite.
4. pyrite plus hematite plus chalcopryrite (Fig. 4-12).
5. hematite plus quartz (Fig. 4-13).
6. quartz, finally developing into vugs.

Figure I-U-3: Paragenetic sequence of minerals in the Champion and Ruakaka veins, Tui Mine. (Modified from Wodzicki & Weissberg, 1970; Robinson, 1974.)

Figure I-U-4: Cut surfaces of hand specimens containing Stage 1 chalcopyrite (bright yellow) pyrite (dull yellow) and hematite (dark red), which is brecciated, veined and coated (e.g. right hand side of specimen at top right) by Stage 2 sphalerite (brown), galena (grey) and quartz (white - translucent). The Stage 1 material also contains native gold, bismuthinite and tetradymite, not visible in hand specimen. Samples from M stope Champion Vein, courtesy of Dr H.W. Kobe. The longest dimension of the largest sample is 17cm.

Stage 2. Renewed fault movement resulted in the formation of a narrow zone (usually less than 0.6m wide, with well defined walls) and the deposition of Stage 2 minerals. These include coarse grained (greater than 10mm) galena and sphalerite followed by minor chalcopryrite, tetrahedrite, pyrite, marcasite and intermittent quartz deposition and brecciation.

Stage 2 chalcopryrite is found enclosing and partly replacing younger Stage 2 pyrite and together these minerals form veinlets in galena and sphalerite. Marcasite forms rims around chalcopryrite and a further generation of chalcopryrite in turn rims the marcasite. This third generation chalcopryrite occurs together with tetrahedrite.

In the Champion lode Stage 2 mineralisation usually occurs within the early part of the lode system (Stage 1) but in parts of 4 level it is in the footwall and in parts of 5 level it is in the hanging wall (Ker & Wodzicki). Stage 2 mineralisation in the Ruakaka Lode occurs in one horizontal ore shoot which has a variable Pb/Zn ratio with depth (low in 5 level and high in 3 and 4 levels). The ore in the lower part of the ore shoot is low grade "breccia type" cemented by Stage 2 quartz and sulphides (Ker & Wodzicki).

Stage 3. Stage 3 mineralisation is represented by quartz, kaolinite, barite, pyrite, hematite, cinnabar, and several carbonate minerals partially filling the remaining cavities and late formed joints.

Supergene sugary calcite, smithsonite coatings and cerussite infillings are shown as Stage 4 in the paragenetic diagram. Ansin (1975) recorded a number of other supergene and secondary minerals including covellite.

FLUID INCLUSIONS

Fluid inclusions in samples of Stage 2 quartz and sphalerite and Stage 3 barite are generally two phase liquid plus vapour normal types although a fibrous solid is also present in some inclusions of samples 14056 (Tui 13), 14064

Figure I-U-5: The single vapour rich primary fluid inclusion identified from Tui Mine (sample 14064, Stage 2 quartz). X63.

(Tui 22), and 14068 (Tui 28), and a vapour rich inclusion was identified in sample 14064 (Tui 22; Fig. I-U-5). The latter indicates that vapour was trapped along with liquid at the time of formation and therefore the parent hydrothermal fluid may have been boiling.

Filling temperature and salinity measurement results are presented as histograms in Figs. I-U-6A (Champion) and I-U-6B (Ruakaka).

Pressure - salinity corrections that must be added to the filling temperatures to equate them with depositional temperature are approximately 10°C . Corrected filling temperatures indicate depositional temperatures between 280 and 310°C for Stage 2 quartz and sphalerite. Filling temperatures of primary and secondary inclusions (their generation could not be determined) in Stage 3 barite record a wide temperature range from approximately 290°C down to 120°C with no well defined peak.

Salinities of primary fluid inclusions in Stage 2 quartz are higher than those of other vein deposits in the province with a maximum measurement of 6.1 eq. wt. % NaCl and an average around 3 eq. wt. % NaCl.

A partial chemical analysis of fluid inclusions in Stage 3 quartz from the Champion Lode (14054), determined by crushing and leaching experiments, indicates the presence of 5200 ppm Na^+ , 1000 ppm K^+ , 170 ppm Li^+ and 8000 ppm Cl^- . The measured Na/K ratio is in agreement with that predicted theoretically by the Na/K geothermometer at a temperature around 270°C .

SULPHUR ISOTOPES

Robinson (1974) determined $\delta^{34}\text{S}$ values for sulphides between -2.4 per mil (galena) and +4.9 per mil (sphalerite) and individual values for barite of +16.0 per mil and +19.5 per mil from samples of Tui Mine material. Fractionation between cogenetic Stage 1 pyrite-chalcopyrite pairs indicated a depositional temperature of around 400°C , whereas a temperature around 320°C was indicated for Stage 2 mineralisa-

Fig. I-U-6A

Fig. I-U-6B

Figure I-U-6: Histograms of primary fluid inclusion filling temperatures and apparent salinities for samples of quartz, sphalerite (14063) and barite (14067) from the Champion Vein (Fig. I-U-6A) and Ruakaka Vein (Fig. I-U-6B), Tui Mine. The individual measurements are listed in Appendix III.

Figure I-U-7: A plot of $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ for hypogene and supergene vein carbonates from Tui Mine (from Fig. 10 of Robinson, 1974). The temperature scale for calcite, defined for a value of $\delta^{18}\text{O}$ fluid = -1 per mil, indicates a decrease in temperature from 250°C down to approximately 60°C during Stage 3. The carbonates indicate a $\delta^{13}\text{C}$ value of -6.4 per mil for the H_2CO_3 in the fluid ($\approx \delta^{13}\text{C}_{\text{FC}}$).

tion by sphalerite - galena pairs.

An additional Stage 1 pyrite - chalcopyrite pair from the Champion Lode and a Stage 3 barite from the Ruakaka Lode were analysed during this study. The $\delta^{34}\text{S}$ values determined, +2.5, +1.7 and +18.8 respectively, conform with Robinson's data.

CARBON AND OXYGEN ISOTOPES OF CARBONATES

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of Stage 3 carbonates ranging from +5.6 to +28.3 per mil and -16.5 to +0.1 per mil respectively, were determined by Robinson (1974). When plotted on a $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ diagram (Fig. I-U-7) these analyses define a trend of decreasing temperature between 250°C and 40°C for a solution having a $\delta^{18}\text{O}$ value of -1 per mil. A $\delta^{13}\text{C}_{\text{calc}}$ value of -6.4 per mil was also calculated by Robinson (1974).

HYDROGEN AND OXYGEN ISOTOPES OF BARITE, QUARTZ, KAOLINITE AND FLUID INCLUSIONS

$\delta^{18}\text{O}$ values for Stage 2 quartz (+6.0 per mil), Stage 3 quartz (+9.2 per mil) and Stage 3 barite (+7.4 and +11.2 per mil) and δD values for Stage 3 kaolinite (-54.6 and -59.3 per mil) were determined by Robinson (1974). He also analysed fluid inclusion waters by decrepitating large (250g) samples of Stage 2 galena (δD of primary inclusions = -70.0 per mil), Stage 2 quartz (δD of secondary inclusions = -35.1 per mil), Stage 2 sphalerite (δD of secondary inclusions = -17.2 per mil) and by crushing a 300g sample of Stage 3 quartz ($\delta^{18}\text{O}$ and δD of primary inclusions were -1.0 and -24.0 per mil respectively).

The δD value of -70 per mil for Stage 2 galena inclusion water was concluded to indicate the presence of primary magmatic water, whereas other δD values were interpreted to represent water of meteoric origin. $\delta^{18}\text{O}$ values of late stage samples were considered to result by "oxygen isotope shift" from meteoric water due to reaction with wall rocks.

Figure I-U-8: Probable depth of mineralisation at Tui Mine during Stage 2 (same surface datum as used for the Waiorongomai depth reconstruction). Stage 1 mineralisation may have occurred at greater depth - pressure.

The hydrogen isotopes of fluid inclusion waters from three samples of quartz were analysed during this study. Waters from late Stage 2 quartz samples 14056 (Tui 13) and 14061 (Tui 19) have δD values of -34.3 and -34.8 per mil respectively, whereas a value of -35.0 per mil was determined for water from inclusions in Stage 3 quartz (sample 14054). These δD values are consistent with a meteoric water origin.

Problems of contamination encountered during crushing and water separation phases of analyses for this study raise some doubt over Robinson's heavy (-24 per mil) and light (-70 per mil) δD values. The former may differ from the values determined in this study because of water contamination or fractionation within the vacuum line, whereas the latter value may result from leakage of water into, or sample out of, the vacuum line.

LEAD ISOTOPES

Cooper & Richards (1969) measured the ratios of lead isotopes in samples of galena and andesite from the Tui Mine (Champion 4 and Champion 5 and 6 levels respectively), in addition to samples of galena, andesite and rhyolite from other locations in the Coromandel Peninsula. Their data, together with measurements of lead isotope ratios in Nanaia Hill Group greywacke by Armstrong & Cooper (1971), indicate that the lead in the hydrothermal veins was derived from the greywacke basement rocks (c.f. Fig. 5 of Robinson, 1974).

DEPTH OF MINERALISATION

A reconstruction of the depth regime during Stage 2 mineralisation is illustrated in Fig. I-U-8. The surface datum is taken at 400m above the summit of Mt Te Aroha, the same as used for the Waiorongonui reconstruction. Stage 1 mineralisation may have occurred at greater depths (e.g. 1km), the difference in depth between Stage 1 and Stage 2 being due to uplift and erosion between mineralising episodes.

THERMOCHEMISTRY

Robinson (1974) modelled the Tui Mine mineralisations on

Figure I-U-9: The geochemical environment of Stages 1 and 2a mineralisations (star) calculated on an fO_2 versus pH diagram at 350°C and $\pm S = 0.01m$ by Robinson (1974, Fig. 7).

Figure I-U-10: The geochemical environment of Stage 3 mineralisation (star) calculated on an fO_2 versus pH diagram at 150°C and $\pm S = 0.001m$ by Robinson (1974, Fig. 8).

fO_2 versus pH diagrams: Stages 1 and 2 at $350^{\circ}C$ (Fig. I-U-9) and Stage 3 at $150^{\circ}C$ (Fig. I-U-10). By combining mineralogical and stable isotope evidence he concluded that the chemical conditions during mineral deposition were represented by the regions marked with stars in Figs. I-U-9 and I-U-10.

Additional information on the temperature of Stage 2 (fluid inclusion studies), mineralogy of Stage 1 (bornite? wolframite?) and fS_2 conditions of Stage 1 (gold compositions) and Stage 2 (sphalerite compositions) mineralisations warrants a reappraisal of the geochemical environment of these systems.

Table I-U-1 lists some of the parameters used here to model Stage 1 and Stage 2 mineralisations.

Stage 1 mineralisation is represented by the shaded area in Fig. I-U-11. It is defined by the fS_2 values indicated by the gold analyses and the presence of pyrite, chalcopyrite, hematite and possibly rare bornite.

An fS_2 versus fO_2 diagram for Stage 2 mineralisation is presented in Fig. I-U-12. The iron content of sphalerites suggest $\log fS_2$ values between -9.3 and -9.6, whereas $\log fO_2$ is limited between -34.4 and -31.0 by the absence of graphite and magnetite respectively.

Kaolinite, sericite and adularia occur in the wall rocks and veins, however only sericite and adularia were in equilibrium with the Stage 2 hydrothermal fluid: kaolinite formed at a later stage. Therefore a pH of around 6.0 (equivalent to the sericite/K-feldspar boundary) is indicated for the Stage 2 fluid.

Contours of concentration of total sulphur in solution shown in Fig. I-U-12 were constructed for a pH of 6.0. A value of $0.01m$ ($\log m \pm S = -2$) was used for this parameter to construct the fO_2 versus pH diagram presented in Fig. I-U-13. The region of mineral deposition is represented by the shaded area in Fig. I-U-13, indicating that sulphur was present in solution in approximately equal concentrations of sulphate and sulphide.

TABLE I-U-1: General thermochemical parameters for the depositional environments of Stage 1 and Stage 2 mineralisations, Tui Mine.

	Stage 1	Stage 2	Reference
Temperature °C	400	300	Table V-1
True ionic strength	0.10	0.19	"
Salinity (m NaCl eq)	0.51	0.38	"
mK ⁺	0.14	0.026	"
pH	5.5	6.1 (Fig.I-U-13)	See text
pH of kaolinite/sericite boundary	4.1	4.5	Table V-1
pH of sericite/K-feldspar boundary	5.5	6.0	"
Total S (log m%S)	-1.3	-2.0	See text
Log fS ₂ (sphalerite comp.)		-9.3to-9.6	Table V-4A
(gold comp.)	-3.9to-4.7		Table V-6A
Log fO ₂	-21.5to-23.5 (Fig.I-U-11)	-31.5to-32.5 (Fig.I-U-13)	figures cited
Log fCO ₂	+1.3	+1.6	Table V-1

Figure I-U-11: f_{S_2} versus f_{O_2} diagram at 400°C showing the geochemical environment (shaded) of Stage 1 quartz + pyrite + chalcopyrite ± hematite ± gold ± bismuthinite ± tetradymite ± wolframite? ± bornite? in the Champion and Ruakaka veins of Tui Mine. (See Table I-U-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-U-12: f_{S_2} versus f_{O_2} diagram at 300°C showing the geochemical environment (shaded) of Stage 2 quartz + sphalerite + galena + pyrite + chalcopryite + tetrahedrite mineralisation in the Champion and Ruakaka veins of Tui Mine. (See Table I-U-1 for relevant thermochemical parameters and Appendix V for methods of construction.)

Figure I-U-13: fO_2 versus pH diagram at $300^\circ C$ and $\pm S = 0.01m$ showing the geochemical environment (shaded) of Stage 2 quartz + sphalerite + galena + pyrite + chalcopyrite + tetrahedrite mineralisation in the Champion and Ruakaka veins, Tui Mine. The environment proposed here is characterised by a higher pH and lower relative oxygen fugacity than that proposed for Stage 2 mineralisation by Robinson (1974; c.f. Fig. I-U-9). The pH of the calcite soluble/insoluble boundary is 5.6. (See Table I-U-1 for other relevant thermochemical parameters and Appendix V for methods of construction.)

GENESIS

Robinson (1974) concluded from the isotopic compositions of vein minerals and ore fluid that the sulphur was originally Jurassic sea water sulphate, leached from underlying greywacke rocks, whereas the carbon (in carbonates) was derived from magmatic CO_2 . He postulated that the initial ore fluid was possibly of magmatic origin, whereas the later ore fluids were deeply circulating meteoric water. Robinson's evidence for magmatic water is considered suspect by the writer although no additional evidence has been presented to either support or refute the hypothesis of the presence of a magmatic water component in the early mineralisation.

The changes in mineralogy and physicochemical parameters from Stage 1 to Stage 2 indicate a general trend of increasing pH, caused by reactions with the wall rocks and decreasing temperature. These factors are considered by the writer to have caused mineral deposition from chloride complexed metals in solution during Stages 1 and 2. Dilution may have also been important. Processes of oxidation, decreasing pH and declining temperature occurred during Stage 3 and were the cause of late stage mineral deposition.

The K - Ar age data suggests that hydrothermal alteration and mineralisation occurred some 9 to 12 my after the formation of the host volcanic rocks and together with Pb isotope data reported by Cooper & Richards (1969) and Armstrong & Cooper (1971) indicate that the mineralisation may have been affiliated to rhyolite volcanism during the Pliocene.

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WAIORONGOMAIINTRODUCTION

The spectacular surface exposure of quartz veins and sulphide mineralisation in the Waiorongomai area tempted considerable investment and mining activity in the late 1800's. The Piako County Council built several kilometres of tramway, including three self acting inclines, linking the mining area with the treatment plants. Unfortunately, due to a succession of treatment problems and low grade ore, the various ventures, with the exception of that by E.F. Hardy (between 1899 and 1905), were complete financial failures. Downey (1935) recorded that the total production for the area was 2.1 million grams (68,961 ounces) of bullion from 51,664 tonnes of quartz.

The geology and mineralisation of the Waiorongomai area were described by Henderson & Bartrum (1913) and Cartwright (1982) although the latter work was not available at the time of completion of this thesis.

GEOLOGY

The rocks of the Waiorongomai area are andesites of the Coromandel Group.

HYDROTHERMAL ALTERATION

The andesites of the Waiorongomai area are hydrothermally altered to propylitic assemblages. The major minerals are quartz, sericite, chlorite, calcite and pyrite: adularia was not apparent in specimens collected by the writer (although a detailed study of the hydrothermal alteration of the area was not made).

MINERALISATION

A large quartz vein known as the "Big Buck Reef" strikes north-south and forms a prominent feature along the western side of the Waiorongomai Valley (Fig. I-V-1). The reef is a

Figure I-V-1: Veins of the Waiorongomai area (from Williams 1974; after Henderson & Bartrum, 1913). See also Fig. VIII-1.

nearly vertical, 10 to 40m wide, zone of interconnecting longitudinal and transverse quartz veins and country rock, with pug zones and breccias present at several localities.

North-east striking branch veins intersect the Big Buck Reef and penetrate without crossing it. Some of the branch veins on reaching the Big Buck Reef change their course and follow its walls for a distance before ultimately penetrating and merging with it (Henderson & Bartrum, 1913).

Although minor quantities of gold and silver were mined from the north-east striking veins the major production was from the New Find, Colonist and Premier sections of the Big Buck Reef (known as the Main Reef at these locations) where it was intersected by the north-east striking veins, No.2, Warrior and Vulcan respectively. In all other locations the Big Buck Reef was essentially barren of mineralisation.

A common feature of the main and branching veins is the coarsely crystalline and vuggy nature of the quartz. Base metal mineralisation occurs in most of the branch veins and in the New Find, Colonist and Premier sections of the main vein. Henderson & Bartrum recorded the major minerals as being quartz, pyrite, sphalerite, galena, chalcopyrite and electrum. They also noted the occurrence of abundant calcite in the lowest adit level of the Premier Lode, hessite from the Premier, cinnabar from an unstated locality and suggested that antimony found in ore analyses may have been present in the form of tetrahedrite or pyrargyrite. The writer has confirmed the presence of tetrahedrite but not pyrargyrite, and also identified barite and very rare altaite.

Although a marked depth zonation of mineralisation, such as present at Karangahake and Waihi, was not observed at Waiorongomai by Henderson & Bartrum (1913) these authors did note that "copper-pyrites [chalcopyrite] of the upper levels showed a tendency to give place to sphalerite in depth. It may also be mentioned that here, as at Karangahake, copper-pyrites is a good indicator for gold." Also "In the Premier the gold - silver ratio was, in the upper levels, 1 to 4; in the lowest level in which stoping has been done the ratio was

1 to 2½." (Both quotes are from p96 of Henderson & Bartrum 1913).

Because of the large number of veins investigated, details of their access and ore petrography are given in Appendix VIII and only a brief summary follows.

The veins generally consist of wall rock breccia cemented by quartz with medium grained sulphides (Stage 1) followed by comby and vuggy quartz (Stage 2) and, in some veins, plates of barite coating the vug quartz crystals (Stage 3).

The sulphides are generally banded with successive bands of quartz and sulphides differing in the proportion of the various minerals and their grain size. Pyrite is often early followed by sphalerite then galena and chalcopyrite. As with the mineralisations at Waitekauri and Petote Stream area, late quartz often contains pyrite and chalcopyrite.

The banded sulphides may be arranged concentrically around the breccia fragments (Fig. 4-7) or be subsequently brecciated themselves and infilled with later quartz, with or without accompanying sulphides.

Textures are generally simple. A common texture resulting from brecciation and later quartz cementation is the occurrence of individual grains of sulphides scattered in quartz. The only unusual texture seen was in a specimen from No.1 Reef in which dendritic-herringbone galena occurs in quartz (Fig.4-24).

FLUID INCLUSIONS

Fluid inclusions in Stage 2 quartz and Stage 3 barite are generally normal two phase, liquid plus vapour, types. Some inclusions in samples 13979 (Wi100), 14081 (Wi45), 14084 (Wi56) and 14087 (Wi64) also contain a fibrous solid phase (Fig.6-12), one inclusion of sample 13979 (Wi100) contains a hexagonal solid phase (Fig. 6-16), and vapour rich and vapour filled inclusions occur, in addition to normal types, in sample 14093 (Wi87). The later indicate boiling of the hydrothermal fluid at the time of fluid inclusion formation.

Figure I-V-2: Histograms of primary fluid inclusion filling temperatures and apparent salinities for samples of quartz and barite from the Wairongomai area (individual measurements are listed in Appendix III; locations of samples are listed in Appendix IX). Sample 14093 contains vapour rich and vapour filled inclusions, in addition to normal liquid-vapour types, indicating that the hydrothermal fluid was boiling during the samples formation.

Histograms of filling temperature and salinity measurements are presented in Fig. I-V-2.

With the exception of sample 14093 (Wi87) the filling temperatures require the addition of a correction for pressure and salinity. Reconstruction of the depth relations during mineralisation (see Depth of Mineralisation section) indicate that corrections ranging from 5 to 10°C are required. The exact figure depends on the vertical location of the individual sample in the mining area.

Corrected filling temperatures indicate that Stage 2 quartz deposition occurred at temperatures between approximately 240 and 290°C but predominantly around 265°C. Stage 3 barite appears to have been deposited at temperatures near 120°C although a single fluid inclusion in sample 14099 (Wi97) has a filling temperature of 196°C indicating that deposition may have also occurred at higher temperatures.

A few inclusions in sample 13979 (Wi100) appear to have unusually high salinities (up to 5.5 eq wt. % NaCl) in comparison to other samples which average 1.6 eq. wt. % NaCl.

The results of crushing and leaching experiments on four samples of quartz are listed in Table 7-7. Partial chemical analyses of the fluid inclusions were determined for samples 14071 (Wi16) and 14090 (Wi67) but only Na/K ratios are reported for samples 14091 (Wi80) and 14098 (Wi94) because the quantity of their inclusion fluid analysed was not measured. Using the theoretical Na/K geothermometer, the average measured Na/K ratio of 4.4 (range from 3.2 to 5.7) indicates a fluid temperature around 290°C compared with a range of approximately 250 - 290°C indicated by the fluid inclusion filling temperatures.

HYDROGEN ISOTOPES

δ D values of -36.8 and -37.3 were measured in fluid inclusion waters of late stage quartz samples 14071 (Wi16) and 14094 (Wi89) respectively (Chapter 8). These values are consistent with a meteoric water origin (possibly during a period of cooler climatic conditions) although their origin

Figure I-V-3: Depth of mineralisation scheme for the Waiorongomai deposits constructed by assuming that boiling occurred in the New Find section under predominantly hydrostatic pressure conditions.

from other types of waters with some modification is also possible.

SULPHUR ISOTOPES

$\delta^{34}\text{S}$ values of measured sulphides and barites are listed in Table 9-1. The sulphides have $\delta^{34}\text{S}$ values ranging from -2.0 per mil (galena) to +2.5 per mil (chalcopyrite), whereas the two samples of barite analysed have values of +18.8 and +18.9 per mil.

Temperatures calculated from fractionations between cogenetic pairs of sphalerite and galena range from 255 to 390°C with the average fractionation value (2.1 per mil) indicating a temperature of 310°C. As would be expected average temperatures of the veins decrease with increasing elevation: Hero 1100' level (sample 14100) 350°C, May Queen 3 level (sample 14080) 350°C, Colonist 3 level (samples 14076a, 14076b, 14077, 14092a and 14092b) 325°C, No. 1 Vein Waterfall (samples 14073 and 14075) 285°C and Main Vein Waterfall (14089) 255°C.

LEAD ISOTOPES

Cooper & Richards (1969) measured the ratios of lead isotopes in galena and andesite (one sample of each) from the Waiorongomai area. When viewed with lead isotope measurements of galena, andesite, rhyolite and greywacke from other locations in the Coromandel Peninsula (Cooper & Richards, 1969; Armstrong & Cooper, 1971; c.f. Fig.5 of Robinson, 1974), a greywacke basement source is indicated for the lead in the hydrothermal veins.

DEPTH OF MINERALISATION

Fig. I-V-3 illustrates a reconstruction of the depth regime at the time of mineralisation. The surface datum is taken at 400m above the summit of Mt Te Aroha. The model is consistent with boiling at a temperature greater than 240°C in the New Find Section provided that the pressure regime was predominantly hydrostatic (at the time of boiling) and the concentration of CO_2 in the fluid was greater than 0.6 mole

Figure I-V-4: fS_2 versus fO_2 diagram at 325°C showing the geochemical environment (shaded) of Stage 1 quartz + sphalerite + galena + pyrite + chalcopryite $\pm$ hessite $\pm$ tetrahedrite $\pm$ electrum mineralisation in veins of the Waiorongomai area. $\leq S = 0.01m$, $pH = 5.4$, $\log fS_2$ from sphalerite compositions = -7.3 to -8.3 , $\log fS_2$ from electrum compositions = -7.2 and $\log fCO_2$ from fluid inclusion measurements = $+1.5$. (See Appendix V for methods of construction.)

7 (data from Merchant, 1978 Fig. 5-6). The same datum is used in the Tui Mine reconstruction.

THERMOCHEMISTRY

Stage 1 mineralisation plots in the pyrite + chalcopyrite field of the fS_2 versus fO_2 diagram illustrated in Fig. I-V-4. The iron content of sphalerites indicate sulphur fugacities of $\log fS_2 = -7.3$ to -8.3 , whereas the mole fraction of silver in electrum suggests a $\log fS_2$ value of -7.2 . fO_2 is limited by the absence of graphite, magnetite and hematite, and in the case of the low levels of the Premier, by the presence of calcite but absence of anhydrite.

A pH of 5.4 (in equilibrium with sericite in the wall rocks) was used to construct the contours of concentration of total sulphur in solution in Fig. I-V-4. A value of $0.01m$ ($\log m \leq S = -2$) for this parameter is consistent with the other data and was used to construct the fO_2 versus pH diagram shown in Fig. I-V-5.

$\delta^{34}S$ values of late stage barite (+18.8 and +18.9 per mil) may be used to determine $\delta^{34}S_{\leq S}$ by assuming that barite was deposited from a fluid in which dissolved sulphur occurred predominantly as sulphate (c.f. Chapter 9). Therefore $\delta^{34}S_{\text{barite}} \approx \delta^{34}S_{SO_4^{2-}} \approx \delta^{34}S_{\leq S}$. A value of +16 per mil is assigned to $\delta^{34}S_{\leq S}$.

Contours of $\delta^{34}S_{H_2S}$ are shown in Fig. I-V-5 for $\delta^{34}S_{\leq S} = +16$ per mil and indicate that Stage 1 sulphides ($\delta^{34}S$ values ranging from -0.2 to $+2.5$ per mil) must have been deposited from a fluid which plots near or on the oxidised sulphur species/reduced sulphur species boundary. The most likely region of mineral deposition is shown by the shaded area in Fig. I-V-5.

The fTe_2 versus fS_2 diagram (Fig. I-V-6) indicates that fTe_2 was relatively high during some stages of the Waiorongomai mineralisation as evidenced by the presence of hessite and rare altaite.

Figure I-V-5: fO_2 versus pH diagram at 325°C and $a_S = 0.01m$ showing the geochemical environment (shaded) of Stage 1 quartz + sphalerite + galena + pyrite + chalcopyrite + hessite + tetrahedrite + electrum mineralisation in the veins of the Waiorongomai area. $\bar{I} = 0.08$, $mK^+ = 0.021$, $pH = 5.4$, $\log fS_2$ from sphalerite compositions = -7.3 to -8.3 , $\log fS_2$ from electrum compositions = -7.2 , $\log fCO_2$ from fluid inclusion measurements = $+1.5$, and the pH of the calcite soluble/insoluble boundary = 5.9 . $\delta^{34}S_{H_2S}$ contours are constructed for $\delta^{34}S_{\text{‰}} = +16$ per mil. (Methods of construction are described in Appendix V.)

Figure I-V-6: $f\text{Te}_2$ versus $f\text{S}_2$ diagram at 325°C showing the possible stability ranges of Stage 1 assemblages containing hessite + electrum (widely spaced diagonally ruled pattern), hessite (widely spaced diagonally ruled pattern plus stippled area), and hessite + altaite (closely spaced diagonally ruled pattern). (Methods of construction are described in Appendix V.)

GENESIS

The value of +16 per mil for $\delta^{34}\text{S}_{\text{S}}$ indicates that the source of sulphur in the Waiorongomai sulphide and sulphate minerals was probably sedimentary sulphur leached from the greywacke basement rocks. In this and several other aspects (e.g. mineralogy and physicochemical conditions of mineral deposition) the mineralisation at Waiorongomai is genetically similar to that at Tui Mine and because of their close proximity they may have been related to the same magmatic - geothermal episode. However, the mineralisations differ in that the early high temperature copper-bismuth-gold (-tungsten?) stage of Tui Mine appears to be absent from the Waiorongomai area and the concentration of Te in solution appears to have been higher at Waiorongomai than Tui Mine.

Stage 1 mineral deposition at Waiorongomai probably occurred due to changes in pH associated with reactions of the fluid with the wall rocks although the high dissolved sulphate/dissolved sulphide ratio indicated for the fluid suggests mineral deposition in a mixing zone where the hydrothermal fluid encountered oxygenated waters (c.f. model of Henley & Seward, in prep).

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MISCELLANEOUS DEPOSITSINTRODUCTION

The locations of the deposits reviewed in this section are shown in Fig. I-W-1. They are described in geographical order from north to south.

Several deposits are not reviewed here because of their small size (Au - Ag production less than 30,000 grams or 1,000 ounces) and because they have not been studied since their description in the early Geological Survey Bulletins. These include the following (locations shown in Fig. I-W-2): Preeces Point (9,450 grams or 304 ounces), Ocean View (5,570 grams or 179 ounces), Moewai (2,580 grams or 83 ounces), Mahakirau (18,256 grams or 587 ounces), Te Mata (6,530 grams or 210 ounces), Waihi Beach (less than 9,000 grams or 280 ounces) and Eliza (160 grams or 5 ounces). The reader is referred to the early Geological Survey Bulletins for information on these deposits.

WAIKAWAU BAY

Several small quartz veins occur in Port Charles Andesite, Kokumata Dacite and Tuataewa Andesite (Coromandel Group formations) of the Waikawau Bay area (c.f. Skinner, 1976). Skinner (1967) considered that they are characterised by the occurrence of arsenopyrite and marcasite in addition to pyrite. Fraser & Adams (1907) noted that veins in Cousin Jack Creek (Cousin Jack Mine), Gisborne Creek and Waikanae Stream (Matamataharakeke area: Mill's Reward and Marcaroni Mines) are auriferous but total production from the area was apparently less than 2000 grams of gold and silver (c.f. Downey, 1935).

COLVILLE AREA

Disseminated arsenical mineralisation and several quartz veins occur in rhyodacitic pyroclastic rocks of the Omoho Formation (Coromandel Group) in the Colville area. The quartz

Figure I-W-1: Location of deposits reviewed in Section I-W.

Figure I-W-2: Locations of deposits not reviewed here. Their production of gold and silver was small (less than 30,000 grams or 1,000 ounces) and they have not been described in the literature since the Geological Survey Bulletins of the early 1900's.

veins contain pyrite, arsenopyrite and marcasite and one in Ngakuku Stream also contains pyrrhotite and chalcopyrite (Skinner, 1967; 1976). Approximately 20,000 grams (600 ounces) of gold and silver were mined from quartz veins in the Jersey, White Star and Bay View Mines (c.f. Fraser & Adams, 1907; Downey, 1935).

WAIKOROMIKO VALLEY

The quartz veins of the Waikoromiko Valley area and the Whangapoua or Lillis Mine (Au - Ag production of 47,000 grams or 1,502 ounces) mostly occur in Beesons Island Volcanics (Coromandel Group), however Skinner (1976) mapped the host rocks of the Four In Hand Mine (Au - Ag production of 332,000 grams or 10,713 ounces) as Tuatawa Andesite (Coromandel Group). Numerous dikes of Kai-iti Porphyrites intrude the Beesons Island Volcanics.

The area was successively investigated by Fraser & Adams (1907), Kear (1958), Skinner (1967) and ASARCO (Neilsen, 1968). Fraser & Adams (1907) noted that in the 10 to 120cm thick Four In Hand vein, electrum occurred with pyrite either in shoots or disseminated in the quartz. Bonanza style ore occurred in a hanging wall branch vein, particularly where it contacted the main vein.

The main vein of the Whangapoua Mine varied in thickness from 5 to 75cm and in the upper levels the ore occurred in rich "pockets". The gold (electrum ?) sometimes "resembled a loosely compressed mass of thread-like metal turnings" (Fraser & Adams, 1907 p125).

Skinner (1967) differentiated two types of quartz veins in surface exposures of the area: (a) veins with sugary quartz, pyrite, rare marcasite and arsenopyrite, and late calcite and vuggy quartz, and (b) "honeycomb" impregnations of quartz in shear zones, containing disseminated or colloform-like bands of pyrite.

Neilsen (1968) noted that the wall rocks adjacent to the veins were only moderately effected by hydrothermal alteration,

although weathering obscures this feature in the vicinity of the Four In Hand Mine.

OWERA

The Owerā mining area (including Murphy's Hill) produced 71,000 grams (2,200 ounces) of gold and silver (Downey, 1935) from quartz veins in Waterangi Andesite (Coromandel Group). Practically all of the production was from the Owerā Vein which averages 60cm wide, dips steeply and strikes NNE (Fraser & Adams, 1907).

BOAT HARBOUR TO TAIRUA

Bell & Fraser (1912) and Ovens (1976) described quartz veins at Boat Harbour (Heather Bell Reef), Neaves Bay and Te Karo Bay, and sinter deposits between Te Karo Bay and Tairua (e.g. Pumpkin Hill). Near these deposits the host rocks, Tapuaetahi Andesites of the Coromandel Group (Ovens, 1976), are altered to propylitic assemblages (chlorite, sericite, pyrite, calcite and quartz) but strong hydrothermal alteration adjacent to some veins and sinters has produced intermediate argillic and advanced argillic alteration with kaolinite predominating (Swindale & Hughes, 1968; Ovens, 1976).

Pyrite occurs in the quartz veins and associated with some sinter deposits but gold and silver are practically absent (the recorded Au - Ag production for the area is only 280 grams or 9 ounces, Downey, 1935).

OHUI

Quartz veins and sinter deposits occur in Whitianga Group rhyolites and Coromandel Group andesites of the Ohui area. Downey (1935) recorded a total Au - Ag production of 7,300 grams (234 ounces), practically all of which came from the Great Mexican and Phoenix Mines.

In the Great Mexican, electrum and pyrite occurred in a quartz vein known as the Maori Dream Reef. This vein had an average width of 40cm (maximum width of 1.2m) and was characterised by a low angle of dip: the northern part was flat lying (Bell & Fraser, 1912). The host rocks are andesites of

the Coromandel Group.

Two thin quartz veins (averaging 18 and 30cm wide, with a maximum width of 60cm) were worked in the Phoenix Mine and these occurred within a narrow zone of brecciated and silicified spherulitic biotite rhyolite (Minden Rhyolite Subgroup of the Whitianga Group). The veins contained milky white quartz with a pronounced ribbon structure, electrum, acanthite, and evidence of pyrite and calcite which had been oxidised and leached out respectively.

A number of sinter deposits occur capping Phoenix Hill, in Whitianga Group rhyolite. A chemical analysis of the sinterous material was given by Bell & Fraser (1912, p61) and demonstrates that gold and silver are present in only extremely low concentrations.

KAUAERANGA VALLEY

Gold, cinnabar and disseminated pyrite mineralisations occur in the Coromandel Group andesites of the Kauaeranga Valley.

Fraser (1910) briefly described auriferous quartz veins of the Otanui Mine in Otanui Stream (Mangakirikiri Valley), however according to production figures given by Downey (1935) they appear to have been unimportant economically, having produced less than 1,000 grams (100 ounces) of bullion.

Near the junction of Mangakirikiri Stream and the Kauaeranga River, cinnabar mineralisation occurs in bands of siliceous sinter, and occasionally in the intensely silicified and brecciated zones of the propylitised andesites which enclose these bands (Fraser, 1910). Less than one tonne of cinnabar ore was mined.

Kear (1957) described disseminated pyrite and marcasite mineralisation (up to 32% sulphur, equivalent to 60 wt. % sulphide) in propylitised andesite lavas, pyroclastics (breccias and tuffs), dikes (up to 2.5m wide) and sediments (siltstone, sandstone and conglomerates) in the Waikato Stream

area. Surface mapping and core from 7 drill holes (maximum depth: 134m in hole G) indicated that the mineralisation was mainly by replacement, conformable to bedding and lithologically controlled, being strongest in carbonaceous sediments.

LUCK AT LAST MINE (WHAREKAWA VALLEY)

The host rocks of the Luck At Last Mine were mapped as Pliocene "Third Period" volcanics by Bell & Fraser (1912) and Minden Rhyolite by Schofield (1967), although Bell & Fraser (1912, p93) described them as pyroxene dacites with "faintly observable" flow structure. The propylitic alteration in these rocks, adjacent to the veins, "differs in no respect from that afforded by a normal andesite" (Bell & Fraser, 1912, p93). Biotite rhyolite was encountered in the northern workings of the mine.

A single quartz vein (with minor branches and loops) was worked in three adit levels and produced 408,000 grams (13,176 ounces) of gold and silver between 1899 and 1901 (Bell & Fraser, 1912; Downey, 1935). It strikes at 020° , dips steeply to the east and varies in width from 0.3 to 5m (average width of 1.5m). The finely crystalline milky white quartz contained gold and silver but "little or no pyrite or other sulphides".

OMAHU VALLEY

Gold and silver were produced from three mines in the Omahu Valley: Sheet Anchour (46,000 grams or 1,480 ounces), We Three (17,000 grams or 539 ounces) and Klondyke (1,000 grams or 35 ounces). The following descriptions are summarised from Bell & Fraser (1912).

In the Sheet Anchour Mine a 1 to 1.5m thick "very flat lying" vein contains fine milky quartz, electrum and acanthite. The vein occurs in rhyolite tuffs (Coroglen Subgroup of the Whitianga Group) at or near their irregular contact with andesites of the Coromandel Group.

The quartz vein in the We Three Mine strikes at 020° , has a maximum width of approximately 30cm and occurs in Coromandel Group andesite. Gold and silver were mined from

the oxidised near surface section.

The Klondyke Mine is situated in rhyolite tuffs of the Coroglen Subgroup (Whitianga Group) which contain intrusions of rhyolite and dacite. The vein consists of "small erratic seams".

WENTWORTH - WHANGAMATA AREA

Several quartz veins were mined in the Wentworth Valley but only two produced significant gold and silver: the Wentworth or Auckland Mine (469,000 grams or 15,086 ounces) and the Goldwater Vein of the Glamorgan Claim (46,000 grams or 1,470 ounces). The country rocks are andesites and dacites (Bell & Fraser, 1912; Main, 1971; 1979). The following description is summarised from Bell & Fraser (1912).

An un-named quartz vein, together with the Raunui Loop Vein were worked on 4 adit levels in the Wentworth Mine. The main vein had an average width of 50cm, with a strike of 020° and dip, 70° , to the east. It contained quartz, pyrite and visible electrum. The ore occurred in the upper levels, mainly between 1 level and the surface.

The Goldwater Vein had an average width of 2.5m or less and contained quartz, quartz pseudomorphs after calcite, some carbonate, pyrite and acanthite, the latter apparently being the only economic mineral. Bell & Fraser (1912, p97) list an assay of the ore in which the Au:Ag ratio is approximately 1:100.

WAIHI MONUMENT

The pyritised sinter deposits of the Waihi Monument were described by Bell & Fraser (1912), Morgan (1924) and Skinner (1975b). They consist of two sinter mounds of slightly pyritic, silicified, partly brecciated, opalised Coromandel Group andesites, 60m apart and each approximately 10m high (Skinner, 1975b). They are surrounded by a 3 to 6m thick layer of pumiceous and quartzose sand and silt (interpreted by Skinner as being the distal part of Whitianga Group tuffs and sediments of the Waihi Plains) covering Coromandel Group andesites.

Prospecting in the late 1800's, in the form of adits and a shaft, revealed strong pyrite mineralisation but very low values of gold and silver. Drilling in the 1960's (a single hole to a depth of 192m at 55° dip, equivalent to a vertical depth of approximately 160m, followed by 20 holes each to a depth of approximately 18m) intersected a strongly kaolinitised and pyritised intrusive rhyolite pipe or plug approximately 60m in diameter. Skinner (1975b) suggested that the pipe may have been a feeder to an overlying Minden Rhyolite dome that has been stripped by erosion.

OWHAROA

The geology and mineralisation of the Owharoa area were described by Bell & Fraser (1912), Morgan (1924) and Rabone (1971, 1975).

Between 1875 and 1933, 2.3 million grams (72,580 ounces) of gold and silver (Downey, 1935) were produced from quartz veins which occur in Whitianga Group (Minden Rhyolite Subgroup) rhyodacite flows.

The rhyodacites have been intensely hydrothermally altered to assemblages of quartz, sericite, adularia and hematite (Rabone, 1971; 1975).

In the largest mine, the Rising Sun, three quartz veins were worked on three levels producing 2 million grams of gold and silver. They strike at 020°, dip steeply to the west or vertically, and have average widths of less than 50cm with a maximum recorded width of 1.5m in No.1 Lode. The veins are mainly finely crystalline milky quartz but they also contain sugary quartz, vug quartz, semi-platy quartz (quartz pseudomorphs after calcite), pyrite, acanthite, electrum ("occasionally visible in association with the sulphides"; Bell & Fraser, 1912) and cinnabar, the latter forming encrustations on quartz.

The Au:Ag ratios in twenty assays of ore from the low level were reported by Morgan (1924, p127) to vary between 1:1.23 and 1:0.77, except in one case, where the ratio was 1:3.8. The assays averaged 1 ounce 10 dwt. 8 grams of gold

Figure I-W-3: Diagrammatic cross section of the cinnabar deposit at the Ascot Mine, Mackaytown (after Bell & Fraser, 1912; Russell, 1980).

and 1 ounce 10 dwt. 15 grams of silver per ton (approximately 42 ppm each).

The ore was confined to a vertical range of approximately 100m. With increasing depth the quartz veins were found to split up into stringers.

The mineralisation in other workings of the Owaharoa area (e.g. Smile of Fortune, 220,000 grams Au - Ag; Radical, 54,000 grams Au - Ag) occurred in a number of NNE trending quartz veins confined to a 150m wide zone. The veins "resembled the stock-work type of deposits, each including numerous parallel stringers and erratically disposed streaks and bunches of quartz and much soft mineralised country rock, the whole of the material being more or less auriferous" (Bell & Fraser, 1912, p118). Ore occurred near the surface but values decreased with increasing depth.

MACKAYTOWN

Bell & Fraser (1912) and Russell (1980) described cinnabar deposits, principally the Ascot Cinnabar Mine, near Mackaytown. The deposits occur in ridges and knobs of intensely silicified Whitianga Group rhyolite which forms thin (approximately 30m) cappings on propylitised Ohinemuri Andesite (Coromandel Group). In other localities the rhyolite is overlain by Omahia Andesite (Coromandel Group).

At the Ascot Mine the mineralisation occurs predominantly in a 1.5m thick kaolinitised horizon sandwiched between two "sinter beds" (Fig. I-W-3). The cinnabar occurs in red puggy seams, pugg filled cavities (often lined with drusy quartz), whitish flinty quartz veinlets and in a fairly persistent thin (maximum width of 30cm) quartz vein located near the base of the 1.5m kaolinitised horizon. The mines were unprofitable.

MUIR'S REEFS (TE PUKE)

Muir's Reefs (also known as Te Puke Reefs and Fleming's Hill) occur approximately 6km south-west of Te Puke in hypersthene augite andesite flows (Bartrum, 1913) of the Coromandel Group. Near the veins the rocks are hydrothermally

altered to propylitic assemblages of chlorite, secondary quartz, carbonate and pyrite (Bartrum, 1913).

Between 1895 and 1928, 1.7 million grams (54,172 ounces) of gold and silver were produced from two NNE trending quartz veins, Muirs Reef and Massey Reef, mined on 5 levels to a depth of 150m below the surface (Downey, 1935). Most of the ore came from Muirs Reef in workings near the surface. The average width of this vein varied from 1.5m in the upper levels to 4.6m in the lower levels, with a maximum width of 18m (Downey, 1935).

Bartrum (1913) noted that on 1 level the accessible parts of the vein (during his visit) contained "greyish fairly friable quartz" although sinterous banded quartz was plentiful in the mullock heaps. Quartz pseudomorphs after calcite occurred on 2 level and Bartrum considered that the vein material resembled that in the upper levels at Waihi. Below 2 level the vein "pinched considerably and was very puggy".

ANTHONY BARRY CHRISTIE

FLUID INCLUSIONS, STABLE ISOTOPES AND GEOCHEMISTRY
OF PORPHYRY COPPER AND EPITHERMAL VEIN DEPOSITS
OF THE HAURAKI GOLD - SILVER PROVINCE,
NEW ZEALAND

VOLUME 3

APPENDICES II TO IX:

ELECTRON MICROPROBE AND FLUID INCLUSION
METHODS AND RESULTS, THERMOCHEMICAL
CALCULATIONS, AND SAMPLE DESCRIPTIONS

August 1982

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APPENDIX IIELECTRON MICROPROBE ANALYSES:METHODS AND RESULTSMETHODSInstrumentation

EPMA analyses were made on the Jeol 733 Superprobe in the Analytical Facility, Victoria University of Wellington, using the ZAF (atomic number, absorption and fluorescence) correction program.

Measuring Conditions

Measuring conditions were generally; 25kv accelerating potential, 2.0×10^{-8} amps specimen current and 3 micrometre beam diameter, with the following counting times: peak, 2 at 20 seconds; background, 2 at 10 seconds. Some analyses of acanthite, electrum and hessite were made at lower accelerating potential and specimen current and/or wider beam diameter.

Standards

Pyrite and galena (Broken Hill, N.S.W.) were used as standards for sulphur and lead respectively, whereas pure elements were used as standards for all other elements.

Detection Limits

Detection limits are listed in Table II-1 and were calculated using the following formula:

$$\text{Detection limit} = \frac{3}{m} \cdot \sqrt{\frac{R_b}{T_b}} \quad (\text{II-1})$$

where R_b = background count rate
 T_b = background counting time
 m = counts per second per %

The values listed are those calculated for analyses of the elements when present in low concentration. Concentrations below the detection limits are considered not significant.

TABLE II - 1: Detection limits for electron
microprobe analyses.

<u>Element</u>	<u>wt. %</u>
Ag	0.10
Au	0.20
As	0.08
Bi	0.40
Cd	0.08
Co	0.04
Cu	0.06
Fe	0.04
Mn	0.03
Ni	0.04
Pb	0.03
S	0.05
Sb	0.08
Se	0.13
Te	0.10
Zn	0.05

Interferences

Interferences of Bi and Pb prevented routine analyses of these elements together. The peaks used for counting Bi and Pb were adjacent and the background count of Bi occurred on the tail of the Pb peak, causing negative corrected counts for Bi in analyses of galena.

RESULTS

The minerals are listed in alphabetical order. The individual samples are listed within each mineral category in order of increasing V.U.W. (or other) sample number. Sample number subscripts (a), (b) and (c) indicate different polished mounts of the same sample. The locations and descriptions of these samples are given in Appendix IX.

n.a. = not analysed

Acanthite, Ag₂S

	14032(GJ3)			14043(WH35)					
	1	2	3	1	2	3	4	5	6
Ag	83.55	83.19	83.96	83.20	82.41	83.24	84.80	84.21	83.49
S	12.33	11.28	11.33	8.89	7.89	9.40	9.64	9.13	9.50
Se	4.45	5.11	4.46	7.62	9.73	6.92	6.50	6.52	6.70
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
As	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Au	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.33	99.58	99.75	99.71	100.03	99.56	100.94	99.86	99.69

				285/37/7(M14)	285/37/8(M32)		M18185
	7	8	9	1	1	2	1
Ag	86.54	85.98	87.00	80.72	84.42	86.14	85.17
S	12.94	12.24	12.15	12.02	13.37	12.49	12.45
Se	0.96	0.98	1.05	1.94	0.13	3.11	2.58
Cu	n.a.	n.a.	n.a.	1.93	0.27	0.09	n.a.
As	n.a.	n.a.	n.a.	1.80	0.04	0.00	n.a.
Au	n.a.	n.a.	n.a.	0.58	1.26	0.00	n.a.
Total	100.44	99.20	100.20	98.99	99.49	101.83	100.20

							M18186		
	2	3	4	5	6	7	1	2	3
Ag	85.28	85.48	84.68	85.70	84.58	85.27	83.70	85.04	86.09
S	12.83	12.57	12.78	12.06	12.61	12.78	11.85	12.23	11.16
Se	2.56	2.74	2.61	2.71	2.54	2.67	4.08	3.78	3.74
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
As	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Au	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.67	100.79	100.07	100.47	99.73	100.72	99.63	101.05	100.99

Argentian Pentlandite, (Fe Ni)_{8+x}Ag_{1-x}S₈

13965 (MH1)

1

Fe	36.51
Ni	18.26
Ag	13.52
S	31.42
Cu	0.70
Zn	0.07
As	0.00
Co	0.01
Total	100.49

Bismuthinite, Bi_2S_3

13915 (Tui 27)									
	1	2	3	4	5	6	7	8	9
Bi	78.30	78.44	76.31	79.83	76.38	78.18	76.54	77.32	79.40
S	17.69	18.00	17.85	17.78	17.98	17.66	17.60	17.50	17.61
Pb	3.73	3.16	4.36	2.18	4.91	3.75	4.49	3.99	2.46
Cu	1.14	0.99	1.39	0.92	1.41	1.13	1.38	1.21	0.81
Te	0.02	0.06	0.16	0.04	0.03	0.02	0.01	0.03	0.02
Total	100.87	100.64	99.93	100.75	100.71	100.75	100.01	100.05	100.30

Chalcopyrite, Cu Fe S_2

13979(Wi 110)		14025(a) (TL22)		14058(Tui 15)			
	1		1	1	2	3	4
Cu	34.23		34.12	34.30	34.15	33.84	34.26
Fe	31.02		30.45	30.07	31.06	30.70	30.56
S	33.90		33.85	34.59	35.17	35.04	34.88
As	0.00		0.36	0.41	0.17	0.00	0.05
Au	n.a.		0.51	n.a.	n.a.	n.a.	n.a.
Zn	0.01		n.a.	0.10	0.02	0.07	0.06
Ni	0.06		n.a.	0.03	0.01	0.01	0.00
Mn	0.00		n.a.	0.00	0.00	0.00	0.01
Cd	0.00		n.a.	0.00	0.03	0.00	0.00
Sb	0.02		n.a.	0.01	0.00	0.03	0.09
Total	99.25		99.29	99.51	100.61	99.69	99.91

	5	6
Cu	34.26	34.53
Fe	29.91	30.79
S	34.83	34.26
As	0.09	0.55
Au	n.a.	n.a.
Zn	0.58	0.09
Ni	0.00	0.00
Mn	0.00	0.01
Cd	0.00	0.02
Sp ₄	0.05	0.08
Total	99.72	100.33

Gold - Electrum AuAg

13909(Tul 30)

	1	2	3	4	5	6	7	8
Au	89.05	89.69	91.03	91.35	91.00	90.32	89.78	89.08
Ag	8.82	8.42	7.05	7.18	7.11	8.11	8.55	8.94
S	0.17	0.12	0.21	0.11	0.19	0.12	0.19	0.13
Cu	0.06	0.07	0.14	0.09	0.09	0.07	0.22	0.23
Fe	0.02	0.03	0.08	0.04	0.04	0.02	0.14	0.14
As	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.02
Te	0.00	0.00	0.02	0.00	0.02	0.03	0.00	0.00
Total	98.12	98.33	98.53	98.78	98.45	98.67	98.88	98.54

13915(Tul 27)

13937(M33)

13961(TK7)

	1	2	1	2	1	2	3	4
Au	87.77	90.22	53.79	55.83	61.54	58.31	60.24	60.13
Ag	11.78	7.75	43.84	44.42	36.15	39.32	38.31	39.19
S	0.07	0.04	0.53	0.35	0.08	0.10	0.16	0.03
Cu	0.00	0.02	0.00	0.03	0.00	0.00	0.00	0.00
Fe	0.00	0.01	0.53	0.62	0.00	0.00	0.00	0.01
As	0.00	0.00	0.00	0.00	0.26	0.18	0.27	0.12
Te	0.09	0.06	0.02	0.01	0.04	0.12	0.00	0.00
Total	99.72	98.10	98.70	101.25	98.07	98.04	98.88	99.47

14025_(a)(TL22₂)

	5	6	7	1	2	3	4	5
Au	61.34	60.61	60.30	73.80	75.27	73.43	74.96	73.29
Ag	39.69	38.17	39.04	27.57	25.35	26.02	26.19	26.40
S	0.05	0.08	0.07	0.00	0.07	0.01	0.01	0.05
Cu	0.00	0.06	0.01	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
As	0.11	0.31	0.00	0.57	0.00	0.00	0.00	0.05
Te	0.00	0.00	0.09	0.00	0.00	0.05	0.00	0.08
Total	101.18	99.24	99.51	101.96	100.69	99.52	101.16	99.89

14025_(b)(TL22₆)

14032(GJ3)

14043(Wh35)

	1	1	2	3	1	2	3	4
Au	71.34	51.76	52.69	52.41	65.98	64.28	65.08	69.38
Ag	26.67	46.82	46.85	46.34	32.55	34.40	34.35	32.40
S	0.06	0.09	0.05	0.00	0.12	0.10	0.08	0.04
Cu	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.03
Fe	0.00	0.09	0.00	0.01	0.03	0.00	0.00	0.02
As	0.00	0.00	0.41	0.96	0.00	0.00	0.00	0.00
Te	0.05	0.03	0.18	0.09	0.13	0.16	0.00	0.03
Total	98.12	98.81	100.22	99.82	98.81	98.94	99.51	101.90

Gold - Electrum (Continued)

14043(Wh35) (Continued)					14046(Wh43)
	5	6	7	8	1
Au	63.51	67.10	67.41	63.26	68.15
Ag	37.01	32.27	32.15	35.80	31.36
S	0.07	0.13	0.06	0.13	0.10
Cu	0.00	0.07	0.01	0.00	0.00
Fe	0.00	0.04	0.02	0.03	0.13
As	0.26	0.19	0.05	0.21	0.00
Te	0.00	0.10	0.00	0.05	0.00
Total	100.85	99.89	99.70	99.46	99.74

14048(Wh45)								14092(Wi83)
	1	2	3	4	5	6	7	1
Au	61.93	63.51	62.35	63.42	64.15	61.43	63.82	80.27
Ag	36.03	36.49	36.25	37.12	36.67	37.41	36.50	19.64
S	0.15	0.13	0.13	0.09	0.10	0.07	0.14	n.a.
Cu	0.11	0.07	0.20	0.05	0.21	0.06	0.17	n.a.
Fe	0.05	0.03	0.02	0.08	0.14	0.07	0.00	n.a.
As	0.29	0.37	0.15	0.00	0.22	0.00	0.02	n.a.
Te	0.00	0.01	0.00	0.01	0.09	0.01	0.04	n.a.
Total	98.56	100.62	99.10	100.77	101.59	99.05	100.69	99.91

285/37/8 (M32)					
	1	2	3	4	5
Au	59.94	58.50	55.71	58.49	60.87
Ag	40.56	40.65	42.50	41.52	38.18
S	0.17	0.30	0.24	0.33	0.18
Cu	0.01	0.08	0.00	0.03	0.00
Fe	0.01	0.01	0.04	0.71	0.23
As	0.00	0.18	0.26	0.00	0.00
Te	0.00	0.02	0.18	0.00	0.11
Total	100.68	99.74	98.92	101.07	99.57

Galena, Pb S

13959(TK1)						13971(DC12)			
	1	2	3	4	5	6	1	2	3
Pb	86.72	86.23	86.80	86.19	86.18	86.42	86.92	86.43	86.65
S	13.02	12.87	13.21	12.94	13.12	13.16	13.16	13.11	13.10
Ag	0.02	0.01	0.04	0.04	0.05	0.04	0.06	0.02	0.00
Sb	0.01	0.01	0.00	0.00	0.06	0.00	0.08	0.03	0.05
Fe	0.00	0.00	0.00	0.00	0.18	0.11	0.02	0.00	0.00
Total	99.78	99.13	100.05	99.17	99.60	99.72	100.45	99.60	99.80

Galena, Pb S (Continued)

13971(DC12) (Continued)				13974(SM11)			
	4	5	6	1	2	3	4
Pb	86.83	86.02	86.99	86.63	86.15	86.08	86.75
S	13.14	13.22	13.30	13.00	13.21	13.04	12.94
Ag	0.03	0.03	0.09	0.05	0.01	0.00	0.02
Sb	0.00	0.05	0.00	0.00	0.03	0.02	0.09
Fe	0.00	0.00	0.00	0.00	0.01	0.00	0.03
Total	100.00	99.31	100.39	99.68	99.41	99.14	99.83

13985(HC3)				13989(HC4 ₁)					
	1	2	3	4	1	2	3	4	5
Pb	86.82	86.95	86.93	87.22	85.82	86.71	86.77	86.28	86.41
S	13.12	13.27	13.22	13.54	13.22	13.09	13.31	13.03	12.96
Ag	0.00	0.02	0.01	0.01	0.00	0.02	0.04	0.03	0.04
Sb	0.06	0.00	0.02	0.02	0.00	0.05	0.05	0.03	0.04
Fe	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.01
Total	100.00	100.24	100.18	100.79	99.06	99.88	100.17	99.39	99.46

14015(WK6)		14025 (b) (TL22 ₆)						14040(Wb29)	
	1	2	1	2	3	4		1	2
Pb	86.02	86.29	86.03	86.76	86.22	86.76		86.02	86.54
S	13.13	13.29	13.24	12.93	13.17	13.24		13.32	13.32
Ag	0.01	0.01	0.08	0.00	0.06	0.02		0.00	0.03
Sb	0.07	0.05	0.03	0.03	0.15	0.06		0.04	0.06
Fe	0.01	0.00	0.03	0.01	0.05	0.00		0.01	0.00
Total	99.23	99.64	99.41	99.73	99.65	100.08		99.39	99.94

				14046(Wb43)		14048(Wb45)		
	3	4	5	6	1	2	1	2
Pb	86.23	86.46	85.89	86.11	85.64	86.16	86.24	86.22
S	13.28	13.17	13.32	13.30	13.36	13.10	13.27	13.37
Ag	0.05	0.00	0.04	0.07	0.04	0.07	0.05	0.11
Sb	0.08	0.05	0.05	0.05	0.10	0.04	0.05	0.02
Fe	0.00	0.05	0.13	0.07	0.08	0.07	0.01	0.00
Total	99.64	99.73	99.42	99.60	99.22	99.44	99.62	99.72

14059(Tul 17)								
	3	4	1	2	3	4	5	6
Pb	86.04	86.21	87.19	96.54	86.62	86.79	86.66	87.18
S	12.95	12.83	13.00	13.09	13.39	13.16	13.39	13.30
Ag	0.07	0.07	0.03	0.05	0.07	0.08	0.09	0.02
Sb	0.02	0.12	0.03	0.00	0.03	0.08	0.05	0.10
Fe	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.00
Total	99.07	99.23	100.25	99.68	100.12	100.10	100.22	100.61

Galena, Pb S (Continued)

	14060(Tul 18)					14061(Tul 19)	
	1	2	3	4	5	1	2
Pb	87.59	86.57	87.30	86.65	87.15	86.22	86.52
S	13.25	12.93	13.32	13.03	13.36	12.74	12.64
Ag	0.02	0.00	0.04	0.00	0.11	0.01	0.08
Sb	0.04	0.00	0.05	0.03	0.00	0.09	0.07
Fe	0.01	0.01	0.00	0.03	0.02	0.00	0.00
Total	100.91	99.52	100.72	99.75	100.63	99.06	99.31

	14100(W198)			
	1	2	3	4
Pb	86.26	86.73	86.57	86.30
S	12.88	12.78	13.15	13.16
Ag	0.06	0.03	0.00	0.06
Sb	0.00	0.00	0.01	0.07
Fe	0.00	0.00	0.00	0.00
Total	99.20	99.54	99.73	99.59

Hessite, Ag₂ Te

	13961(TK7)									
	1	2	3	4	5	6	7	8	9	10
Ag	63.17	63.26	62.29	63.30	62.17	63.49	63.40	63.36	62.48	62.99
Te	37.41	37.23	36.97	37.18	37.10	37.26	37.18	36.71	37.07	36.51
S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Fe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Au	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
As	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Se	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.58	100.49	99.26	100.48	99.27	100.75	100.58	100.07	99.55	99.50

	14092(W183)				14094(W198)			
	11	1	2	3	1	2	3	4
Ag	63.42	62.61	60.06	61.05	62.16	58.21	60.54	61.44
Te	36.94	37.60	38.47	37.14	38.07	41.11	40.08	37.45
S	n.a.	0.07	0.22	0.22	0.04	0.03	0.02	0.09
Cu	n.a.	0.17	0.28	0.14	0.00	0.01	0.01	0.10
Fe	n.a.	0.00	0.00	0.02	0.00	0.01	0.00	0.00
Au	n.a.	0.00	0.19	0.00	0.00	0.00	0.22	0.00
As	n.a.	0.38	0.54	0.75	0.52	0.00	0.12	0.50
Se	n.a.	0.72	0.38	0.00	0.00	0.00	0.00	0.00
Total	100.36	101.55	100.14	99.32	100.79	99.37	100.99	99.58

Hessite, Ag₂Te (Continued)

	14094(W198)	285/37/2 (M12)				
	5	1	2	3	4	5
Ag	62.02	61.70	62.42	63.12	63.59	62.74
Te	37.71	37.11	36.36	36.81	37.15	37.45
S	0.08	0.12	0.34	0.11	0.10	0.12
Cu	0.13	0.00	0.01	0.04	0.00	0.00
Fe	0.00	0.00	0.00	0.00	0.04	0.00
Au	0.00	0.00	0.08	0.00	0.57	1.44
As	0.11	0.07	0.14	0.00	0.26	0.00
Se	0.00	0.18	0.41	0.27	0.12	0.00
Total	100.05	99.18	99.76	100.35	101.83	101.75

	285/37/6 (M13)				
	1	2	3	4	5
Ag	63.28	62.77	61.27	62.43	62.80
Te	37.45	36.99	37.15	36.78	37.39
S	0.10	0.17	0.09	0.10	0.09
Cu	0.00	0.01	0.00	0.00	0.00
Fe	0.00	0.05	0.02	0.00	0.00
Au	0.00	0.86	0.82	0.25	0.00
As	0.00	0.13	0.00	0.00	0.25
Se	0.00	0.00	0.00	0.00	0.00
Total	100.83	100.98	99.35	99.56	100.53

Pyrite, Fe S₂

	13909(Tul 30)	13915(Tul 27)		14025(c)(TL22 ₉)	14032(6J3)	
	1	1	2	1	1	2
Fe	46.81	46.94	46.29	46.90	45.35	45.92
S	53.54	53.15	53.43	53.31	52.90	52.36
Cu	0.39	0.00	0.07	0.03	0.00	0.06
Au	0.02	0.18	0.00	0.25	0.26	0.33
Ag	0.00	0.00	0.04	0.03	0.05	0.00
As	0.00	0.00	0.00	0.23	1.50	1.46
Te	0.03	0.00	0.00	0.00	0.00	0.00
Se	0.02	0.06	0.68	0.16	0.56	0.00
Total	100.81	100.33	100.52	100.91	100.61	100.14

Pyrite, Fe S₂ (Continued)

	14046(Wh43)		14048(Wh45)		14058(Tui 15)	
	1	2	1		1	
Fe	46.42	46.84	46.33		47.48	
S	52.13	52.93	53.58		53.15	
Cu	0.01	0.00	0.16		0.02	
Au	0.00	0.00	0.00		n.a.	
Ag	0.04	0.00	0.00		0.01	
As	1.06	0.44	0.01		0.00	
Te	0.00	0.00	0.00		n.a.	
Se	0.00	0.00	0.83		n.a.	
Total	99.66	100.21	100.91		100.66	

	285/37/7 (M14)		285/37/8 (M32)	
	1		11	2
Fe	47.46		46.14	46.21
S	52.44		53.36	52.98
Cu	0.03		0.02	0.10
Au	0.00		0.00	0.76
Ag	0.00		0.00	0.05
As	0.56		0.03	0.00
Te	0.05		0.00	0.00
Se	0.00		0.00	0.00
Total	100.53		99.54	100.10

Pyrrhotite, Fe S

	13965 _(a) (MH1)			13965 _(b) (MH1)					
	1	2	3	1	2	3	4	5	6
Fe	59.75	59.93	59.23	59.60	59.46	59.77	59.92	59.29	59.77
S	40.07	39.55	39.48	39.74	39.45	39.03	39.12	39.33	39.26
Zn	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cu	0.20	0.13	0.38	0.15	0.05	0.02	0.12	0.10	0.08
Mn	0.06	0.03	0.05	0.06	0.05	0.08	0.06	0.06	0.04
As	0.03	0.01	0.08	0.00	0.00	0.02	0.02	0.00	0.00
Co	0.22	0.25	0.25	0.43	0.42	0.33	0.28	0.38	0.35
Ag	0.00	0.00	0.03	0.00	0.02	0.00	0.00	0.03	0.00
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.33	99.90	99.50	99.98	99.45	99.25	99.52	99.19	99.50

Pyrrhotite, Fe S (Continued)

	13965 ^(b) (MH1) (Continued)		13965 ^(c) (MH1)	
	7	8	1	2
Fe	59.93	59.82	59.79	59.86
S	39.24	39.00	39.29	38.98
Zn	n.a.	n.a.	n.a.	n.a.
Cu	0.18	0.09	0.20	0.21
Ni	0.07	0.05	0.05	0.08
As	0.02	0.07	0.00	0.01
Co	0.24	0.33	0.33	0.32
Ag	0.00	0.01	0.01	0.02
Cd	0.00	0.00	0.00	0.00
Total	99.68	99.37	99.67	99.48

14040(Wh29)							
	1	2	3	4	5	6	7
Fe	58.77	59.38	59.04	59.11	58.82	58.53	57.85
S	39.37	40.09	39.40	38.81	40.41	40.17	39.78
Zn	1.05	1.41	1.45	1.46	1.58	1.38	1.08
Cu	0.00	0.01	0.01	0.02	0.00	0.00	0.01
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As	0.37	0.08	0.11	0.10	0.14	0.37	0.99
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ag	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Cd	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.56	100.97	100.01	99.50	100.95	100.45	99.71

Sphalerite, Zn S

13908(GB 5)								
	1	2	3	4	5	6	7	8
Zn	65.94	65.88	65.86	65.65	65.99	64.12	65.85	66.01
Fe	0.91	1.00	0.97	1.13	1.02	2.44	1.00	0.81
S	32.05	32.80	32.71	32.28	32.07	32.82	32.28	32.10
Cd	0.13	0.15	0.13	0.16	0.13	0.17	0.17	0.16
Mn	0.07	0.08	0.07	0.09	0.06	0.02	0.04	0.05
Cu	0.01	0.00	0.02	0.06	0.00	0.35	0.00	0.02
Total	99.11	99.91	99.76	99.37	99.27	99.92	99.34	99.15

13937(M33)					13959(TK1)					
	1	2	3	4		1	2	3	4	5
Zn	66.55	66.52	66.94	65.64		65.13	63.42	64.23	64.32	65.48
Fe	0.28	0.26	0.26	0.43		2.16	3.65	2.29	2.31	1.52
S	32.99	32.47	33.11	32.31		32.03	33.07	32.69	33.11	32.65
Cd	0.30	0.19	0.23	0.28		0.26	0.26	0.18	0.15	0.22
Mn	0.27	0.33	0.18	0.90		0.15	0.46	0.42	0.30	0.30
Cu	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.39	99.77	100.72	99.56		99.73	100.86	99.81	100.19	100.17

Sphalerite, Zn S (Continued)

13966 _(a) (MH1)								
	1	2	3	4	5	6	7	8
Zn	57.04	57.64	57.52	56.88	56.67	55.91	56.57	56.73
Fe	9.29	8.86	8.72	9.36	9.24	9.79	9.62	9.51
S	32.29	33.45	32.42	33.46	32.59	33.49	32.27	33.14
Cd	0.52	0.53	0.54	0.55	0.49	0.57	0.52	0.56
Mn	0.11	0.11	0.11	0.11	0.11	0.06	0.10	0.11
Cu	0.09	0.04	0.04	0.15	0.15	0.14	0.31	0.25
Total	99.34	100.63	99.35	100.51	99.25	99.96	99.39	100.30

13966 _(b) (MH1)									
	1	2	3	4	5	6	7	8	9
Zn	56.57	56.45	56.37	56.15	56.10	56.00	57.03	56.26	55.00
Fe	9.60	9.79	9.75	9.42	9.50	9.55	8.94	9.47	10.41
S	33.53	32.58	33.55	32.70	33.96	32.71	33.34	32.97	33.65
Cd	0.54	0.52	0.53	0.52	0.53	0.48	0.56	0.52	0.56
Mn	0.08	0.09	0.09	0.10	0.10	0.09	0.10	0.09	0.06
Cu	0.27	0.42	0.44	0.13	0.25	0.36	0.20	0.15	0.58
Total	100.59	99.85	100.73	99.02	100.44	99.19	100.17	99.46	100.26

	13966 _(c) (MH1)				13966 _(d) (MH1)				
	1	23	3		1	2	3	4	5
Zn	56.33	56.78	56.47		56.78	57.10	57.59	57.30	57.33
Fe	9.34	9.35	9.64		9.29	8.95	8.91	8.89	8.96
S	32.92	33.47	33.12		32.40	33.32	33.26	32.30	33.05
Cd	0.51	0.55	0.59		0.56	0.62	0.59	0.62	0.62
Mn	0.10	0.10	0.11		0.10	0.09	0.09	0.10	0.10
Cu	0.22	0.20	0.30		n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.42	100.45	100.23		99.13	100.08	100.44	99.21	100.06

13971(DG12)										
	1	2	3	4	5	6	7	8	9	10
Zn	63.85	64.86	64.86	64.49	63.78	64.13	62.88	62.32	64.05	63.91
Fe	2.82	3.01	2.97	2.66	3.04	2.94	3.66	4.27	3.32	3.09
S	32.03	31.89	32.44	32.65	32.59	32.42	32.74	32.92	32.03	33.08
Cd	0.35	0.27	0.38	0.20	0.37	0.24	0.33	0.32	0.32	0.32
Mn	0.25	0.22	0.25	0.24	0.31	0.25	0.56	0.37	0.30	0.50
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.29	100.25	100.90	100.24	100.10	99.98	100.17	100.19	100.02	100.91

Sphalerite, Zn S (Continued)

	13971(DC12)	13974(SM11)							
	11	1	2	3	4	5	6	7	8
Zn	63.80	66.29	65.78	66.24	65.74	66.30	66.91	65.99	66.15
Fe	2.86	0.71	0.81	0.78	1.05	0.89	0.80	0.98	0.94
S	32.15	32.62	32.63	32.59	32.24	32.50	31.77	32.63	32.58
Cd	0.25	0.42	0.53	0.50	0.44	0.40	0.37	0.31	0.37
Mn	0.34	0.05	0.08	0.06	0.05	0.12	0.09	0.16	0.13
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.40	100.09	99.83	100.17	99.52	100.21	99.94	100.07	100.17

	13979(W1110)					13982(AS5)			
	1	2	3	4	5	1	2	3	4
Zn	66.38	66.10	67.12	66.83	67.45	65.79	64.67	66.48	65.97
Fe	0.93	0.62	0.48	0.55	0.54	1.71	1.72	1.72	1.75
S	31.62	32.21	31.90	31.90	32.12	32.22	32.85	32.19	32.05
Cd	0.17	0.24	0.24	0.28	0.12	0.33	0.29	0.31	0.33
Mn	0.23	0.15	0.11	0.09	0.26	0.08	0.10	0.11	0.08
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.33	99.32	99.85	99.66	100.48	100.14	99.63	100.81	100.18

	13985(HC3)								
	5	1	2	3	4	5	6	7	8
Zn	65.38	65.77	67.05	64.78	66.51	66.92	66.11	66.49	66.52
Fe	1.71	0.65	0.73	1.24	0.99	0.49	0.96	0.86	0.90
S	32.41	33.21	32.05	32.76	32.80	32.78	33.09	33.13	32.58
Cd	0.36	0.19	0.21	0.24	0.25	0.29	0.32	0.25	0.33
Mn	0.11	0.10	0.16	0.14	0.19	0.16	0.20	0.19	0.17
Cu	n.a.	0.08	0.10	0.84	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.98	100.01	100.29	99.99	100.74	100.64	100.68	100.92	100.52

	13989(HC4)								
	9	10	1	2	3	4	5	6	
Zn	66.70	66.66	66.42	65.86	65.92	66.05	66.89	66.41	
Fe	0.79	0.81	0.82	0.85	0.80	0.77	0.67	0.86	
S	32.11	32.85	32.21	33.29	32.01	32.49	32.44	32.55	
Cd	0.17	0.22	0.29	0.28	0.31	0.25	0.29	0.17	
Mn	0.15	0.14	0.21	0.22	0.22	0.23	0.19	0.19	
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Total	99.92	100.69	99.95	100.50	99.26	99.80	99.89	100.18	

Sphalerite, Zn S (Continued)

13991(PS4)							14000(PS21c)		
	1	2	3	4	5	6	1	2	3
ZZ	67.45	66.34	66.53	65.71	67.07	66.09	66.49	65.52	65.54
Fe	0.73	1.33	1.16	1.29	1.07	1.12	1.13	1.45	1.41
S	32.11	32.28	32.90	32.59	31.61	32.44	32.75	33.58	31.85
Cd	0.27	0.22	0.18	0.26	0.31	0.34	0.24	0.23	0.30
Mn	0.06	0.05	0.10	0.07	0.05	0.11	0.05	0.05	0.07
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.63	100.21	100.86	99.93	100.11	100.11	100.66	100.84	99.17

14002(PS21h)									
	4	5	6	1	2	3	4	5	6
Zn	65.67	64.93	66.07	66.69	66.84	66.75	67.05	67.07	65.96
Fe	1.00	1.66	1.10	0.82	0.87	0.86	0.49	0.54	1.75
S	32.10	32.27	32.54	31.87	32.26	32.31	32.60	32.49	31.16
Cd	0.33	0.16	0.27	0.29	0.29	0.22	0.21	0.28	0.28
Mn	0.06	0.06	0.05	0.25	0.20	0.17	0.18	0.06	0.16
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.17	99.09	100.04	99.93	100.46	100.30	100.53	100.45	99.30

14015(WK6)							14020(WK13)	
	7	1	2	3	4	5	1	2
Zn	66.23	67.33	67.14	66.87	65.31	66.41	65.84	66.00
Fe	0.92	0.27	0.31	0.31	1.52	0.54	0.77	0.98
S	32.50	32.28	32.46	33.15	33.55	32.17	31.93	32.28
Cd	0.32	0.22	0.27	0.26	0.23	0.23	0.25	0.35
Mn	0.00	0.18	0.30	0.30	0.28	0.31	0.56	0.56
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.06	100.28	100.48	100.89	100.89	99.66	99.36	100.21

	3	4	5	6	7	8	9	10	11
Zn	65.43	64.22	64.27	64.27	64.61	64.92	65.44	65.01	65.09
Fe	1.34	1.86	1.90	1.86	1.58	1.07	0.81	1.26	0.94
S	32.12	31.96	32.21	32.00	32.51	32.10	32.26	32.13	32.55
Cd	0.30	0.37	0.36	0.29	0.31	0.34	0.29	0.35	0.40
Mn	0.55	0.59	0.58	0.61	0.63	0.60	0.56	0.53	0.54
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.73	99.00	99.30	99.04	99.64	99.03	99.36	99.28	99.52

14023(TI.17)						14025 _(a) (TI22 ₂)		
	1	2	3	4	5	1	2	3
Zn	63.27	64.15	62.48	63.72	63.37	63.84	63.68	63.72
Fe	2.22	2.04	2.72	2.28	2.71	1.46	1.35	1.21
S	32.92	33.09	32.99	33.37	33.00	33.03	33.28	33.24
Cd	0.37	0.38	0.40	0.38	0.38	0.16	0.18	0.21
Mn	0.53	0.48	0.55	0.54	0.55	0.96	0.97	0.88
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.31	100.14	99.14	100.29	100.01	99.45	99.46	99.26

Sphalerite, Zn S (Continued)

14025 _(b) (TL22 ₆)					14025 _(c) (TL22 ₉)			
	1	2	3	4	1	2	3	4
Zn	64.76	65.04	64.65	64.30	62.55	63.67	64.01	62.37
Fe	1.53	1.46	1.57	1.57	1.80	1.34	1.10	1.43
S	32.65	32.11	32.20	32.32	34.08	33.28	33.57	33.53
Cd	0.19	0.12	0.15	0.15	0.27	0.25	0.24	0.23
Mn	0.87	0.87	0.91	0.86	1.87	1.22	0.79	1.53
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.99	99.60	99.48	99.19	100.57	99.76	99.71	99.09

14040(Wh29)						14046(Wh43)			
	1	2	3	4	5	6	1	2	3
Zn	53.78	53.31	54.09	54.42	53.88	54.13	60.64	61.89	59.79
Fe	11.76	12.11	11.83	10.80	11.12	11.21	5.69	4.03	6.51
S	33.62	33.31	33.81	33.59	33.37	33.28	32.01	33.10	33.43
Cd	0.10	0.07	0.08	0.10	0.08	0.10	0.05	0.09	0.06
Mn	0.92	1.03	0.89	0.72	0.79	0.70	0.69	0.77	0.71
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.18	99.83	100.70	99.63	99.24	99.42	99.08	99.88	100.50

						14047(Wh44)			
	4	5	6	7	8	9	1	2	3
Zn	59.15	59.77	59.29	59.43	58.44	59.34	66.13	65.10	64.25
Fe	7.13	6.80	6.82	6.39	7.49	6.11	1.43	2.08	1.92
S	33.21	33.38	32.29	33.53	33.26	33.21	33.01	32.46	32.34
Cd	0.09	0.09	0.04	0.08	0.08	0.10	0.11	0.18	0.13
Mn	0.74	0.72	0.66	0.72	0.75	0.77	0.27	0.52	0.40
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.32	100.76	99.10	100.15	100.02	99.53	100.95	100.34	99.04

					14048(Wh45)				
	4	5	6	7	8	1	2	3	4
Zn	63.93	63.97	65.90	66.46	65.01	65.63	66.36	66.39	65.26
Fe	2.64	2.41	1.10	1.02	1.42	1.00	0.70	0.60	1.20
S	32.26	32.90	31.94	32.12	32.73	32.89	31.81	32.71	32.93
Cd	0.18	0.15	0.08	0.09	0.09	0.14	0.16	0.15	0.19
Mn	0.53	0.53	0.42	0.39	0.46	0.56	0.48	0.48	0.72
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.54	99.96	99.44	100.08	99.71	100.22	99.51	100.33	100.30

							14052(Wh50)		
	5	6	7	8	9	10	11	1	2
Zn	65.31	65.30	65.30	66.17	66.17	65.04	65.47	60.51	60.83
Fe	1.28	1.23	1.36	0.48	0.98	1.33	1.22	6.02	5.99
S	32.13	33.03	32.09	32.34	32.66	32.75	32.97	32.24	31.89
Cd	0.12	0.16	0.14	0.12	0.17	0.19	0.17	0.08	0.07
Mn	0.60	0.67	0.89	0.40	0.46	0.65	0.49	0.27	0.33
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.44	100.39	99.78	99.51	100.44	99.96	100.32	99.13	99.10

Sphalerite, Zn S (Continued)

14052(Wh50)(Cont'd)							14057(Tui 14)	
	3		1	2	3	4	5	6
Zn	60.87		65.96	65.36	66.04	65.10	66.69	65.65
Fe	5.67		1.20	1.29	1.30	1.34	1.07	1.10
S	32.44		32.25	31.91	31.87	32.24	31.12	32.48
Cd	0.12		0.50	0.34	0.34	0.29	0.44	0.10
Mn	0.30		0.04	0.15	0.10	0.08	0.05	0.41
Cu	n.a.		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.40		99.95	99.04	99.65	99.06	99.37	99.80

14058(Tui 15)								14059(Tui 17)	
	1	2	3	4	5	6	7	1	2
Zn	65.73	65.78	66.01	64.93	65.32	66.46	65.22	65.62	65.32
Fe	1.16	1.67	2.12	2.09	1.41	1.36	1.28	1.32	1.40
S	32.03	32.59	31.78	31.90	32.05	32.06	32.25	32.23	33.07
Cd	0.28	0.38	0.38	0.37	0.62	0.53	0.37	0.47	0.48
Mn	0.09	0.11	0.11	0.08	0.09	0.07	0.11	0.08	0.11
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.01	0.01
Total	99.29	100.52	100.40	99.36	99.50	100.48	99.22	99.74	100.40

								14060(Tui 18)		
	3	4	5	6	7	8		1	2	3
Zn	64.53	64.00	64.31	65.97	64.89	64.03		65.60	66.01	66.25
Fe	2.07	1.93	1.84	1.39	1.68	2.02		1.29	1.34	1.16
S	33.05	32.87	32.53	32.79	32.31	33.01		32.64	32.90	33.21
Cd	1.09	0.91	0.69	0.43	0.78	0.95		0.36	0.24	0.21
Mn	0.12	0.11	0.10	0.07	0.11	0.14		0.06	0.04	0.06
Cu	0.00	0.00	0.00	0.02	0.02	0.08		n.a.	n.a.	n.a.
Total	100.87	99.81	99.47	100.66	99.78	100.21		99.95	100.54	100.90

								14061(Tui 19)	
	4	5	6	7		1	2	3	4
Zn	64.79	65.50	65.33	65.64		64.65	65.65	65.45	65.60
Fe	1.42	1.36	0.93	1.02		1.50	1.48	1.43	1.34
S	33.05	32.89	32.54	32.71		33.05	33.06	33.11	32.63
Cd	0.51	0.37	0.32	0.22		0.51	0.67	0.50	0.64
Mn	0.08	0.07	0.17	0.05		0.04	0.07	0.06	0.06
Cu	n.a.	n.a.	n.a.	n.a.		0.00	0.00	0.00	0.02
Total	99.85	100.20	99.29	99.63		99.74	100.93	100.55	100.29

14072(Wi21)								
	1	2	3	4	5	6	7	8
Zn	65.70	66.91	66.60	66.31	66.69	66.12	66.49	66.81
Fe	0.58	0.49	0.65	0.68	0.66	0.60	1.63	0.83
S	32.86	32.60	32.19	31.43	31.87	31.98	32.23	32.13
Cd	0.31	0.43	0.48	0.59	0.57	0.51	0.42	0.41
Mn	0.07	0.12	0.10	0.16	0.16	0.15	0.09	0.08
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.52	100.56	100.02	99.17	99.95	99.36	100.87	100.27

Sphalerite, Zn S (Continued)

14075(w127)								14082(w153)	
	1	2	3	4	5	6	7	1	2
Zn	66.22	66.27	66.05	65.29	65.92	65.95	66.20	66.04	65.76
Fe	1.03	0.95	1.03	1.75	0.87	1.74	1.29	0.55	0.41
S	32.13	32.22	31.63	32.96	32.43	32.68	32.79	32.54	32.53
Cd	0.16	0.20	0.24	0.06	0.26	0.18	0.11	0.36	0.23
Mn	0.05	0.11	0.09	0.03	0.05	0.06	0.06	0.10	0.15
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.60	99.76	99.03	100.09	99.63	100.60	100.45	99.60	99.08

								14086(W158)	
	3	4	5	6	7	8	9	1	2
Zn	66.44	66.57	64.80	65.78	65.97	66.24	66.32	65.80	65.48
Fe	0.51	0.58	1.57	1.60	1.03	0.76	0.70	1.15	1.13
S	33.21	32.27	32.84	32.18	32.13	32.48	32.49	32.59	32.44
Cd	0.29	0.27	0.40	0.38	0.23	0.31	0.38	0.18	0.28
Mn	0.07	0.16	0.07	0.04	0.06	0.09	0.07	0.09	0.08
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.53	99.84	99.80	99.98	99.42	99.88	99.97	99.82	99.41

14092(w183)									
	3	4	5	6	1	2	3	4	5
Zn	66.05	65.47	64.77	64.22	65.90	66.34	66.31	66.19	66.11
Fe	1.16	1.39	2.03	1.73	0.48	0.34	0.47	0.46	0.50
S	32.30	32.67	32.43	32.70	32.23	32.42	32.05	32.25	32.14
Cd	0.21	0.09	0.22	0.30	0.30	0.26	0.29	0.27	0.24
Mn	0.09	0.09	0.07	0.07	0.35	0.33	0.33	0.32	0.34
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.81	99.71	99.51	99.03	99.26	99.69	99.45	99.48	99.33

14100(w198)									
	6	7	8	9	10	1	2	3	4
Zn	65.84	67.39	66.32	66.60	66.67	65.56	65.25	66.20	66.40
Fe	0.52	0.48	0.37	0.40	0.39	0.73	0.72	0.67	0.64
S	32.31	31.68	32.23	32.13	32.48	33.12	32.68	33.09	32.44
Cd	0.30	0.30	0.13	0.23	0.33	0.24	0.24	0.21	0.27
Mn	0.36	0.34	0.37	0.33	0.36	0.14	0.14	0.09	0.15
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.33	100.20	99.41	99.69	100.22	99.79	99.03	100.26	99.90

285/37/6(M13)									
4	5	6	1	2	3	4	5	6	7
Zn	66.08	66.07	65.46	64.13	64.77	64.04	65.32	64.98	65.49
Fe	0.69	0.54	0.47	1.08	0.60	0.40	0.41	0.53	0.59
S	32.78	32.09	33.64	33.59	33.27	34.12	33.71	34.16	33.97
Cd	0.27	0.23	0.76	0.72	0.73	1.14	1.15	0.80	0.75
Mn	0.10	0.19	0.04	0.05	0.04	0.06	0.06	0.04	0.05
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.92	99.12	100.37	99.57	99.41	99.76	100.65	100.51	100.85

Sphalerite, Zn S (Continued)

	285/37/7(M14)		285/37/8(M32)		3	4	5	6	7
	1	2	1	2					
Zn	66.95	67.01	66.64	66.98	66.97	66.89	66.94	66.65	66.43
Fe	0.32	0.30	0.37	0.28	0.30	0.33	0.31	0.36	0.36
S	31.34	31.44	31.37	33.07	31.83	32.72	32.95	31.29	32.97
Cd	0.27	0.24	0.32	0.23	0.29	0.33	0.21	0.23	0.26
Mn	0.36	0.38	0.40	0.27	0.33	0.29	0.46	0.50	0.45
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	99.24	99.37	99.01	100.83	99.72	100.56	100.87	99.03	100.47

						M18185			
	8	9	10	11	12	1	2	3	4
Zn	66.33	65.67	65.96	66.86	65.48	65.37	65.52	65.52	65.18
Fe	0.29	0.49	0.28	0.21	0.35	0.31	0.32	0.32	0.30
S	32.83	32.38	32.77	31.41	32.91	34.59	33.87	34.11	33.63
Cd	0.27	0.22	0.28	0.25	0.28	0.20	0.22	0.19	0.19
Mn	0.43	0.65	0.48	0.27	0.57	0.30	0.45	0.50	0.42
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.15	99.41	99.77	99.00	99.59	100.77	100.38	100.64	99.72

						M18186			
	5	6	7	8	9	1	23	3	4
Zn	64.93	65.54	65.89	65.31	65.84	66.20	65.52	65.10	65.42
Fe	0.26	0.25	0.23	0.28	0.23	0.17	0.20	0.51	0.31
S	33.92	34.07	33.70	33.46	33.83	33.79	33.48	33.59	33.77
Cd	0.17	0.22	0.17	0.21	0.18	0.20	0.20	0.20	0.19
Mn	1.62	0.67	0.53	0.49	0.54	0.43	0.39	0.40	0.58
Cu	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Total	100.90	100.75	100.52	99.75	100.62	100.79	99.79	99.80	100.27

	5	6	7	8
Zn	66.02	65.96	64.96	64.82
Fe	0.29	0.26	0.02	0.01
S	33.35	32.24	33.30	33.12
Cd	0.18	0.23	0.18	0.19
Mn	0.57	0.51	1.23	1.39
Cu	n.a.	n.a.	n.a.	n.a.
Total	100.41	99.20	99.69	99.53

Tetradymite, $\text{Bi}_2\text{Te}_2\text{S}$

13915(Tui 27)

1

Bi	60.91
Te	32.44
S	4.71
Cu	0.07
Pb	0.00
Se	0.00
Fe	0.00
Total	<u>98.13</u>

Tetrahedrite, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ - Tennantite, $\text{Cu}_{12}\text{As}_4\text{S}_{13}$

13979(Will10) Tetrahedrite

14058(Tui 15) Tetrahedrite

	1	2	3	4	1	2	3	4	5
Cu	39.11	40.10	39.55	38.48	36.12	36.10	36.38	36.61	35.85
S	25.45	26.00	25.06	24.79	23.82	24.62	24.12	24.75	23.97
Sb	20.47	17.37	22.67	23.99	29.41	28.71	29.42	27.51	29.98
As	6.81	9.32	4.89	5.07	0.62	0.84	0.95	2.30	0.85
Zn	5.96	6.48	5.79	6.65	4.83	4.79	4.43	5.53	4.81
Fe	1.69	1.57	1.72	1.05	2.64	2.42	2.59	1.96	2.46
Ag	0.10	0.09	0.11	0.20	2.36	2.62	2.60	2.32	2.54
Ni	0.01	0.04	0.01	0.01	0.02	0.00	0.05	0.00	0.04
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cd	0.00	0.00	0.11	0.13	0.05	0.05	0.00	0.00	0.06
Total	99.60	100.96	99.90	100.37	99.87	100.15	100.54	100.98	100.56

Tennantite

	6	1	2
Cu	36.44	42.52	43.06
S	24.07	27.83	27.56
Sb	29.88	0.38	0.15
As	0.52	18.95	19.39
Zn	4.81	6.75	6.78
Fe	2.77	2.56	2.22
Ag	1.72	0.17	0.04
Ni	0.00	0.00	0.00
Mn	0.02	0.00	0.00
Cd	0.00	0.07	0.07
Total	<u>100.23</u>	<u>99.23</u>	<u>99.27</u>

APPENDIX IIIPROCEDURES AND RESULTS OF FLUID INCLUSION
FILLING TEMPERATURE, FREEZING TEMPERATURE
AND APPARENT SALINITY MEASUREMENTSPROCEDURESSample preparation for optical examination

Plates of barite were separated from quartz crystals with a pair of pliers and used without further preparation.

Most of the plates of calcite and sphalerite studied were obtained by cleaving them off samples with a pocket knife or fine cold chisel. Other samples of calcite and sphalerite and all samples of quartz were cut into thin plates and ground and polished on both sides.

Considerable problems were experienced in polishing samples of quartz (and ore mounts) during the course of this thesis. However, by experimenting with different polishing materials, the following technique was finally adopted.

Samples were glued to glass slides with lakeside cement. The glass slides were attached with candle wax to special aluminium holders to facilitate hand holding during the following procedures.

- Grinding:
- (1) diamond lap, water lubricant
 - (2) carborundum powders on glass plates or rotating zinc laps; 280, 400 and 600 grades, water lubricant (approximately 3 minutes on each grade on rotating zinc laps)
 - (3) Aluminium oxide powders on glass plates; 12.5 μ m and 5 μ m grades, water lubricant (2-3 minutes each grade)

Polishing: Samples were hand held on a Struers DP10 machine using Bueler cloths and diamond pastes.

- (1) 6 μ m on nylon cloth, water lubricant (drip fed), 20 minutes.

- (2) 1 μ m on microcloth, polishing oil lubricant, 10-15 drops applied to dry cloth or less to damp cloth before commencement of run, then one or two drops added periodically. 10 minutes polishing time.

After final polishing and cleaning the slides were removed from the aluminium holders, heated, the quartz plates turned over, and the slide reattached to the aluminium holder. The exposed rough side was ground and polished as above.

Polishing difficulties encountered before the adoption of the technique described above are attributed to:

- (1) use of coarse diamond paste (15 μ m) for initial polishing (followed by 6 μ m and 1 μ m grades)
- (2) incorrect cloths for diamond grade
- (3) use of oil lubricant for initial polishing stages causing difficulties in cleaning. Small quantities of contamination lodged in open inclusions and probably contaminated finer grades.
- (4) insufficient polishing time on initial stages.

Plates were generally made to a thickness of approximately 1mm and maximum diameter of 25mm. Selected areas of the large plates were trimmed to fit into the heating and freezing stages by grinding on a diamond lap or alternatively cut from the plates, while cemented on glass slides, with a 20mm diameter diamond disc mounted in a dentists drill (KaVo workshop hand-piece 277 and motor 520).

Selection of inclusions and their storage

Plates were scanned under the microscope at room temperature for selection of inclusions suitable for filling temperature and freezing point determinations. Suitable fields of view were drawn, noting the magnification (for later measurement of inclusion size from the drawings) and the plate transferred to the heating stage on another microscope.

Plates used for filling temperature measurements were subsequently mounted on a glass slide with "sellotape",

Figure III-1: Leitz 1350 heating stage mounted on a Leitz SM Lux Pol microscope with vertical illuminator attachment. The temperature is adjusted by regulating the current supplied to the stage from the transformer in the right background, and is read directly off the meter in the foreground. The outer parts of the stage are water cooled.

retaining the same orientation as in the drawing. Depending on the width of the sellotape used, up to 4 plates can be mounted on a single 25x76mm glass slide with room for the label. Mounting in this way allowed for quick location of inclusions for freezing point determinations or later reference.

Determination of Filling Temperatures

All filling temperatures are liquid - vapour homogenisation in the liquid phase. They were determined using a Leitz 1350 heating stage. Initially this was mounted on a Leitz DIALUX-Pol microscope fitted with binocular head, X10 eyepieces and X3.5 and X10 objectives. Special long focus H20 and H32 objectives were later used for higher magnification but required an infinity tube length, not obtainable on the standard DIALUX-Pol microscope. This was achieved using a SM-LUX-Pol microscope, Fig III-1, fitted with the vertical illuminator attachment and binocular head, but still used in transmitted light mode. The NPL (incident light) 5x/0.09P and 10x/0.20P objectives, fitted with 6mm and 15mm extension rings respectively, provided a parafocal objective set with the H20 and H32 (the normal transmitted light 4 and 10x objectives give a poor image with the vertical illuminator in place). 18x eyepieces were experimented with but gave no better resolution with the H32 than the normal 10x. Therefore the latter were used throughout.

The stage was periodically calibrated using organic melting point standards from a Thomas 6608-M10 Test Reagent Set (obtained from Arthur H. Thomas Co., Philadelphia, Pa, U.S.A) for the temperature range 43°C - 328°C and $K_2Cr_2O_7$ for 398°C.

Precision of filling temperatures and standards was found to be within $\pm 3^\circ\text{C}$ at approximately 300°C. Once the stage is calibrated the accuracy of a filling temperature measurement is dependant on the thickness of the sample used and the height of the fluid inclusion within the sample (because of thermal gradients set up within the system). Some "thick" plates (up to 2mm) were used in this study. The accuracy of individual measurements is therefore probably no better than $\pm 10^\circ\text{C}$. Therefore an overall experimental error of $\pm 10^\circ\text{C}$ is assigned to the filling temperature measurements reported in this thesis although in most samples it will be considerably less but in a few perhaps slightly greater.

Figure III-2: Freezing stage mounted on a Leitz Dialux microscope (see also Fig. III-5). The temperature is read directly off the meter in the foreground.

Determination of Salinities

Freezing point depressions (last point of ice melting temperatures) of inclusion fluids were measured in two instruments; a "homemade" freezing stage (Fig III-2), described below, and a Chaix-Meca combined heating-freezing stage installed at the Institute of Nuclear Sciences. The operation and calibration of the latter is described by Duckworth and Robinson (1979). The freezing point depression results were converted to salinities using the equation in Potter et al (1978).

Experimental errors in freezing point measurements, translated into errors in salinity values are considered to be within ± 0.5 wt.% NaCl over the range of measurements quoted. These large errors for equipment with apparently very accurate temperature measuring devices are due to thermal gradients in the Chaix-Meca stage with thick plates and changing gas flow conditions between measurement of sample and standard in the "homemade" stage.

Freezing Stage Construction

The freezing stage, constructed by the Victoria University Workshop, is based on the design suggested by Smith (1973) but differs in materials used and temperature measuring instrumentation. Figs III-3 and III-4 illustrate the general details of construction.

The body was made by milling out a block of 62mm diameter PTFE teflon rod and adding a teflon base plate incorporating a perspex window. A perforated copper gas delivery tube and three copper gauzes, for mixing the cooling gas, are held in place within the chamber by circular perspex spacers. The sample sits on a clear circular plate sample holder from the Leitz heating stage (Leitz catalogue No. 515052) resting in a lip on the top copper gauze. The top window is also a spare part from the heating stage (the lower window, part No. 515043) and sits in a recess milled into the top of the stage.

Misting of the top window, encountered in trial runs, was later prevented by the incorporation of a glass collar surrounding the microscope objective and fed with dry nitrogen gas.

Figure III-3: Cross section of the freezing stage constructed by the University Workshop (see Fig. III-4 for parts description).

Figure III-4: Parts of the freezing stage (see Fig. III-3 for dimensions):
 1 = top window; 2, 4, 6 and 8 = perspex spacing collars; 3, 5 and 7 = copper gauzes; 9 = demisting collar; 10 = sample holder; 11 = stage body; 12 = lower plate of stage with bottom window; 13 = screws, 14 = gas delivery tube; 15 = mounting, with translation screws; 16 = mounting screws; 17 = substage with blue filter.

Figure III-5: Diagrammatic layout of freezing stage apparatus. Dry nitrogen, supplied from a bottle, is cooled by passing it through a copper coil immersed in liquid nitrogen and then fed to the stage via a rubber delivery hose. The latter is insulated with polystyrene collars to prevent frosting and icing. The temperature of the stage is adjusted by varying the flow of cold gas with the needle valve. Dry nitrogen (at room temperature) is also supplied to a glass collar around the microscope objective, to prevent misting. Misting of the bottom window did not occur, probably because of the double window arrangement consisting of the bottom window of the freezing stage and the blue filter in the substage.

The collar rests on the top window, preventing it from lifting and allowing exit of the gas, as in the original design. Therefore a series of holes were drilled into the body of the stage around the edge of the top window.

The stage is mounted via a set of translational screws (off an old Swift microscope) to a perspex substage which is screwed onto the microscope stage.

Dry nitrogen from a cylinder is supplied separately, via needle valves and flow metres, to the demister and a copper coil immersed in liquid nitrogen. The cold nitrogen gas from the cooling coil is fed to the stage via a rubber tube insulated with polystyrene collars.

Temperature measurement is by copper-constantan thermocouple (made from 0.005mm teflon coated matched thermocouple wire obtained from OMEGA Engineering Inc. P.O. Box 4047 Stamford, Conn. 06907, U.S.A.) connected to a Comark 1624 electronic thermometer giving a readable range down to -60°C .

Freezing Stage Operating Instructions

The system is assembled as shown in Figs. III-2 and III-5. Dry nitrogen gas is run through the cooling system for several minutes to remove all traces of water vapour which might otherwise condense as ice in the next step.

While still maintaining a slow flow of dry nitrogen gas through the system, liquid nitrogen is poured into the cooling coil dewar. When the liquid nitrogen has ceased boiling vigorously the flow of gas can be reduced to a level just sufficient to prevent air backing into the system.

The Comark electronic thermometer can be turned on, its batteries checked and the control set to the ambient temperature range.

The sample is placed on the sample holder, the top window seated in its recess and the objective with demister collar swung into position (the demister collars are made to fit a Leitz x10/0.25P objective found on the DIALUX-Pol microscopes). A slow flow of dry nitrogen is supplied to the demister.

When a suitable inclusion is located in the sample the gas supply to the cooling system is opened and the temperature within the stage reduced while adjusting the range on the electronic thermometer. Most inclusions freeze between -30 and -40°C , shown by a sudden reduction in bubble size and loss of spherical shape. The temperature can be raised to near the last point of melting by reducing the gas flow. Great care is needed near the end point, especially if reversibility is to be tested. In the latter technique, the ice crystals are allowed to melt until only a very small fraction of ice remains, at which point the system is cooled slightly to allow the crystals to regrow and then warmed to complete melting. Ideally this can all be accomplished within a 0.2 to 0.3°C temperature range.

Although the scale of the electronic thermometer can be read to 0.1°C and estimated to 0.01°C , its accuracy and the precision of measurements are limited by its internal reference junction to $\pm 0.5^{\circ}\text{C}$. To obtain greater accuracy a sealed capillary tube containing a very small quantity of double-distilled water is placed in the stage alongside or on the sample and its freezing point determined immediately after that of the sample, during the same warm up run. Thus the last point of melting measurement of the sample will be a freezing point deviation from the pure water standard and not a reading from the electronic thermometer calibrated at some other time. However, if this procedure is used care must be taken to ensure that the same number of gas exit holes surrounding the top window remain uncovered throughout the manoeuvre of shifting position and focus from the sample to the capillary tube, otherwise the gas flow conditions may change within the chamber resulting in a different temperature balance between the thermocouple, sample and capillary.

RESULTS

Method of Listing

The filling temperature, freezing temperature and apparent salinity result for each sample are listed together. The samples are grouped geographically north to south into the various mining centres discussed in Appendix I. They are arranged within these groups in order of increasing V.U.W.

sample number. Field numbers and mineral identification are also given. The location and a brief description of each sample is given in Appendix IX.

Units

Filling and freezing temperatures are given in degrees centigrade, whereas apparent salinities are in units of equivalent weight percent sodium chloride (eq.wt.% NaCl).

MINERS HEAD

13966 (MH2) Quartz

FILLING TEMPERATURE	Primary inclusions	(47): 365, 371, 381 ⁽⁵⁾ , 382, 387, 390, 391, 392 ⁽⁸⁾ , 393 ⁽³⁾ , 394 ⁽¹⁰⁾ , 395, 396 ⁽²⁾ , 397 ⁽⁴⁾ , 398 ⁽⁴⁾ , 399, 400 and 402 ⁽²⁾ .
	Secondary inclusions	(21): 322 ⁽³⁾ , 329, 336, 337, 339 ⁽³⁾ , 341 ⁽²⁾ , 342, 346, 370 ⁽³⁾ and 371 ⁽⁵⁾ .
FREEZING TEMPERATURE	Primary inclusions	(26): -2.7 ⁽¹⁰⁾ , -2.8, -10.4, -10.5 ⁽¹³⁾ and -10.7
	Secondary inclusions	(11): -0.3, -0.4 ⁽³⁾ , -0.7 ⁽²⁾ , -0.9, -1.0 and -1.1 ⁽³⁾ .
APPARENT SALINITY	Primary inclusions	(26): 4.5 ⁽¹⁰⁾ , 4.6, 14.5, 14.6 ⁽¹³⁾ and 14.8
	Secondary inclusions	(11): 0.5, 0.7 ⁽³⁾ , 1.3 ⁽²⁾ , 1.6, 1.7 and 1.9 ⁽³⁾ .

TE AHUMATA

13952 (GB10) Quartz

FILLING TEMPERATURE	Primary inclusions	(37): 197, 201, 215, 221 ⁽²⁾ , 222, 223 ⁽³⁾ , 224 ⁽³⁾ , 226, 227 ⁽²⁾ , 228, 229 ⁽³⁾ , 231 ⁽²⁾ , 232 ⁽⁴⁾ , 244 ⁽²⁾ , 245, 249, 253, 254 ⁽²⁾ , 255, 258 ⁽³⁾ and 262.
FREEZING TEMPERATURE	Primary inclusions	(12): -0.3 ⁽²⁾ , -0.4 ⁽⁹⁾ and -0.5.
APPARENT SALINITY	Primary inclusions	(12): 0.5 ⁽²⁾ , 0.7 ⁽⁹⁾ and 0.9.

13953 (GB9) Quartz

FILLING TEMPERATURE	Primary inclusions	(24): 214, 222, 225, 226 ⁽²⁾ , 227 ⁽³⁾ , 229, 233, 234, 236 ⁽²⁾ , 239 ⁽³⁾ , 241, 253 ⁽²⁾ , 254, 261, 263 and 265.
FREEZING TEMPERATURE	Primary inclusions	(6): -0.6 ⁽⁴⁾ , -0.7 and -1.0
APPARENT SALINITY	Primary inclusions	(6): 1.1 ⁽⁴⁾ , 1.3 and 1.7

13954 (GB12) Quartz

FILLING TEMPERATURE	Primary inclusions	(36) 180, 204, 206, 210 ⁽³⁾ , 213 ⁽³⁾ , 215 ⁽²⁾ , 217 ⁽²⁾ , 218 ⁽²⁾ , 219, 221, 222 ⁽²⁾ , 223, 224 ⁽²⁾ , 225 ⁽²⁾ , 227, 232, 235, 240 ⁽³⁾ , 243, 246, 247, 248, 252 and 254.
	Secondary inclusions	(6): 176 ⁽²⁾ , 200, 215, 218 and 254.

NORTHERN COLVILLE PENINSULA

13971 (DC12) Quartz

FILLING TEMPERATURE	Primary inclusions	(54): 262, 263 ⁽²⁾ , 267, 271, 273, 274, 275, 276, 281, 282 ⁽²⁾ , 283 ⁽³⁾ , 284, 286, 287, 289, 290, 291, 292, 293 ⁽⁷⁾ , 294 ⁽²⁾ , 295 ⁽²⁾ , 296, 297 ⁽²⁾ , 300, 302 ⁽²⁾ , 303 ⁽²⁾ , 309, 313, 314 ⁽⁴⁾ , 317, 326, 329, 330, 331 ⁽²⁾ and 346.
	Secondary inclusions	(11): 225 ⁽²⁾ , 246, 252, 273, 274, 275 ⁽²⁾ , 278 and 279 ⁽²⁾ .
FREEZING TEMPERATURE	Primary inclusions	(1): -1.1
APPARENT SALINITY	Primary inclusions	(1): 1.9

13972 (SM4) Quartz

FILLING TEMPERATURE Primary inclusions (16): 254, 264, 265, 272₍₂₎, 273₍₂₎,
274, 275, 282, 283, 288₍₂₎, 292,
293 and 302.

13973 (SM7) Quartz

FILLING TEMPERATURE Secondary inclusions (10): 255, 257, 258₍₂₎, 259, 260,
262₍₂₎ and 263₍₂₎.
FREEZING TEMPERATURE Primary inclusions (2): -0.7 and -1.0
APPARENT SALINITY Primary inclusions (2): 1.3 and 1.7

KUAOTUNU

14007 (K 3) Quartz

FILLING TEMPERATURE Primary inclusions (2): 192 and 250.

14008 (K 4) Quartz

FILLING TEMPERATURE Primary or Secondary (5): 184, 187, 195, 196 and 249.
inclusions

14009 (GL1) Quartz

FILLING TEMPERATURE Primary inclusions (35): 224, 229₍₂₎, 243, 244, 245, 251,
252₍₅₎, 253, 255₍₂₎, 256, 260,
261₍₂₎, 262₍₃₎, 263₍₃₎, 264,
265₍₃₎, 268, 272, 273, 274, 282
and 291.
Secondary inclusions (25): 156, 161, 197, 202, 244, 245, 247,
249₍₂₎, 250, 252₍₃₎, 254, 255,
256, 258₍₂₎, 261, 263, 265, 270,
271, 273 and 291.

TOKATEA, COROMANDEL

13955 (RO1) Quartz

FILLING TEMPERATURE Primary inclusions (37): 183, 187, 190₍₃₎, 193, 205, 207,
208, 213₍₃₎, 214, 215₍₇₎, 216,
219₍₂₎, 220₍₃₎, 221, 222, 223,
224₍₂₎, 229, 230, 233, 234, 237
and 239.
FREEZING TEMPERATURE Primary inclusions (1): -0.5
APPARENT SALINITY Primary inclusions (1): 0.9

13956 (RO7) Quartz

FILLING TEMPERATURE Primary inclusions (12): 187, 195₍₂₎, 203, 206, 210, 226,
229, 236, 239, 244 and 277.

13957 (TK2) Quartz

FILLING TEMPERATURE Primary inclusions (38): 176₍₆₎, 185₍₃₎, 187, 190, 197₍₄₎,
218, 219₍₂₎, 222, 224, 225, 227,
229₍₄₎, 232, 234₍₃₎, 237, 241₍₄₎,
242, 243 and 246.
FREEZING TEMPERATURE Primary inclusions (7): -0.6, -1.1, -1.3, -1.4 and -1.7₍₃₎.
APPARENT SALINITY Primary inclusions (7): 1.1, 1.9, 2.2, 2.4 and 2.8₍₃₎.

13958 (BO2) Quartz

FILLING TEMPERATURE Primary inclusions (11): 244, 245, 246₍₂₎, 249, 253,
254₍₃₎, 262 and 263.
Secondary inclusions (8): 170, 172, 174₍₂₎, 176, 185, 200
and 244.

PETOTE STREAM, COROMANDEL

13980 (AS1) Quartz

FILLING TEMPERATURE Primary inclusions (31): 207, 226, 231, 232, 243, 244₍₄₎,
245₍₂₎, 255, 257, 258₍₅₎, 261,
271, 281, 284, 285, 287₍₂₎, 288,
289, 293, 297₍₂₎ and 301.
Secondary inclusions (11): 180, 186₍₂₎, 187, 188, 191, 193₍₂₎,
197, 201 and 275.

13981 (AS2) Quartz

FILLING TEMPERATURE Secondary inclusions (16): 166, 177, 186₍₂₎, 190, 193, 195,
197, 198, 200, 203₍₂₎, 204, 208,
213 and 215.

13984 (HC3) Quartz

FILLING TEMPERATURE Secondary inclusions (4): 206, 210, 215 and 219.

13991 (PS4) Calcite

FILLING TEMPERATURE Primary inclusions (14): 183, 213, 240, 241, 244, 245₍₂₎,
246₍₃₎, 249, 252, 258 and 261.
Secondary inclusions (1): 168
FREEZING TEMPERATURE Primary inclusions (2): -0.9 and -1.4
APPARENT SALINITY Primary inclusions (2): 1.6 and 2.4

13992 (PS5) Quartz

FILLING TEMPERATURE Secondary inclusions (2): 250₍₂₎

13993 (PS7) Calcite

FILLING TEMPERATURE Primary inclusions (7): 180, 204, 205, 208, 211, 213 and
215.
Secondary inclusions (1): 171

13993 (PS7) Quartz

FILLING TEMPERATURE Secondary inclusions (4): 197, 200, 202 and 249.

13995 (PS10) Quartz

FILLING TEMPERATURE Primary inclusions (46): 254, 257, 258, 261, 263₍₃₎, 265₍₄₎,
266, 268₍₂₎, 269₍₂₎, 271, 273₍₃₎,
275, 277, 283₍₅₎, 288₍₄₎, 292, 297,
306, 308, 310, 312, 313, 314, 316,
317, 318, 323, 327 and 331₍₂₎.
FREEZING TEMPERATURE Primary inclusions (11): -0.7₍₄₎, -0.9₍₃₎, -1.0₍₃₎ and -1.3
APPARENT SALINITY Primary inclusions (11): 1.3₍₄₎, 1.6₍₃₎, 1.7₍₃₎ and 2.2

13996 (PS14a) Quartz

FILLING TEMPERATURE Primary inclusions (25): 216, 222, 224₍₆₎, 228₍₂₎, 234₍₃₎,
250, 267, 273, 274, 275, 281,
283, 285, 288₍₂₎, 290 and 293.

13997 (PS14) Quartz

FILLING TEMPERATURE Primary inclusions (30): 254, 256, 258, 259, 260, 261, 262,
263, 268, 270, 271, 272, 273₍₃₎,
274₍₂₎, 275, 276, 278, 285,
288₍₂₎, 291₍₂₎, 297₍₂₎, 299, 302
and 303.

14005 (PS24) Quartz

FILLING TEMPERATURE Primary inclusions (13): 244, 253, 254, 258₍₂₎, 261₍₅₎,
265 and 271₍₂₎.

Secondary inclusions (21): 117, 171, 180, 184, 185(2), 186, 188(2), 195, 200(3), 203(2), 204, 205, 226, 229, 242 and 261.

FREEZING TEMPERATURE Primary inclusions (2): -0.9 and -1.8.
Secondary inclusions (2): -1.5(2)

APPARENT SALINITY Primary inclusions (2): 1.6 and 3.0
Secondary inclusions (2): 2.6(2)

14006 (PS26) Quartz

FILLING TEMPERATURE Primary inclusions (51): 215(5), 224, 230, 254(2), 263(2), 265, 268(2), 270(2), 273, 280, 283, 288(3), 290(2), 291, 292(2), 293(2), 294(3), 296, 297(3), 300(5), 302, 303, 304, 308(3), 310, 314, 317 and 322.

FREEZING TEMPERATURE Primary inclusions (13): -0.7(3), -1.3, -1.5(3), -1.7, -1.9(3) and -2.1(2).

APPARENT SALINITY Primary inclusions (13): 1.3(3), 2.2, 2.6(3), 2.8, 3.2(3) and 3.5(2).

WHANGAPOUA

13910 (Wg9) Quartz

FILLING TEMPERATURE Primary inclusions (2): 190(2)

BROKEN HILLS

13950 (TR9) Quartz

FILLING TEMPERATURE Primary inclusions (35): 200, 210, 215(2), 216, 222, 223, 224(2), 225, 232(2), 233, 235(2), 236(2), 239, 243(3), 244(2), 245(4), 247, 249, 255(2), 256, 262, 273 and 274.

Secondary inclusions (12): 210(2), 215(3), 217, 222(5) and 222.

FREEZING TEMPERATURE Primary inclusions (11): -0.3, -0.4(7), -0.6(2) and -0.7

APPARENT SALINITY Primary inclusions (11): 0.5, 0.7(7), 1.1(2) and 1.3

13951 (TR6) Quartz

FILLING TEMPERATURE Primary inclusions (25): 203, 204(3), 205(2), 206, 215, 216(2), 217, 221, 222, 223, 232, 233, 235, 237, 242, 243, 245, 255, 268, 283 and 293.

Secondary inclusions (26) 221, 222, 229, 234(2), 235(4), 236, 237, 238(3), 239(2), 244, 245(4), 246(3), 251 and 289.

FREEZING TEMPERATURES Primary inclusions (6): -0.4, -0.5(2), -0.6, -1.1 and -1.3

APPARENT SALINITY Primary inclusions (6): 0.7, 0.9(2), 1.1, 1.9 and 2.2

NEAVESVILLE

13940 (N26) Quartz

FILLING TEMPERATURE Primary inclusions (10): 188, 206, 209, 212, 213(4), 215 and 254.

13941	(N14) Quartz		
FILLING TEMPERATURE	Primary inclusions	(20): 232, 239 ₍₂₎ , 241, 243 ₍₂₎ , 244, 245 ₍₃₎ , 249, 252, 253 ₍₂₎ and 254 ₍₆₎	
FREEZING TEMPERATURE	Primary inclusions	(7): -0.3 ₍₂₎ , -0.4 ₍₂₎ , -0.5 ₍₂₎ and -0.6	
APPARENT SALINITY	Primary inclusions	(7): 0.5 ₍₂₎ , 0.7 ₍₂₎ , 0.9 ₍₂₎ and 1.1	
13942	(N42) Quartz		
FILLING TEMPERATURE	Primary inclusions	(20): 193, 207, 215, 229, 234 ₍₂₎ , 239, 245, 246, 248, 249 ₍₂₎ , 253, 254, 255 ₍₂₎ , 258 ₍₂₎ , 265 and 274.	
FREEZING TEMPERATURE	Primary inclusions	(3): -0.4 and -0.5 ₍₂₎	
APPARENT SALINITY	Primary inclusions	(3): 0.7 and 0.9 ₍₂₎	
13943	(N39) Quartz		
FILLING TEMPERATURE	Primary inclusions	(2): 221 and 224	
13944	(N47) Quartz		
FILLING TEMPERATURE	Primary inclusions	(30): 190, 193 ₍₃₎ , 194 ₍₅₎ , 195 ₍₂₎ , 196 ₍₉₎ , 197, 201, 203, 204, 205, 206, 212, 215, 231 and 249.	
FREEZING TEMPERATURE	Primary inclusions	(6): -0.1, -0.2 ₍₂₎ , -0.3 and -0.4 ₍₂₎	
APPARENT SALINITY	Primary inclusions	(6): 0.2, 0.3 ₍₂₎ , 0.5 and 0.7 ₍₂₎	
13945	(N28) Quartz		
FILLING TEMPERATURE	Primary inclusions	(14): 126, 205 ₍₃₎ , 211, 215 ₍₃₎ , 222 ₍₂₎ , 225, 234, 241 and 283.	
	Secondary inclusions	(3): 215 ₍₃₎	
FREEZING TEMPERATURE	Primary inclusions	(2): -0.4 and -0.5	
APPARENT SALINITY	Primary inclusions	(2): 0.7 and 0.9	
13946	(N46) Quartz		
FILLING TEMPERATURE	Primary inclusions	(11): 206, 208, 210, 214 ₍₃₎ , 215 ₍₄₎ and 222.	
FREEZING TEMPERATURE	Primary inclusions	(6): -0.4 ₍₅₎ and -0.5	
APPARENT SALINITY	Primary inclusions	(6): 0.7 ₍₅₎ and 0.9	

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13916	(CNS)		
FILLING TEMPERATURE	Primary inclusions	(17): 220, 250 ₍₂₎ , 251 ₍₂₎ , 252, 254, 256 ₍₂₎ , 257, 258, 260 ₍₃₎ , 263, 265 and 290.	
	Secondary inclusions	(9): 240 ₍₂₎ , 250, 256, 260, 273, 275, 276 and 277.	
FREEZING TEMPERATURE	Primary inclusions	(3): -0.5 ₍₃₎	
APPARENT SALINITY	Primary inclusions	(3): 0.9	
13917	(M1) Quartz Core		
FILLING TEMPERATURE	Primary inclusions	(14): 222, 230, 256, 259, 262, 263 ₍₃₎ , 267, 268, 272, 273, 278 and 282.	
	Secondary inclusions	(13): 260 ₍₂₎ , 261, 262 ₍₂₎ , 264, 265, 267, 268 ₍₂₎ , 270 ₍₂₎ and 298.	
FREEZING TEMPERATURE	Primary inclusions	(2): -0.1 and -0.6	
APPARENT SALINITY	Primary inclusions	(2): 0.2 and 1.1	
	Quartz growth zone around core		
FILLING TEMPERATURE	Primary inclusions	(6): 255, 258, 259 ₍₂₎ , 260 and 276.	
	Calcite zone		
FILLING TEMPERATURE	Primary inclusions	(31): 195, 208 ₍₂₎ , 210 ₍₂₎ , 212, 222, 235, 238, 240, 243 ₍₂₎ , 245, 248, 251, 253,	

258, 260₍₃₎, 261, 262₍₂₎, 268,
273, 277, 278, 281, 288, 290 and 306.

FREEZING TEMPERATURE Primary inclusions (2): -0.1 and -0.2
APPARENT SALINITY Primary inclusions (2): 0.2 and 0.3

13918 (M2 Calcite) Calcite

FILLING TEMPERATURE Primary inclusions (40): 230, 238, 239, 240, 242, 245₍₂₎,
247, 248₍₂₎, 250₍₃₎, 251₍₂₎, 254,
256, 258₍₃₎, 260₍₃₎, 262₍₄₎, 263,
266₍₃₎, 267, 268, 270₍₂₎, 275,
278₍₂₎, 290 and 292.

FREEZING TEMPERATURE Primary inclusions (4): -1.1₍₂₎, -1.2 and -1.7
APPARENT SALINITY Primary inclusions (4): 1.9₍₂₎, 2.1 and 2.8

13919 (M2 quartz) Quartz

FILLING TEMPERATURE Primary inclusions (29): 202, 209, 210, 213, 217, 218, 220₍₂₎,
221₍₂₎, 222, 223, 225, 228, 229₍₂₎,
230₍₄₎, 232, 237₍₂₎, 238, 240, 245
249, 261 and 269.

Secondary inclusions (22): 210, 218, 220₍₂₎, 222, 226, 228₍₂₎,
230₍₄₎, 240₍₃₎, 248₍₂₎, 250₍₂₎,
252 and 255₍₂₎.

FREEZING TEMPERATURE Primary inclusions (5): -0.1, -0.3₍₂₎, -0.4 and -0.5
Secondary inclusions (27): 0 to -0.1₍₂₆₎ and -0.3
APPARENT SALINITY Primary inclusions (5): 0.2, 0.5₍₂₎, 0.7 and 0.9
Secondary inclusions (27): 0 to 0.2₍₂₆₎ and 0.5

13920 (M3) Quartz

FILLING TEMPERATURE Primary inclusions? (54): 230₍₂₎, 240, 243, 244, 248₍₂₎,
250₍₃₎, 251₍₂₎, 252₍₄₎, 253₍₂₎,
255₍₂₎, 258, 260₍₅₎, 262₍₅₎, 265,
268₍₂₎, 270, 272, 275₍₃₎, 277, 278,
280₍₆₎, 285, 290, 300₍₂₎, 305, 320 and 323.

FREEZING TEMPERATURE Primary inclusions? (5): -0.1₍₃₎ and -0.7₍₂₎
APPARENT SALINITY Primary inclusions? (5): 0.2₍₃₎ and 1.3₍₂₎.

13921 (M4)

FILLING TEMPERATURE Primary inclusions (37): 215, 222₍₂₎, 226, 233, 235₍₂₎,
242₍₃₎, 243, 245₍₃₎, 247, 248₍₂₎,
250₍₂₎, 251₍₂₎, 252₍₂₎, 253₍₃₎, 255,
258, 262₍₂₎, 264, 267, 268, 269, 270,
278 and 290.

FREEZING TEMPERATURE Primary inclusions (5): -0.1, -0.4₍₂₎ and -0.7₍₂₎.
APPARENT SALINITY Primary inclusions (5): 0.2, 0.7₍₂₎ and 1.3₍₂₎.

13922 (M5) Quartz

FILLING TEMPERATURE Primary inclusions (69): 215, 218, 219, 220, 230₍₂₎, 232,
234, 240, 241, 242, 243, 244,
245₍₂₎, 247, 248₍₂₎, 250₍₂₎, 251,
252₍₂₎, 253, 254₍₂₎, 255₍₃₎, 257₍₂₎,
258₍₂₎, 259, 260₍₃₎, 262₍₂₎, 263, 264,
265₍₂₎, 266, 267, 268, 269₍₂₎, 272, 274,
275, 276, 280, 285₍₃₎, 286, 288₍₄₎, 290₍₃₎,
293, 295₍₃₎ and 300.

Secondary inclusions (21): 208, 216, 218, 220, 225₍₃₎, 243, 245, 247,
248, 252₍₂₎, 260, 261, 267, 268, 269,
272₍₂₎ and 275.

FREEZING TEMPERATURES Primary inclusions (5): -0.1, -0.2, -0.5, -1.4 and -2.0
Secondary inclusion : all near 0.
APPARENT SALINITY Primary inclusions (5): 0.2, 0.3, 0.9, 2.4 and 3.4
Secondary inclusions : all near 0.

13923 (M6)

FILLING TEMPERATURE Primary inclusions (32): 230₍₂₎, 241, 242₍₃₎, 245₍₂₎, 250₍₄₎, 251, 252₍₂₎, 258, 260, 261, 266, 270₍₅₎, 271, 273, 278₍₂₎, 280, 282, 290 and 292.

FREEZING TEMPERATURE Primary inclusions (6): -0.1, -0.2, -0.4, -1.0₍₂₎ and 1.1

APPARENT SALINITY Primary inclusions (6): 0.2, 0.3, 0.7, 1.7₍₂₎ and 1.9

13924 (M8b) Quartz Quartz band close to sulphide band

FILLING TEMPERATURE Primary inclusions (18): 225₍₂₎, 228₍₂₎, 231, 235, 239₍₂₎, 242, 243, 250₍₃₎, 253, 255, 260, 264 and 267.

Intermediate Quartz band

FILLING TEMPERATURE Primary inclusions (34): 228, 231, 238, 239, 240, 242, 243₍₂₎, 245₍₃₎, 249, 251₍₂₎, 252, 253₍₂₎, 254, 255₍₃₎, 256, 258, 259₍₃₎, 263, 266, 267, 270, 273, 275, 285₍₂₎

FREEZING TEMPERATURE Primary inclusions (11): -0.1₍₆₎, -0.2₍₄₎ and -1.2

APPARENT SALINITY Primary inclusions (11): 0.2₍₆₎, 0.3₍₄₎ and 2.1

Quartz band further away from sulphide band

FILLING TEMPERATURE Primary inclusions (6): 275, 278, 280, 290, 292 and 295.

FREEZING TEMPERATURE Primary inclusions (1): -0.2

APPARENT SALINITY Primary inclusions (1): 0.3

13925 (M9)

FILLING TEMPERATURE Primary inclusions (36): 258, 260, 270, 271, 275, 278₍₄₎, 280₍₂₎, 281, 282, 283, 284₍₂₎, 285, 286₍₂₎, 288, 290₍₂₎, 291₍₃₎, 292₍₃₎, 293, 295, 299, 301, 309, 310 and 320₍₂₎.

Secondary inclusions (13): 190, 235, 237, 239, 250₍₂₎, 260, 265, 267, 269, 275, 278 and 286.

FREEZING TEMPERATURE Primary inclusions (1): -0.3

APPARENT SALINITY Primary inclusions (1): 0.5

13926 (M10)

FILLING TEMPERATURE Primary inclusions (60): 172, 178, 180, 192, 255, 260₍₂₎, 261₍₂₎, 262₍₃₎, 264₍₂₎, 265₍₁₁₎, 266, 267₍₃₎, 269₍₄₎, 270₍₂₎, 271₍₅₎, 272, 273₍₃₎, 275₍₃₎, 276, 280₍₅₎, 281, 282, 285₍₃₎ and 290₍₂₎.

FREEZING TEMPERATURE Primary inclusions (2): -0.5₍₂₎

APPARENT SALINITY Primary inclusions (2): 0.9₍₂₎

13927 (M11) Banded quartz Quartz band close to sulphide band

FILLING TEMPERATURE Primary inclusions (30): 230, 232, 245, 250₍₂₎, 252₍₂₎, 255, 256, 257, 260₍₄₎, 261, 262, 263₍₄₎, 264₍₃₎, 265₍₂₎, 268, 270₍₃₎ and 275.

FREEZING TEMPERATURE Primary inclusions (1): -0.1

APPARENT SALINITY Primary inclusions (1): 0.2

Intermediate quartz band

FILLING TEMPERATURE Primary inclusions (11): 259₍₂₎, 260₍₂₎, 261, 262₍₂₎, 265, 266, 267 and 275.

Quartz band further away from sulphide band

FILLING TEMPERATURE Primary inclusions (9): 246, 250, 251, 255, 260, 262, 263, 268 and 272.

13928 (M19) Quartz

FILLING TEMPERATURE Primary inclusions (43): 239, 241, 248₍₂₎, 260₍₄₎, 261, 262, 263, 265, 267, 268₍₃₎, 269, 270₍₃₎, 272₍₄₎, 273₍₃₎, 277, 278₍₅₎, 279, 280₍₂₎, 281, 283, 289, 292, 295, 310 and 315.

FREEZING TEMPERATURE Primary inclusions (4): -1.5₍₂₎ and -1.6₍₂₎.

APPARENT SALINITY	Primary inclusions	(4): 2.6(2) and 2.7(2).
13929 (M28)		
FILLING TEMPERATURE	Primary inclusions	(18): 225, 230, 232, 247(3), 248, 249(3), 250(2), 251, 255, 268, 270, 277 and 281.
	Secondary inclusions	(4): 199, 200, 202 and 205.
FREEZING TEMPERATURE	Primary inclusions	(3): -0.3(2) and -0.4
APPARENT SALINITY	Primary inclusions	(3): 0.5(2) and 0.7
13930 (M8a)		
FILLING TEMPERATURE	Primary inclusion	(33): 240, 245(2), 248(2), 250, 252(2), 253, 254, 255, 256, 257(2), 260(4), 261, 263, 265, 268(4), 269, 272(2), 274, 275(2), 278, 287.
FREEZING TEMPERATURE	Primary inclusions	(3): -0.3(2) and -0.5
APPARENT SALINITY	Primary inclusions	(3): 0.5(2) and 0.9
13945 (M22)		
FILLING TEMPERATURE	Primary inclusions	(42): 224, 227, 231, 233, 239, 240, 241, 242(2), 243(5), 244(5), 245, 246(2), 247, 248(2), 249(2), 250, 252, 253(2), 254, 255(2), 256(2), 261, 270, 273, 288(2) and 291.
<u>KOMATA</u>		
13947 (Km15) Quartz		
FILLING TEMPERATURE	Primary inclusions	(33): 144, 149, 152, 167, 186, 188, 190, 191(2), 194(2), 195, 204, 206, 210(2), 213, 214(4), 215, 220, 221, 223, 224, 234, 241, 245, 272, 273, 282 and 297.
FREEZING TEMPERATURE	Primary inclusions	(3): -0.4, -1.0 and -1.8
APPARENT SALINITY	Primary inclusions	(3): 0.7, 1.7 and 3.0
Calcite		
FILLING TEMPERATURE	Primary inclusions	(38): 215(2), 218, 230, 231, 233, 234(2), 235, 239(2), 240, 241, 242(2), 243, 244(4), 245(4), 250, 251(3), 252(2), 254, 258, 261, 263, 264, 266, 272 and 273.
FREEZING TEMPERATURE	Primary inclusions	(9): -0.9, -1.0(3), -1.1(4) and -1.7
APPARENT SALINITY	Primary inclusions	(9): 1.6, 1.7(3), 1.9(4) and 2.8
13948 (Km18) Quartz		
FILLING TEMPERATURE	Primary inclusions	(12): 219, 224(2), 239, 241, 243, 244(3), 249, 252 and 261.
FREEZING TEMPERATURE	Primary inclusions	(7): -0.5, -0.6, -0.7(4) and -1.7
APPARENT SALINITY	Primary inclusions	(7): 0.9, 1.1, 1.3(4) and 2.8
Calcite		
FILLING TEMPERATURE	Primary inclusions	(38): 232, 235, 244, 245(2), 249(2), 251, 254(6), 255(2), 259(2), 260, 261(3), 262, 263, 265(2), 266, 267(2), 269(3), 275, 278(3), 283 and 284.
13949 (Km10) Quartz		
FILLING TEMPERATURE	Primary inclusions	(28): 231, 233, 234, 236(2), 239(4), 241, 244, 247, 252(6), 255, 258, 263, 264, 268, 269, 271 and 275(3).
	Secondary inclusions	(27): 227(2), 228(2), 229(4), 230, 231(2), 233(5), 234(2), 235(2), 236(2), 242, 245, 246, 247 and 258.

FREEZING TEMPERATURE	Primary inclusions	: -0.5 and -1.8
APPARENT SALINITY	Primary inclusions	: 0.9 and 3.0

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14010 (WK1) Quartz

FILLING TEMPERATURE	Primary inclusions	(48): 236, 241, 245, 251(2), 252(2), 253(3), 254(5), 255, 256, 260, 261, 262(3), 265, 268(5), 269, 270, 272(5), 273(3), 274, 276, 279, 280, 281(2), 282, 283, 285 and 290.
	Secondary inclusions	(44): 229, 232(2), 239, 242(2), 243(2), 244, 245, 249, 252, 253(3), 254, 255, 257(4), 258(3), 259, 261(4), 262(2), 263(2), 271, 272, 274, 275(3), 276, 279, 282 and 283(2).
FREEZING TEMPERATURE	Primary inclusions	(1): -0.4
APPARENT SALINITY	Primary inclusions	(1): 0.7

14011 (WK2) Quartz

FILLING TEMPERATURE	Primary inclusions	(38): 234, 236, 244, 246(5), 247, 248(2), 249, 252, 253(2), 254, 257, 259(2), 261(5), 263(2), 264(4), 265, 267, 271, 272(2), 275(2) and 281.
FREEZING TEMPERATURE	Primary inclusions	(2): -0.3 and -0.4
APPARENT SALINITY	Primary inclusions	(2): 0.5 and 0.7

14012 (WK3) Quartz

FILLING TEMPERATURE	Primary inclusions	(47): 227, 240, 242, 241, 245, 246(2), 247(2), 248, 250(2), 252, 253(3), 254(4), 255, 256, 258, 260, 261, 262(2), 263(4), 264(5), 265(2), 266, 272, 273, 276, 292(2), 296 and 312(2).
FREEZING TEMPERATURE	Primary inclusions	(10): -0.5(3), -0.6, -0.9, -1.0(2), -1.3(2) and -1.9
APPARENT SALINITY	Primary inclusions	(10): 0.9(3), 1.1, 1.6, 1.7(2), 2.2(2) and 3.2

14013 (WK 4) Quartz

FILLING TEMPERATURE	Primary inclusions	(42): 171, 190, 210, 213, 227, 229(2), 232, 235, 237, 238(2), 242, 243(2), 244(2), 245(2), 249(2), 251, 252, 254(2), 256, 258, 261(2), 262, 263, 264, 267, 268, 271(4), 274, 275, 279 and 286.
FREEZING TEMPERATURE	Primary inclusions	(8): -0.4(4), -0.5(3) and -0.9
APPARENT SALINITY	Primary inclusions	(8): 0.7(4), 0.9(3) and 1.6

14014 (WK 5) Quartz

FILLING TEMPERATURE	Primary inclusions	(59): 206, 224, 225(3), 226(3), 234(3), 239(3), 242(2), 243, 244(2), 248, 249(3), 250, 251, 254(3), 255, 258(2), 261(7), 262, 263(5), 264(2), 265(5), 268(4), 269(2), 271 and 272.
	Secondary inclusions	(23): 220, 222(2), 226, 236(5), 238, 242, 244(2), 254(4), 255(2), 257, 262, 263 and 265.
FREEZING TEMPERATURE	Primary inclusions	(12): -0.4(2), -0.6, -0.7(2), -0.9(3), -1.0(2) and -1.1(2).
APPARENT SALINITY	Primary inclusions	(12): 0.7(2), 1.1, 1.3(2), 1.6(3), 1.7(2) and 1.9(2).

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13913	(Wh24) Quartz		
	FILLING TEMPERATURE	Primary inclusions	(14): 158, 161, 166, 167, 168, 177 ₍₂₎ , 185, 189 and 190 ₍₂₎ , 194, 195 and 200.
14030	(GJ1) Calcite		
	FILLING TEMPERATURE	Primary inclusions	(20): 212, 216, 219, 224, 228, 231 ₍₂₎ , 242, 243 ₍₃₎ , 244 ₍₅₎ , 247, 252, 253 and 254.
	FREEZING TEMPERATURE	Primary inclusions	(4): -0.7, -0.9, -1.0 and -1.1
	APPARENT SALINITY	Primary inclusions	(4): 1.3, 1.6, 1.7 and 1.9
14031	(GJ2) Calcite		
	FILLING TEMPERATURE	Primary inclusions	(14): 169, 176, 179, 185 ₍₂₎ , 190, 192, 197, 203, 213 ₍₂₎ , 215, 216 and 219.
		Secondary inclusions	(3): 187, 203 and 206.
	FREEZING TEMPERATURE	Primary inclusions	(1): -0.9
	APPARENT SALINITY	Primary inclusions	(1): 1.6
14032	(GJ3) Quartz		
	FILLING TEMPERATURE	Primary inclusions	(4): 229, 243 and 244 ₍₂₎ .
14035	(Wh4b) Quartz		
	FILLING TEMPERATURE	Primary inclusions	(3): 229 ₍₃₎
		Secondary inclusions	(18): 187 ₍₂₎ , 205, 210 ₍₃₎ , 215 ₍₆₎ , 219 ₍₂₎ , 224, 229, 232 and 293.
14036	(Wh8) Quartz		
	FILLING TEMPERATURE	Primary inclusions	(1): 274
		Secondary inclusions	(11): 189, 224 ₍₂₎ , 226 ₍₂₎ , 229, 230 ₍₂₎ , 232, 233 and 234.
14037	(Wh10) Quartz		
	FILLING TEMPERATURE	Primary inclusions	(2): 199 and 204
		Secondary inclusions	(4): 146, 177 ₍₂₎ and 193.
14038	(Wh15) Quartz		
	FILLING TEMPERATURE	Secondary inclusions	(27): 156, 183, 191, 192, 219 ₍₂₎ , 222, 223, 225 ₍₂₎ , 226 ₍₂₎ , 228, 229, 230, 234, 235, 236, 241, 243, 244 ₍₂₎ , 257, 258, 261, 263 and 287.
14042	(Wh32) Quartz		
	FILLING TEMPERATURE	Primary inclusions	(18): 185 ₍₂₎ , 209, 213, 226 ₍₂₎ , 229 ₍₂₎ , 231, 235, 236, 239, 242, 246, 249, 254, 265 and 276.
		Secondary inclusions	(15): 215 ₍₃₎ , 216, 217, 218 ₍₃₎ , 219, 220 ₍₂₎ , 222 and 224 ₍₃₎ .
	FREEZING TEMPERATURE	Primary inclusions	(6): -1.3 ₍₂₎ , -1.5, -1.9 ₍₂₎ and -2.3
	APPARENT SALINITY	Primary inclusions	(6): 2.2 ₍₂₎ , 2.6, 3.2 ₍₂₎ and 3.9
14044	(Wh40) Calcite		
	FILLING TEMPERATURE	Primary inclusions	(6): 159, 164, 177, 184, 186 and 199.
	FREEZING TEMPERATURE	Primary inclusions	(3): -0.4, -0.5 and -1.3
	APPARENT SALINITY	Primary inclusions	(3): 0.7, 0.9 and 2.2
14045	(Wh41).		
	FILLING TEMPERATURE	Primary inclusions	(5): 254, 259, 261, 264, and 271.

FREEZING TEMPERATURE Secondary inclusions (7): 228, 231, 234, 235(3) and 237.
 Primary inclusions (7): -2.2(6) and -2.3
 APPARENT SALINITY Primary inclusions (7): 3.7(6) and 3.9

14051 (Wh49)

FILLING TEMPERATURE Primary inclusions (36): 177, 207, 213, 214(3), 217, 221, 238,
 250, 251, 253, 254(2), 261, 263(3),
 268, 271, 272(2), 273(3), 274, 275(4),
 278, 282, 283, 287, 288 and 296.
 FREEZING TEMPERATURE Primary inclusions (5): -0.6(4) and -0.7
 APPARENT SALINITY Primary inclusions (5): 1.1(4) and 1.3

74/7/10 (Wh46)

FILLING TEMPERATURE Primary inclusions (23): 213, 215(3), 216, 222(2), 224(2),
 226, 228, 230, 232, 234(4), 235,
 239, 240, 245, 254 and 273.
 FREEZING TEMPERATURE Primary inclusions (10): -0.5(3), -0.6, -0.7, -2.7, -3.0,
 -3.1 and -3.2(2).
 APPARENT SALINITY Primary inclusions (10): 0.9(3), 1.1, 1.3, 4.5, 4.9, 5.1
 and 5.2(2).

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14021 (TL2) Quartz

FILLING TEMPERATURE Primary inclusions. (21): 244(2), 246, 248, 250, 252, 254,
 257(2), 261, 265, 262(2), 268,
 273, 274(2), 279, 281(2) and 283.
 Secondary inclusions (5): 219, 247, 248, 285 and 290.
 FREEZING TEMPERATURE Primary inclusions (3): -1.3 and -1.4(2).
 APPARENT SALINITY Primary inclusions (3): 2.2 and 2.4(2).

14022 (TL8) Quartz

FILLING TEMPERATURE Primary inclusions (35): 224(3), 225, 226(5), 229(11),
 232(2), 234(2), 237, 239, 240(2),
 242, 243(4), 254 and 257.
 FREEZING TEMPERATURE Primary inclusions (7): -1.5(7)
 APPARENT SALINITY Primary inclusions (7): 2.6(7)

14029 (MM2) Quartz

FILLING TEMPERATURE Primary inclusions (25): 195(2), 210(2), 215, 219, 222(2),
 227, 240, 242, 245, 247(2), 252,
 253, 254(2), 255, 257, 258, 261,
 267, 269 and 289.
 Secondary inclusions (19): 190, 191, 194(4), 195(2), 200, 202,
 203, 215(2), 216, 219, 236, 254, 265 and
 293.

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14053 (Tui3) Quartz

FILLING TEMPERATURE Primary inclusions (3): 271, 273 and 285.
 Secondary inclusions (9): 174(2), 260, 269(2), 270 and 273(3).

14055 (Tui12) Quartz

FILLING TEMPERATURE Primary inclusions (25): 270, 272(2), 273(2), 274(4), 275(3),
 277, 278, 280, 283, 284, 285(2), 286,
 288(2), 289, 290 and 293.
 FREEZING TEMPERATURE Primary inclusions (6): -2.4, -2.5, -2.7, -3.0, -3.1, -3.3.
 APPARENT SALINITY Primary inclusions (6): 4.0, 4.2, 4.5, 4.9, 5.0 and 5.4

14056	(Tui13)	Quartz		
FILLING TEMPERATURE	Primary inclusions	(58):	261, 262, 263, 264(2), 265(2), 266(2), 268(2), 269, 270, 271, 272(3), 273, 274(2), 275(4), 276, 278, 280(3), 282, 283, 284(2), 285(3), 286, 289, 290, 292(3), 293(10), 294, 296, 300(3) and 303.	
FREEZING TEMPERATURE	Primary inclusions	(12):	-0.1, -0.2(2), -0.4(5), -0.5(3) and -0.6.	
APPARENT SALINITY	Primary inclusions	(12):	0.2, 0.3(2), 0.7(5), 0.9(3) and 1.1.	
14060	(Tui18)	Quartz		
FILLING TEMPERATURE	Primary inclusions	(13):	283(6), 288(2), 290, 293, 294(2) and 295.	
14061	(Tui19)	Quartz		
FILLING TEMPERATURE	Primary inclusions	(27):	249(3), 252(3), 254(3), 256(2), 258(6), 261(4), 262(3), 263, 265, and 271.	
14062	(Tui20)	Quartz		
FILLING TEMPERATURE	Primary inclusions	(29):	232, 234, 239, 254, 270, 272, 273(2), 274(2), 275(3), 276, 277(2), 278, 281(2), 282(2), 283(2), 284, 287, 292 and 293(3).	
FREEZING TEMPERATURE	Primary inclusions	(7):	-1.4, -1.6, -2.2, -2.4, -2.8, -3.6 and -3.8	
APPARENT SALINITY	Primary inclusions	(7):	2.4, 2.7, 3.7, 4.0, 4.7, 5.8 and 6.1	
14063	(Tui21)	Sphalerite		
FILLING TEMPERATURES	Primary inclusions	(6):	273, 275, 276(3) and 284.	
14064	(Tui22)	Quartz		
FILLING TEMPERATURE	Primary inclusions	(87):	255(2), 261(3), 263, 264, 265(3), 266(3), 268(4), 269, 271(2), 272(4), 273(3), 274(4), 275(6), 276(2), 277(2), 278(4), 279, 281(3), 282, 283(2), 284(3), 285(4), 286, 288, 289(2), 290, 291(4), 292, 293(2), 294(3), 295, 296, 297, 298(2), 299, 300, 302(3), 304(2) and 308.	
FREEZING TEMPERATURE	Primary inclusions	(20):	-0.3, -0.5(3), -0.6(3), -0.7(4), -0.8(3), -1.0, -1.4, -1.9(2), -2.2 and -3.3	
APPARENT SALINITY	Primary inclusions	(20):	0.5, 0.9(3), 1.1(3), 1.3(4), 1.5(3), 1.7, 2.4, 3.2(2), 3.7 and 5.4.	
14065	(Tui23)	Quartz		
FILLING TEMPERATURE	Primary inclusions	(41):	273(2), 275, 283, 289, 290, 291(3), 292(2), 293(2), 299, 300(4), 301(3), 302(3), 303(4), 307(2), 309, 310(3), 311(2), 312(2), 322, 337 and 355.	
FREEZING TEMPERATURE	Primary inclusions	(8):	-1.4, -2.1(2), -2.5, -2.7, -2.8, -2.9 and -3.0	
APPARENT SALINITY	Primary inclusions	(8):	2.4, 3.5(2), 4.2, 4.5, 4.6, 4.8 and 4.9.	
14067	(Tui26)	Barite		
FILLING TEMPERATURE	Primary or Secondary inclusions	(24):	132, 143, 146, 156, 163, 166, 169, 177, 184, 205, 216, 219, 226, 232, 234(3), 241, 244, 268, 273, 275, 286 and 288.	

14068 (Tui28) Quartz

FILLING TEMPERATURE Primary inclusions (72): 266, 265, 270, 271, 272(3), 273(3), 274, 275(4), 276(2), 277, 278(11), 279(4), 280(2), 281(9), 282(6), 283(4), 284, 285(2), 286, 288(3), 289(2), 290, 292, 294(2), 301, 302, 304, 307, and 327.

FREEZING TEMPERATURES Primary inclusions (8): -1.0, -1.3(3), -1.4(2) and -1.5(2).

APPARENT SALINITY Primary inclusions (8): 1.7, 2.2(3), 2.4(2) and 2.6(2).

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13914 (W1100) Quartz

FILLING TEMPERATURE Primary inclusions (44): 253, 254, 262, 263(5), 264(2), 265(3), 266, 267, 268, 269, 271(3), 272(2), 273(3), 274(3), 276(2), 277, 281, 282(2), 283(4), 284, 285, 287, 290, 292 and 303.

FREEZING TEMPERATURE Primary inclusions (14): -0.2(7), -0.6(3), -0.9, -2.3(2) and -3.4.

APPARENT SALINITY Primary inclusions (14): 0.3(7), 1.1(3), 1.6, 3.9(2) and 5.5.

14070 (W13) Quartz

FILLING TEMPERATURE Primary inclusions (17): 213, 215, 224, 234, 236, 246, 249, 258(2), 262, 263, 265(2), 270, 273, 274 and 301.

Secondary inclusions (4): 232, 234, 252 and 265.

Barite

FILLING TEMPERATURE Primary inclusions (6): 98, 105, 107(2), 117 and 128.

14074 (W125) Quartz

FILLING TEMPERATURE Primary inclusions (39): 232, 234(2), 235, 236, 237, 241(2), 251, 252, 254(3), 261(2), 262(3), 263(4), 264(4), 265, 267, 270, 271(2), 272(3), 273(2) and 274(3).

Secondary inclusions (13): 193(2), 224, 225, 230, 232, 234, 235, 236, 237, 261, 265 and 309.

FREEZING TEMPERATURE Primary inclusions (6): -0.4, -0.6 and -1.7(4).

APPARENT SALINITY Primary inclusions (6): 0.7, 1.1 and 2.8(4).

14081 (W145) Quartz

FILLING TEMPERATURE Primary inclusions (40): 183, 227, 229, 231, 232, 234(2), 235, 236(5), 238(2), 242, 244(3), 245(2), 246, 247(3), 249(3), 250(2), 251(2), 252, 253, 254(3), 257, 261 and 271.

FREEZING TEMPERATURE Primary inclusions (2): -0.5(2)

APPARENT SALINITY Primary inclusions (2): 0.9(2)

14084 (W156) Quartz

FILLING TEMPERATURE Primary inclusions (37): 214, 232, 233(2), 234(5), 235(10), 236(5), 240, 242, 243(3), 244, 245(2), 246(2), 247, 275 and 288.

14087 (W164) Quartz

FILLING TEMPERATURE Primary inclusions (51): 236, 242, 243, 244(2), 245(3), 248, 250(2), 251, 252(7), 254(6), 255(3), 256, 258(3), 259, 261(2), 263(4), 265, 266(2), 268, 269(2), 276(3), 282 and 283(2).

FREEZING TEMPERATURE Primary inclusions (7): -0.7(2), -1.0(4) and -1.3

APPARENT SALINITY Primary inclusions (7): 1.3(2), 1.7(4) and 2.2

14093 (W187) Quartz

FILLING TEMPERATURE Primary inclusions (25): 234, 235, 238(2), 241(3), 244, 245, 246, 249, 252, 260, 261, 265, 266(2), 267(2), 270(2), 271, 273(2) and 274.

FREEZING TEMPERATURE Primary inclusions (7): -0.5, -0.6(3), -0.7, -1.4 and -1.5.

APPARENT SALINITY Primary inclusions (7): 0.9, 1.1(3), 1.3, 2.4 and 2.6

14094 (W189) Quartz

FILLING TEMPERATURE Primary inclusions (11): 236, 237, 239, 241, 242, 244, 248, 252, 254, 265 and 266.

14099 (W197) Barite

FILLING TEMPERATURE Primary inclusions (6): 98, 107, 112(3) and 196.

APPENDIX IVFLUID INCLUSION CRUSHING AND
LEACHING EXPERIMENTSSAMPLE PREPARATION

Clear chips were selected from the samples in order to obtain a high percentage of primary inclusions. In the case of vug quartz this was achieved by cutting off and collecting the clear tips of the crystals.

Quartz samples were boiled successively in concentrated acids (HF followed by HCl, HNO₃ and finally H₂SO₄), tap water, distilled water and deionised water, whereas a short immersion in dilute HCl was substituted for the boiling acid stages in the case of calcite samples. Finally, all samples were electrolytically cleaned in an apparatus similar to that described by Roedder (1958): a bank of four cells (Fig.IV-1) was constructed and wired in parallel and the total current drawn at 90 volts was monitored by an ammeter. The samples are cleaned by drawing off surface absorbed ions causing an increase in the conductivity of the water and a corresponding rise in the current drawn by the circuit (monitored on the ammeter). The water (initially deionised but later double deionised) was changed periodically until the rise in current over a period of a few days was only small. This process required between 10 days and four weeks, the calcite samples being the most difficult to clean. Table IV-1 is a typical log of a batch of four samples. The values given are only applicable to the system described as different values would be obtained with changes in cell dimensions and surface area of the electrodes.

CRUSHING PROCEDURE

Stainless steel tubes (17mm inside diameter, 19mm outside diameter, approximately 300mm long, welded at one end and open at the other) were cleaned with a solution of HNO₃, detergent and water (in the proportions 1:1:2) followed by rinsing in tap water, distilled water, deionised water and double deionised water.

A tube, loaded with up to 60g of sample, was attached to a vacuum line (Fig.IV-2), heated to a temperature of approximately

Figure IV-1: Bank of four electrolytic cleaning cells. The individual "U" tube cells are each filled with a sample and water. Positive platinum electrodes are immersed in one side and negative platinum electrodes in the other. The cells are wired in series, and the current drawn at 90 volts is monitored on the ammeter. A cover is placed over the cells during operation to prevent dust settling into the tubes.

TABLE IV-1: Cleaning cell log for quartz samples 13939 (N16),
13939 (N14), 13980 (AS1) and 14054 (Tui6)

<u>DATE</u>	<u>TIME</u>	<u>CURRENT (mA)</u>
24 August 1977	Loaded samples into cells and filled with deionised water	
"	5.20 p.m.	0.109
"	5.30 p.m.	0.111
25 August	2.00 p.m.	0.119
26 August	8.45 a.m.	0.130
"	2.00 p.m.	0.134
"	Changed water, refilled with deionised water	
"	2.05 p.m.	0.079
"	4.25 p.m.	0.079
"	5.00 p.m.	0.091
29 August	8.15 a.m.	0.121
"	Changed water, refilled with deionised water	
"	8.40 a.m.	0.114
"	9.15 a.m.	0.115
"	11.10 a.m.	0.117
"	4.30 p.m.	0.114
31 August	8.30 a.m.	0.125
"	Changed water, refilled with deionised water	
"	8.45 a.m.	0.087
"	3.15 p.m.	0.098
1 September	8.10 a.m.	0.099
"	Changed water, refilled with deionised water	
"	8.30 a.m.	0.104 (filled very high)
"	10.15 a.m.	0.108
5 September	9.30 a.m.	0.119
"	Changed water, refilled with double deionised water	
"	10.30 a.m.	0.082
"	1.10 p.m.	0.090
"	3.30 p.m.	0.098
"	4.15 p.m.	0.101
"	Changed water, refilled with double deionised water	
"	4.20 p.m.	0.066
7 September	8.00 a.m.	0.100
"	Changed water, refilled with double deionised water	
"	9.05 a.m.	0.090
"	9.40 a.m.	0.092
"	12.00 noon	0.094
"	12.40 p.m.	0.095
"	2.30 p.m.	0.096
	Removed samples

Figure IV-2: Schematic layout of the glass vacuum line (at the Institute of Nuclear Sciences) used to extract water from fluid inclusions in samples of quartz and calcite. The sample, contained in the stainless steel sample tube was pumped down for approximately 48 hours to remove water adsorbed onto the surfaces. The stainless steel sample tube, with the attached glass tap closed, was removed and crushed three times in a hydraulic press, to open the inclusions, and then reattached to the line. Released fluid inclusion water and CO_2 were separated by vacuum distillation using the liquid nitrogen (condenses CO_2 and water) and acetone-dry ice (condenses water) traps. The water was condensed into the sample bottle and transferred to another vacuum line for hydrogen separation and D/H ratio measurement in a mass spectrometer. Between runs the line was pumped down and cleaned with a tessler coil (high voltage spark source) to remove adsorbed water from the glass surfaces.

120°C by means of a heating tape wound around it and pumped down by diffusion pump for approximately 48 hours to remove water absorbed onto the surfaces. The condition of the sample was monitored by closing the line off from the vacuum pump and observing the rise in pressure in the line over a period of 10 minutes. When this was negligible (0.001 torr) the tube was removed from the line and, with the sample still under vacuum, crushed three times. Between crushings the tube was turned through 90° to restore its shape.

The tube was reattached to the line and again heated. The vapour released on opening the tube to the line was separated into H₂O, CO₂ and non-condensable fractions by vacuum distillation. The non-condensable and CO₂ fractions were always small (c.f. Table 7-8); the latter being too small for oxygen isotope analysis. H₂O was condensed into a sample bottle and transferred to another vacuum line for hydrogen separation (by passing over hot zinc) and subsequent D/H analysis in the mass spectrometer. The D/H ratios for the samples are given in Table 8-1.

LEACHING

Three different leaching solutions were used: double deionised water, ammonium nitrate solution and nitric acid solution. To obtain a low level of contamination in the reagents, analytical grade nitric acid was distilled in a sub-boiling distillation apparatus (Fig. IV-3) constructed from the design described by Mattinson (1971). The "pure" nitric acid was mixed with double deionised water to make the nitric acid solution and with "MERCK Pro analysi ammonia solution GR (0.91)" (supplied in 5 litre plastic containers) and double deionised water to neutral pH for the ammonium nitrate solution. Table IV-2 lists analyses of these reagents.

Initially only a single water or nitric acid solution was used to leach samples, but later a multiple leaching scheme was adopted (Fig. IV-4). The crushed samples were transferred from the stainless steel tubes to pre-cleaned 250ml polyethylene bottles (obtained from Industrial Moldings Ltd, Seaview, Petone). Approximately 30g of leaching solution was added, agitated periodically for 10 minutes, centrifuged at 2,000 r.p.m. for one hour, and siphoned off into a pre-cleaned 100ml polyethylene bottle (similar to those made by Nalgene). Only two-thirds

Figure IV-3: Teflon sub-boiling acid distillation apparatus constructed from the design described by Mattinson (1971). Analytical grade nitric acid was heated in one bottle by the lamp and the vapour condensed in the other. During operation aluminium foil was used to screen the condensing bottle from the lamp and a piece was also used over the top of the other bottle to reflect heat back into the bottle. The system gave an output of approximately 100 millilitres per week.

TABLE IV-2: Concentrations, in parts per billion, of Na^+ , K^+ , Mg^{2+} , and Al^{3+} in the fluid inclusion leaching reagents. Analyses by Mr J.E. Paterson, Chemistry Division D.S.I.R.

	<u>Water</u>	<u>20% ammonium nitrate solution</u>	<u>20% nitric acid solution</u>
Na^+	2	36	2
K^+	2	7	2
Mg^{2+}	1	5	1
Al^{3+}	10	10	10

FIG.IV-4: Flow diagram of the crushing and leaching procedure used for extraction and analysis of dissolved salts from fluid inclusions in quartz samples.

of the leach could be siphoned off the top of the crushed sample without contamination from the sludge. Therefore, for the second leach, 20g of 20% ammonium nitrate solution was added to the crushed sample giving a 30g leaching solution of approximately 13% ammonium nitrate. Similarly, after this was centrifuged and siphoned off 10g of 13% ammonium nitrate solution remained in with the crushed sample. The third leach of 13% nitric acid solution was obtained by adding 20g of 20% nitric acid solution to the crushed sample. The residues left after each leach have been corrected for in the analyses presented in Tables IV-3 and 7-1 so that the individual figures in these tables represent the weights dissolved by only the single leach and do not include traces of previous leaches.

The water and ammonium nitrate leaches were acidified with distilled nitric acid to make 2% solutions and all leaches were analysed for Na, K, Mg and Al by atomic absorption, Ca and Li by flame emission and Cl by the colourimetric technique described by Swain (1956). Zn, Rb and Cs were also analysed for in some samples: Zn and Rb by atomic absorption and Cs by flame emission. The cation analyses were by Dr. R.L. Goguel and Mr J. Paterson at Chemistry Division, DSIR, using Perkin-Elmer equipment, whereas the chloride analyses were by the writer using a Beckman Model B spectrophotometer, housed in the Geology Department, Victoria University of Wellington. The standards used were a set of multi-element solutions (to minimise errors due to interference) containing concentrations of the cations and chloride bracketing and equal to those encountered in the analyses.

RESULTS

Table IV-3 lists the leach analyses and these have been corrected by the dilution factor (calculated from the fluid inclusion water yield measurements) to give the apparent fluid inclusion compositions presented in Table 7-1.

TABLE IV-3: Micrograms of some cations and chloride leached from crushed samples of quartz and calcite. The analyses for each leach solution represent only the quantity of ion leached by the reagent specified. Solutions from multiple leach analyses have been corrected by subtracting the residues left by previous leaches (see text).

TABLE IV-3A Quartz Samples

Petote Stream Area

Tokatea

Tokatea				Petote Stream Area					Whangapoa		Neavesville	
13957 ₁ TK2 ₁	13957 ₂ TK2 ₂	13958 _a BO2 _a	13907 Hutt 2	13980 _a ASL _a	13980 _b ASL _b	13980 _c ASL _c	13980 _d ASL _d	13998 PS15	14006 PS26	13910 WG9	13938 N14	13939 N16
Wt quartz	58	43	33	66	27	63	45	23	29	21	8.4	42
Wt water	23	7	8	22	n.a.	30	8	6	6	8	n.a.	29
Na ⁺	{	29	26	-	2.32	-	-	7.10	19	16.4	0.94	-
	{	16	-	-	2.38	-	-	2.63	45	1.79	0.72	-
	{	5.3	-	83	0.29	n.d.	106	0.10	80	0.51	n.d.	33
K ⁺	{	9.0	1.15	-	0.23	-	-	0.41	4.5	2.26	0.19	-
	{	6.9	-	-	0.38	-	-	0.44	63	0.99	0.42	-
	{	1.9	-	3.9	0.40	n.d.	4.7	0.18	0.82	0.23	0.036	110
Ca ²⁺	{	1.0	24.3	-	n.d.	-	-	0.11	198	4.92	4.99	-
	{	47	-	6.5	13.2	-	-	2.22	300	22.3	12.9	-
	{	n.d.	-	-	n.d.	11	n.a.	n.d.	623	2.00	0.56	135
Al ³⁺	{	0.67	n.a.	-	n.d.	-	-	0.25	0.76	n.a.	n.d.	-
	{	n.d.	-	-	5.76	-	-	320	0.61	10.4	1.64	-
	{	40	-	29	1.98	32	29	1.25	218	2.02	n.d.	180
Mg ²⁺	{	0.20	0.27	-	0.068	-	-	0.10	2.5	0.36	0.13	-
	{	0.74	-	-	0.50	-	-	0.33	2.7	0.99	0.34	-
	{	0.14	-	0.52	0.18	1.5	1.0	0.11	n.a.	0.24	0.05	9.1
Li ⁺	{	3.0	2.78	-	2.54	-	-	0.92	1.5	1.32	0.11	-
	{	1.2	-	-	1.09	-	-	0.21	0.51	0.039	0.007	-
	{	0.24	-	9.63	0.42	9.5	8.1	n.d.	2.6	0.049	0.0004	1.8
Zn ²⁺	{	0.27	n.a.	-	n.a.	-	-	n.a.	1.8	n.a.	n.a.	-
	{	0.19	-	-	n.a.	-	-	n.a.	n.a.	n.a.	n.a.	-
	{	2.3	-	n.a.	n.a.	n.a.	n.a.	n.a.	4.9	n.a.	n.a.	n.a.
Rb ⁺	{	n.d.	n.a.	-	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	-
	{	0.08	-	-	n.d.	-	-	n.d.	0.11	n.d.	n.d.	-
	{	n.d.	-	0.026	n.d.	0.043	0.018	n.d.	0.98	n.d.	n.d.	0.82
Cs ⁺	{	n.a.	n.a.	-	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	-
	{	n.a.	-	-	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	-
	{	n.a.	-	0.039	0.033	0.029	0.079	n.d.	0.16	n.d.	n.d.	0.24
Cl ⁻	{	n.a.	31.44	-	20.58	-	-	9.0	49	25.7	9.7	-
	{	18	-	-	n.d.	-	-	n.a.	n.d.	4.1	1.9	-
	{	16	-	n.a.	9.58	n.a.	84	2.3	14	n.d.	0.3	32

TABLE IV-3A: Continued

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	Neavesville	Maratoto	Konata Waitekauri	Waihi	Tui Mine	
	13941 ^a N14 ^a	13926 M10	13928 ¹ M19 ¹	13948 Km18	14013 Wk4	14035 Wh4
	13941 ^b N14 ^b	13919 M2 ^q	13928 ² M19 ²	13948 Km18	14013 Wk4	14037 ² Wh10 ²
	13941 ^c N14 ^c	13919 M2 ^q	13928 ¹ M19 ¹	13948 Km18	14013 Wk4	14037 ² Wh10 ²
	13941 ^d N14 ^d	13919 M2 ^q	13928 ¹ M19 ¹	13948 Km18	14013 Wk4	14037 ² Wh10 ²
Wt quartz	52	45	49	42	31	28
Wt water	20	55	28	31	7	7
Na ⁺	{	32	12	16	12	12
	{	-	5.3	4.8	4.1	4.1
	{	21	-	-	-	-
K ⁺	{	28	8.6	18	2.0	2.0
	{	-	8.5	17	1.2	1.2
	{	15	-	-	2.7	2.7
Ca ²⁺	{	4.7	n.d.	n.d.	31	31
	{	-	4.6	58	60	60
	{	28	-	-	80	80
Al ³⁺	{	n.a.	n.d.	n.d.	n.a.	n.a.
	{	-	11	14	1.33	1.33
	{	62	-	-	0.27	0.27
Mg ²⁺	{	0.90	n.d.	n.d.	0.17	0.17
	{	-	2.3	2.6	0.65	0.65
	{	0.28	-	-	0.08	0.08
Li ⁺	{	1.4	0.68	0.72	0.11	0.11
	{	-	0.071	0.14	n.d.	n.d.
	{	0.90	-	-	0.001	0.001
Zn ²⁺	{	0.90	0.27	0.41	0.21	0.21
	{	-	0.002	0.24	0.13	0.13
	{	n.a.	0.84	2.3	0.35	0.35
Rb ⁺	{	n.a.	n.a.	n.a.	n.d.	n.d.
	{	-	n.a.	n.a.	n.d.	n.d.
	{	n.a.	-	-	0.035	0.035
Cs ⁺	{	-	n.a.	n.a.	n.d.	n.d.
	{	-	n.a.	n.a.	n.d.	n.d.
	{	0.059	-	-	0.022	0.022
Cl ⁻	{	55	38	67	13.3	24
	{	-	48	33	n.a.	n.a.
	{	18	37	39	3.77	36

TABLE IV-3a: Continued

			Tui Mine				Waiorongomai				Tokatea		Waihi	
			14061 ₁	14061 ₂	14071	14090	14091	14094	14098			13958 _b	14034	grams milligrams
			Tui 19 ₁	Tui 19 ₂	W116	W167	W180	W189	W194			BO _{2b}	W15	
Wt quartz	36	39	36	39	59	35	9	53	24			43	n.a.	
Wt water	12	20	12	20	47	3	n.a.	9	n.a.			12	n.a.	
Na ⁺	A	38	29	29	-	3.88	1.77	8.95	6.39	Na ⁺	{ A ₁ A ₂ A ₃	39	30.3	
	B	58	57	-	-	2.55	0.38	12.0	1.19			0.4	n.d.	
	C	63	53	165	165	n.d.	n.d.	3.17	0.97			n.d.	n.d.	
K ⁺	A	3.2	3.6	-	-	0.75	0.21	0.60	0.79	K ⁺	{ A ₁ A ₂ A ₃	11.9	2.16	
	B	46	50	-	-	0.13	0.27	0.10	0.55			n.d.	n.d.	
	C	24	19	50	50	0.53	0.055	1.07	3.7			n.d.	0.12	
Ca ²⁺	A	68	74	-	-	47.3	0.45	0.53	78.4	Ca ²⁺	{ A ₁ A ₂ A ₃	23.9	2.62	
	B	21	29	-	-	312	0.88	3.49	92.2			n.d.	0.68	
	C	64	73	42	42	20.4	n.d.	1.75	21.9			n.d.	0.35	
Al ³⁺	A	9.1	10	-	-	n.d.	n.d.	n.d.	0.69	Al ³⁺	{ A ₁ A ₂ A ₃	3.46	n.d.	
	B	n.d.	n.d.	-	-	1.42	2.03	10.44	6.6			n.d.	n.d.	
	C	262	267	69	69	0.29	n.d.	2.64	8.9			n.d.	n.d.	
Mg ²⁺	A	7.7	7.8	-	-	0.35	0.12	0.12	0.37	Mg ²⁺	{ A ₁ A ₂ A ₃	2.78	0.28	
	B	1.1	1.2	-	-	4.29	0.24	0.13	0.35			n.d.	0.14	
	C	10	4.6	4.2	4.2	1.41	0.057	n.d.	0.17			n.d.	0.04	
Li ⁺	A	1.8	1.3	-	-	0.36	0.19	2.03	2.1	Li ⁺	{ A ₁ A ₂ A ₃	4.68	2.18	
	B	0.52	0.54	-	-	0.20	n.d.	1.96	0.09			n.d.	n.d.	
	C	1.1	0.95	4.2	4.2	n.d.	0.001	0.58	0.05			n.d.	n.d.	
Zn ²⁺	A	8.9	18	-	-	n.a.	n.a.	n.a.	n.a.	Zn ²⁺	{ A ₁ A ₂ A ₃	29.9	25.2	
	B	n.d.	n.a.	-	-	n.a.	n.a.	n.a.	n.a.			1.63	6.3	
	C	56	85	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.			1.21	n.d.	
Rb ⁺	A	n.d.	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	Rb ⁺	{ A ₁ A ₂ A ₃	n.d.	n.d.	
	B	0.11	0.082	-	-	n.d.	n.d.	n.d.	n.d.			n.d.	n.d.	
	C	0.043	0.020	0.21	0.21	n.d.	n.d.	n.d.	n.d.			n.d.	n.d.	
Cs ⁺	A	n.d.	n.d.	-	-	n.d.	n.d.	n.d.	n.d.	Cs ⁺	{ A ₁ A ₂ A ₃	n.d.	n.d.	
	B	n.d.	n.d.	-	-	n.d.	n.d.	n.d.	n.d.			n.d.	n.d.	
	C	0.084	0.091	0.20	0.20	0.03	n.d.	n.d.	n.d.			n.d.	n.d.	
Cl ⁻	A	68	63	-	-	7.46	18.5	20	20.9	Cl ⁻	{ A ₁ A ₂ A ₃	29.9	25.2	
	B	10	12	-	-	0.06	n.d.	0.17	5.0			1.63	6.3	
	C	31	84	n.a.	n.a.	0.0	10.0	n.d.	5.6			1.21	n.d.	

TABLE IV-3B: Calcite Samples
 Northern Ngawha
 Coville Geothermal
 Peninsula Field
 13970
 DC 4 NG5

		Tokatea	
		13962	RO3
		n.a.	13
		grams	
		milligrams	
Na ⁺	{ A ₁ A ₂	Na ⁺	{ A 4.5 B 4.8
K ⁺	{ A ₁ A ₂	K ⁺	{ A 3.6 B 1.3
Ca ²⁺	{ A ₁ A ₂	Al ³⁺	{ A n.d. B n.d.
Al ³⁺	{ A ₁ A ₂	Mg ²⁺	{ A 7.2 B 17
Mg ²⁺	{ A ₁ A ₂	Li ⁺	{ A 0.09 B 0.11
Li ⁺	{ A ₁ A ₂	Zn ²⁺	{ A 0.24 B 0.25
Cl ⁻	{ A ₁ A ₂	Rb ⁺	{ A n.d. B n.d.
		Cl ⁻	{ A 22 B 0.64

* Leach solution: A = water, B = ammonium nitrate and C = nitric acid.

- = not leached with that specific solution

n.a. not analysed

n.d. not detected

TABLE IV - 4: Analyses of blanks: μg of some cations leached from two samples (Blank 2 and Blank 3) of Spectrosil silica glass tubing. The glass tubing was broken into small chips and cleaned, crushed and leached by the same methods as used for the quartz samples. A third sample (Blank 1) was also processed but the concentrations were recorded only as "not detectible". The analyses include the concentration of ions in the reagents (see Table IV - 2).

Cation	leaching reagent	Blank 2 (26g)	Blank 3 (26g)
Na^+	water	0.05	0.01
	ammonium nitrate	0.25	0.47
	nitric acid	< 0.01	< 0.01
K^+	water	0.15	0.20
	ammonium nitrate	0.20	0.18
	nitric acid	0.05	0.09
Ca^{2+}	water	< 0.03	< 0.03
	ammonium nitrate	0.66	0.76
	nitric acid	< 0.03	< 0.03
Al^{3+}	water	< 0.25	< 0.25
	ammonium nitrate	0.69	0.67
	nitric acid	< 0.25	< 0.25
Mg^{2+}	water	< 0.03	< 0.03
	ammonium nitrate	0.31	0.44
	nitric acid	< 0.03	< 0.03
Li^+	water	< 0.0003	0.001
	ammonium nitrate	< 0.0003	< 0.0003
	nitric acid	0.002	0.002

ASSESSMENT OF EXPERIMENTAL CONTAMINATION

Three blanks were prepared by cutting lengths of silica glass tubing (Spectrosil) into small pieces. They were cleaned, crushed and leached at different times by the same techniques used with the samples. Analyses of the leaches (Table IV-4) show that the ions of interest were not detectable, or present in only trace quantities, indicating that contamination during the experimental procedure is minimal.

PRECISION: DUPLICATES AND SAMPLE GROUPS

Sufficient material for several crushing and leaching experiments was available for some samples. Chips of the sample were sorted according to their quality (=clarity) to give a series of samples identified by the subscripts a,b,c, etc. in decreasing order of quality.

In cases where the material could not be separated, due to homogeneity of the sample, the separates are regarded as duplicates and are given the subscripts 1 and 2.

Four pairs of duplicates were crushed but only three; 12928 (M19), 14037 (Wh10) and 14061 (Tui19), were leached with the identical solvents.

The two samples of 12928 (M19) show very good agreement except for Na^+ which is lower in 12928₁ than 12928₂ (Tables IV-3 and 7-1). The two analyses of 14037 (Wh10) have similar ionic ratios and the concentration values, uncorrected for inclusion water yield, are also similar. When the analyses are corrected for the inclusion water weight (Table 7-1) the agreement is diminished suggesting that one of the water yield measurements is incorrect. Corrected and uncorrected analyses of 14061 (Tui19) are in good agreement except for K^+ which, in the corrected analyses, is higher in 14061₂. The use of a succession of different solvents on 13957₂ (TK2₂) compared with the single solvent used on 13957₁ (TK2₁) and possibly inaccurate water yield results may contribute to the poor agreement in absolute concentrations of some ions between the two samples, although Na^+ , Li^+ and Cl^- are not very different.

TABLE IV-5: Major ion analyses of fluid inclusions in calcite from the Ngawha geothermal system, and modern bore fluids. Concentrations are given in mg/kg (ppm).

	Fluid inclusion water analysis (Sample NG5)	Average analyses of modern water in wells 1,2,4 and 9.	
		A ^{*1}	B ^{*2}
Na ⁺	652	1,028	1,086
K ⁺	126	89	92
Ca ²⁺	2,400	13	4
Al ³	74	2	0.5
Mg ²⁺	2,140	1	0.1
Li ⁺	15	13	14
Cl ⁻	1,900	1,476	1,610
Na/K	5.2	11.6	11.8

*¹ average of all analyses of well water and steam listed in Table 6-4 of Browne et al (1981).

*² average of well water analyses only (same source as above)

The samples separated into quality series generally also show good agreement. Three analyses of the 13980 (AS1) series are in reasonable agreement but a fourth, 13980_b, although having a similar Na/K ratio to the others in the series has much greater relative concentration of the other ions.

Considering that the five samples of the 13939 + 13941 (N16 + N14) series were leached with different solvents four samples are in good agreement, whereas the fifth, 13939 (N16), contains much higher relative concentrations of K^+ and Mg^{2+} .

The two 14054 (Tui6) samples are the best pair, having very similar ionic ratios but slightly different absolute concentrations, the latter presumably due to incorrect water yield measurements.

In conclusion, the duplicate and group samples generally show good agreement, but indicate that the water yield measurements are not very accurate.

ACCURACY: TEST SAMPLE

A sample of calcite cuttings from approximately 1000m in drillhole 5 of the Ngawha geothermal field, Northland, was processed along with the other samples. Unfortunately no other modern geothermal samples could be obtained which had sufficient material for the procedure.

The sample was crushed and leached with water twice. Table IV-5 presents the analyses of the combined water leaches (they are shown separately in Table IV-3) along with an analyses of the modern bore water. Agreement of Na^+ , K^+ , Li^+ and Cl^- is good. High values of Mg^{2+} , Ca^{2+} and Al^{3+} in the leaches (Table IV-5) are due to contamination from the calcite host. Differences in Na^+ and K^+ concentrations between the fluid inclusion analyses and the modern waters are opposite (Na^+ in the inclusion analysis is about 35% lower than in the modern water, whereas K^+ is about 40% higher than in the modern water) and lead to a large difference in Na/K ratio: 5.2 in the fluid inclusion waters and approximately 11.5 in the modern bore water.

These results are very encouraging if the chemistry of the

modern geothermal water is assumed to be similar to the waters present when the inclusions formed.

ASSESSMENT OF ANALYSES OF INDIVIDUAL SAMPLES

Introduction

The results of the crushing and leaching experiments on each sample (Tables 7-1 and IV-3) are discussed individually in the following sections to determine the presence and degree of contamination in the fluid inclusion analyses. The criteria used for assessing the degree of contamination are discussed in Chapter 7.

Quartz and calcite are grouped separately and the samples of each mineral are listed in the geographical order of their location (north to south).

Quartz Samples

Tokatea

Sample 13957 (TK2)

Sample 13957 consists of quartz crystals from a comby quartz vein within the Tokatea Big Reef near Tokatea Saddle. The sample was split into two duplicates 13957₁ and 13957₂.

13957₁ gave a good yield of water (23mg). The crushed sample was leached with nitric acid only. Aluminium contamination is low and comparisons with Na/Al, Na/Li and K/Al ratios in the quartz analysis suggest that contamination of Na and K in the leach, if present, is negligible. The Ca/Mg ratio of the quartz analysis indicates that most of the Ca present in the leach is from contamination. Na and K are only slightly out of balance with Cl.

13957₂ gave a water yield less than half that of 13957₁ (9mg). The crushed sample was leached with the three different leaching solutions. Al contamination is very high but comparisons with the Na/Al and K/Al ratios in the quartz analysis indicate that Na and K contamination from this source would be insignificant. In contrast if the Al is considered to predominantly come from particles of sericite in the fluid

inclusions, half of the K would also be from this source. Compensation for this, changes the Na/K ratio of the leaches to a value similar to 13957₁. Practically all of the Ca in the leaches is from contamination. There is insufficient Cl to balance with the Na and remaining K even after adjustment for possible sericite contamination.

In appraisal the Na, K and Cl concentrations of the fluid inclusions is considered to be best represented by 13957₁: 3400ppm Na, 1600ppm K and 4600ppm Cl.

Sample 13958 (B02)

Sample 13958 consists of large quartz crystals from a comby quartz vein within the Tokatea Big Reef at the Buffalo Mine. The sample was split into two of different quality, 13958_a and 13958_b.

13958_a gave a poor water yield (7mg from 43g of quartz). The crushed quartz was leached with the three different solutions. Na and K display good leaching patterns. Al contamination is very high, however Na/Al, Na/Li and K/Al ratios of the quartz analysis and leaches indicate that contamination of Na and K would be insignificant from this source. Ca contamination is also high and is matched with the quantity of Mg expected by comparison with the Mg/Ca ratio of the quartz analysis. The leaching pattern of Cl follows the general trend but the total concentration of Cl is slightly defficient for a good charge balance with Na and K.

13958_b gave a low yield of water (12mg from 43g of quartz). The crushed sample was leached three times with water. The second and third leaches contained extremely low concentrations of ions except for small quantities of Cl and Na. Al, Ca and Mg contamination are much greater in 13958_b than 13958_a as indicated by their higher concentrations in the water leaches of 13958_b compared with the single initial water leach of 13958_a. Nevertheless the Na/K ratios are similar when calculated from the three different leaches of 13958_a and the three water leaches of 13958_b.

In appraisal the Na and K concentrations of the fluid inclusions are considered to be best represented by 13958_a: 7600ppm Na and 2700ppm K although a Na/K ratio close to 3 may be more appropriate. 8300ppm Cl is present.

Petote Stream Area

Sample 13907 (Hutt 2)

Sample 13907 consists of large vug crystals from the Hutt Creek area. The sample gave a low to moderate yield of water (8mg from 33g of quartz). The crushed sample was leached once with water.

Ca contamination is evident but Li, Mg and Al concentrations are very low, although this is to be expected with a water leach and therefore does not discount the possibility of these values being from contamination. The concentration of Cl balances very well with the Na and K.

The indicated partial composition of the inclusions is: 3300ppm Na, 140ppm K and 4000ppm Cl. These are probably minimum values, whereas the Na/K ratio of 24 is a maximum (K is proportionately higher).

Sample 13980 (AS1)

Sample 13980 consists of large vug quartz crystals from Aitken Stream. The sample was split into four of varying quality. Water yields of 13980_a, and 13980_c were good (22 and 30 mg respectively). The glass tap attachment to the evacuated stainless steel tube broke after the first crushing of 13980_d allowing air into the tube. After repairs the sample was pumped down and crushed again yielding 8mg of water indicating that the original inclusion weight (from which the leached salts are derived) was probably between 20 and 30mg. 13980_b was not crushed under vacuum because of the small quantity of sample.

13980_a, 13980_c and 13980_d were leached only once each with nitric acid solution, whereas 13980_b was leached with all three leaching solutions including several additional nitric acid leaches.

The leaches of 13980_a, 13980_c and 13980_d have very similar

concentrations of the various ions. Ca and Mg contamination is very low compared with other samples, whereas Al and Li contamination is about average. Comparison with the Na/Al, Na/Li and K/Al ratios of the quartz analysis indicate that significant Na and K contamination has not occurred, although similarly high Na/K ratios occur in the leaches and quartz analysis. Cl was only analysed from 13980_d and although not balancing perfectly with Na and K its concentration is of the right order.

In contrast to the above samples the concentrations of various ions leached from 13980_b are very low indicating a low content of leached fluid inclusions. Ca, Mg, Al and Li (the latter nearly as much as Na) concentrations, in proportion to Na and K, are much higher than in previous samples. The Na/K ratio is considerably lower indicating that the analysis may have been contaminated with K in addition to Ca, Mg, Al and Li.

The successive acid leaches experimented with on 13980_b failed to yield any more Na and K but the last leach contained considerable quantities of Ca and Cl indicating possible contamination of the leach during handling.

In appraisal an average of 13980_a and 13980_c is considered representative of the fluid inclusion composition: 4900ppm Na and 320ppm K with consideration that the Na/K ratio is similar to that of the quartz. Cl must be extrapolated from 13980_d, indicating 3900ppm Cl.

Sample 13998 (PS15)

Sample 13998 consists of small vug quartz crystals, intergrown with Stage 2 chalcopyrite and pyrite, from the Chalcopyrite lode of Petote Stream. The water yield was low (6mg), however only a small quantity of quartz was crushed (23g). The crushed sample was leached with all three different solutions.

Ca and Mg contamination is very low with no Ca detected in the nitric acid leach. Al and Li contamination also appears to be low compared with other samples. The leaching patterns of Na and K are very good and follow the expected behaviour for

these ions. The pattern of Cl is not so good but the total quantity balances very well with the Na and K.

A few fluid inclusions in polished plates of another sample of quartz (13995) from this stage contain a fibrous solid mineral (sericite?), however the high Na/K ratio and good Cl balance suggest that contamination from this mineral is insignificant.

In appraisal the leaches of 13998 appear to be some of the better analyses although the suggested fluid inclusion partial analysis of 1800ppm Na, 180ppm K and 2000ppm Cl gives a high Na/K ratio of 10.

Sample 14006 (PS26)

Sample 14006 consists of small vug quartz crystals from a vein crossing the Petote Stream track. The sample gave a low yield of water (6mg from 29g of quartz). The crushed sample was leached with the three different solutions.

Ca and Al concentrations are extremely high particularly in the nitric acid leach, whereas Mg and Li are comparatively low (with reference to their ratios in the quartz analysis of this sample). Comparison with the Na/Al, Na/Li and K/Al ratios of the quartz analysis suggests that contamination of Na and K could account for only 4 and 15% respectively of that recorded in the leaches. However, Na contamination has occurred as evidenced by the increasing quantities of Na in successive leaches. Cl is far too low for a reasonable balance with the total Na and K.

Particles of a fibrous mineral were observed in some of the fluid inclusions of plates prepared for heating and freezing study.

In conclusion the leaches of this sample are considered to be generally contaminated.

Whangapoua

Sample 13910 (Wg9)

Sample 13910 consists of small vug quartz crystals inter

grown with stibnite from Waingaro Stream. A moderate to good yield of water (8mg from 21g of quartz) was obtained. The crushed sample was leached with the three different solutions.

Na and K exhibit good leaching patterns and Cl balances well with these ions. Contamination of Ca, Al, Mg and Li is about average compared with other samples. The Na/K ratio of 5.4 indicates a temperature of approximately 260°C (Na/K geothermometer) compared with the fluid inclusion filling temperatures of 190°C (Na/K $\approx$ 9).

In appraisal the partial analysis of 2300ppm Na, 450ppm K and 3700ppm Cl is considered to be representative of the fluid inclusion water.

Neavesville

Sample 13938 (N44)

Sample 13938 consists of large vug quartz crystals picked off the Ajax 1 level mullock heap. Because of the small sample size (8g) the sample was not crushed under vacuum and therefore the weight of inclusion water is not known.

The crushed sample was leached with the three different solutions. Ca, Mg, Al and Li contamination are present. The leaching patterns of Na and K indicates that significant contamination of these ions has not occurred. Inclusions of sericite present in the quartz of Ajax 2 level may also occur in quartz of 1 level, implying that K contamination of the inclusions is possible. The high concentration of Cl in the water leach indicates that contamination of this ion occurred during handling.

In appraisal a Na/K ratio of 2.6 is indicated for the inclusion water, provided K contamination has not occurred.

Samples 13939 (N16) and 13941 (N14)

Samples 13939 and 13941 are large vug quartz crystals from Ajax 2 level. Because of experimentation with the different leaching solutions, the large quantity of material collected was eventually portioned into five samples of different grade (13939, 13941a, 13941b, 13941c and 13941d) crushed individually or in pairs at different times with batches of other samples.

All five samples gave good water yields, 13941_b being exceptionally good at 55mg.

13941_b was the first sample crushed in this study and was leached once with water to test the viability of the technique. 13941_a and 13939 were each leached once with nitric acid solution, whereas 13941_c and 13941_d were successively leached with water and ammonium nitrate solution.

The quartz analysis indicates the presence of sericite inclusions and therefore K contamination may have occurred during leaching. This appears to be the case in the nitric acid leach of 13939 where the concentration of K is three times that of Na. Ca, Mg and Al contamination is also high in 13939 relative to the 13941 samples.

In contrast the remaining samples have Na/K ratios close to 1 with Na predominating in 13941_a, 13941_b and 13941_c but K predominating in 13941_d. Ca, Al and Mg contamination is moderate in leaches of these samples and Mg is very low in 13941_a. Li values are near modern geothermal water levels and may be representative of the inclusion waters. Because the quartz contains little Li (quartz analysis, Table 7-2), contamination from this source would be minor. The Cl concentration is fairly consistent in all samples, having an average indicated concentration of 1200ppm. Except for 13939 and 13941_a the Cl balances with the Na and K.

In appraisal, a partial analysis of 740ppm Na, 630ppm K, 31ppm Li and 1220ppm Cl is obtained by average total values of these ions from the various leaches of 13941_a, 13941_b, 13941_c and 13941_d. However, the K value may be too high because of contamination from sericite as indicated in 13939.

Maratoto

Sample 13919 (M2q)

Sample 13919 consists of large vug quartz crystals from the Camoola vein. The 28g sample gave a low water yield (7mg). The crushed sample was leached with the three different solutions.

Ca and Mg contamination are very high and in a similar Ca/Mg ratio to that in the host quartz as indicated by the quartz analysis. Al and Li contamination are extremely low and the concentration of Li in the leaches may be representative of the inclusion waters. The leaching patterns of Na and K differ from the general patterns with possible K contamination in the nitric acid leach. However, comparison of Na/Al, Na/Li and K/Al ratios with the quartz analysis suggest contamination is not from this source. The total Cl concentration is very high compared with Na and K as in other samples from Maratoto (see following).

In appraisal the partial analysis of 3000ppm Na, 880ppm K, 40ppm Li and 12000ppm Cl suggests either Cl contamination or the presence of Ca rich fluids.

Sample 13926 (M10)

Sample 13926 consists of small vug quartz crystals from the Silver Queen vein. The sample gave a moderate yield of water (11mg) considering the quantity of quartz crushed (29g). The crushed sample was leached with the three different solutions.

Minor Ca, Al, Mg and Li contamination is present in the leaches.

The leaching patterns of Na and K follow the general Na pattern. Although the Na/K ratio of the leaches and the quartz are similar (5.3 and 5.2 respectively), comparison of the Na/Al, Na/Li and K/Al ratios suggests that contamination of Na and K is insignificant. Particles of a fibrous mineral occur in fluid inclusions of plates prepared for heating and freezing work and provide a possible contamination source if present in large numbers. If these particles are sericite a balance with the Al contamination can account for all of the K present in the leaches. The total concentration of Cl is high compared with Na and K as in other Maratoto samples.

In appraisal the partial analysis of 2700ppm Na, 550ppm K and 11000ppm Cl suggests Cl contamination or the presence of Ca rich fluid.

Sample 13928 (M19)

Sample 13928 consists of small vug quartz crystals from the Camoola vein. The sample was split into two duplicates 13928₁ and 13928₂ of equal quality. These samples gave similar water yields; 13928₁, 27mg from 55g of quartz and 13928₂, 15mg from 39g of quartz. The crushed samples were each leached with the three different solutions.

The concentrations of various ions in the leaches of the two samples show good agreement (when corrected for water yields) except that Na and Mg are slightly lower in 13928₁ than 13928₂. Ca, Mg, Al and Li contamination has occurred. Comparisons with the quartz analysis shows that the Mg/Ca ratios of the leaches are almost identical to that of the host quartz. Similarly the Na/K ratios are very close. However the leaching patterns of Na and K follow the general trends for these ions and comparison with the Na/Al, Na/Li and K/Al ratios of the quartz analysis suggest that both Na and K, proportional to Al, contamination is insignificant. Particles of a fibrous mineral were present in the inclusions of plates prepared for heating and freezing work. Approximately half of the K present in the leaches can be balanced with Al if contamination from sericite occurred. The low Na/K ratios of the 13928 samples relative to the other Maratoto analyses (13919 and 13926) and the ratio predicted by the Na/K geothermometer (5 at 270°C) suggests K contamination. The total concentration of Cl is high compared with Na and K as in other Maratoto samples and requires balancing with Ca.

In conclusion, although the water yield and the leaching patterns of Na and K appear to be satisfactory the low Na/K ratios of the analyses are believed to indicate that contamination of K, in addition to Ca, Mg, Al and Li may have occurred.

Komata

Sample 13948 (Km18)

Sample 13948 consists of vug quartz crystals from 8 level. Because of the small quantity of sample (14g) it was not crushed under vacuum. The crushed sample was leached with the three different solutions. Although the quartz analysis indicates that the sample contains very little Ca, Ca contamination in

the leaches appears to be at a high level. Al, Mg and Li contamination appear to be low. The leaching patterns of Na and K and the Na/K ratio of 4.8 suggest that no significant contamination of these ions has occurred. The total quantity of Cl present is very high compared with Na and K and requires balancing with some Ca.

Waitekauri

Sample 14013 (WK4)

Sample 14013 consists of large vug quartz crystals from the Maoriland vein. The sample was crushed under vacuum but the stainless steel tube cracked admitting a small quantity of air into the system. The water yield of 10mg is therefore considered to be a maximum value.

The crushed sample was leached with the three different solutions. Al and Li contamination is low and may be present only in the nitric acid leach, whereas Ca and Mg contamination is more general and present in larger quantities. The Mg/Ca, Li/Al and also Na/K ratios of the combined leaches are similar to those of the quartz analysis. Na and K contamination may also be indicated by the increase in Na in the nitric acid leach, the progressive increase in K through the three leaches and the overall low Na/K ratio (1.4). If Na and K contamination has occurred it is in a much greater proportion than Al and Li as indicated by the Na/Al, Na/Li and K/Al ratios of the quartz analysis. The total concentration of Cl is high compared with Na and K and requires some Ca for an adequate charge balance.

In conclusion the sample is considered to be generally contaminated and not representative of the original inclusion waters.

Waihi

Sample 14034 (Wh5)

Sample 14034 consists of small vug quartz crystals from the mullock heap of No.5 Shaft. Because of the small quantity of quartz it was not crushed under vacuum. The crushed sample was leached with water three times. Little additional material

was dissolved by the second and third water leaches. Ca and Mg contamination may be present but the degree of contamination is difficult to assess without ammonium nitrate and nitric acid leaches. However, Li contamination is evident. The concentration of K must be considered a minimum value in relation to Na because of the absence of ammonium nitrate leach values. The total concentration of Cl indicates that if a full analysis were available a good charge balance with Na and K might be achieved.

In conclusion if Na and K contamination is minor a maximum Na/K ratio of 14 is indicated for the inclusion fluids.

Sample 14035 (Wh4)

Sample 14035 consists of small vug quartz crystals picked off the mullock heap of No.5 Shaft. The sample gave a low water yield (6mg from 44g of quartz). The crushed sample was leached with the three different solutions.

Al and Mg contamination is low. Except for a small increase in Na concentration from the water to the ammonium nitrate leach the leaching patterns of Na and K look satisfactory. Li may be uncontaminated. The total concentration of Cl is slightly high relative to Na and K and may require balancing with a small quantity of Ca but not to the concentration present. Therefore most of the Ca is from contamination.

In appraisal a Na/K ratio of 3.6 is indicated for the inclusion fluids and a small quantity of Ca is required to balance Cl. The partial analysis is 2800ppm Na, 780ppm K, 47ppm Li and 5300ppm Cl.

Sample 14037 (Wh10)

Sample 14037 consists of small vug quartz crystals from 3 level. The sample was split into two duplicates, 13037₁ and 13037₂. Both samples gave very poor water yields: 2 and 4mg respectively from about 50g of quartz.

The crushed samples were each leached with water and ammonium nitrate solutions. The leaches of the two samples are very consistent.

Although nitric acid leaches were not used, strong contamination of Ca, Al, Mg and Li is indicated by the ammonium nitrate leaches. Cl is present in greater quantities than can be balanced with Na and K and some Ca is required to complete the balance. Both samples gave Na/K ratios of 0.6 suggesting K contamination.

The absolute values of the various ions in the two sets of leaches are very close but when corrected for fluid inclusion water yields they are considerably different. This can be taken to indicate that the original water yields were identical and the measurements in error or that because the water yields are so low the leach analyses only reflect equal levels of contamination.

In conclusion if the leach analyses of Na, K and Cl are believed to be correct, an average of the two analyses gives an indicated partial composition for the fluid inclusion water as; 2900ppm Na, 4600ppm K and 13000ppm Cl. Ca must be considered as a major component to balance Cl.

Tui Mine

Sample 14054 (Tui 6)

Sample 14054 consists of large vug quartz crystals from 5 level of the Champion vein. The sample was split into two of different quality, 14054_a and 14054_b. The crushed samples were leached only once with nitric acid. Although the samples gave different water yields (14054_a 12mg and 14054_b 21mg) the uncorrected leach analyses are remarkably consistent. After correction for water yields the agreement is not so good. A possible explanation is that 14054_b contained more secondary inclusions resulting in a more dilute solution. Alternatively one of the water yield measurements may be incorrect.

Ca contamination is high, whereas contamination of Al and Mg is moderate. The Li/Al, Na/K, Na/Al and Na/Li ratios of the leaches and quartz analyses are very different indicating that Na, K and Li contamination may be minor.

Particles of a fibrous mineral were identified in fluid

inclusions of plates prepared for heating and freezing work and all the K present in the leaches can be balanced with the Al if these result from contamination by sericite. However, the Na/K ratio of 5.2 gives a temperature (Na/K geothermometer) in reasonable agreement with fluid inclusion filling temperatures, suggesting that K contamination has not occurred.

Cl, analysed only in the leach of 14054_a, balances well with the Na and K.

In conclusion 14054_a is considered to be the most representative analysis and indicates a partial fluid inclusion composition of 5200ppm Na, 1000ppm K, 170ppm Li and 8000ppm Cl.

Sample 14056 (Tui 13)

Sample 14056 (vein quartz from Raise 17, Champion 5 level) gave a moderate yield of water (18mg from 62g of quartz). The crushed sample was leached with the three different leaching solutions.

The leaches contain strong Al and moderate Ca, Mg and Li contamination. The leaching patterns of Na and K suggest that contamination has also occurred with these ions. Both have minimum concentrations in the water leach and maximum concentrations in the ammonium nitrate leach. The Na/K and Mg/Ca ratios of the combined leaches and quartz analyses are similar although the Li/Al, Na/Al and K/Al are different.

Particles of a fibrous mineral occur in fluid inclusions of plates prepared for heating and freezing work, and balancing K and Al in the leaches as sericite can account for most of the K as contamination from this source.

The total concentration of Cl is insufficient to balance even Na.

In conclusion the leaches of 14056 have been generally contaminated.

Sample 14061 (Tui 19)

Sample 14061 consists of vein quartz from DD cross-cut, 5 level Champion vein. The sample was split into two duplicates,

14061₁ and 14061₂. The two samples gave different water yields, 12mg and 20mg respectively, from similar quantities of quartz. Both crushed samples were leached with the three different solutions.

The leaches contain similar concentrations of the various ions before correction for the different water yields, but when the latter correction is made the agreement, although reasonable, is not as good. If the samples are duplicates as originally considered, one of the water weight measurements may be in error or alternatively the leaches may reflect equal amounts of contamination rather than fluid inclusion composition.

Al, Ca, Mg and Li contamination are strong. The leaching patterns of Na and K suggest contamination of these ions also. The combined leaches and quartz analyses have similar Na/K ratios but different Na/Al, K/Al, Mg/Ca and Li/Al ratios. Small particles of a fibrous mineral occur in fluid inclusions of plates prepared for heating and freezing work. Balancing K and Al of the leaches as sericite can account for all of the K, but only half of the Al, as contamination from this source.

The quantity of Cl, is insufficient to balance Na + K.

In conclusion the leaches of 14061 are considered to have been generally contaminated.

Wairongomai

Sample 14071 (Wi16)

Sample 14071 consists of large vug quartz crystals collected from a boulder in Canadian Creek, Wairongomai.

The sample gave a large yield of water, 47mg from 59g of quartz. The crushed sample was leached only once with nitric acid solution.

Ca and Al concentrations are moderate but when corrected for the dilution factor are very low. Mg and Li may be representative of the inclusion fluids. The various ionic ratios for

the leach analysis are different from those of the quartz analysis. Cl was not analysed.

In conclusion, the high water yield and relatively low Ca and Al contamination indicate that the leach is generally representative of the inclusion fluids, with a partial analysis of 3500ppm Na, 1100ppm K, 89ppm Mg, 89ppm Li, 4.5ppm Rb and 4.3ppm Cs.

Sample 14090 (Wi 67)

Sample 14090 consists of vug quartz crystals from the Main Vein. The sample gave a very low water yield, 3mg from 35g of quartz.

The crushed sample was leached with the three different solutions. Ca and Mg contamination is very high, whereas Al and Li contamination is low. The leaching pattern of Na follows the general trend but K rises slightly in the nitric acid leach. A charge balance of Na, K and Cl is acceptable.

In conclusion a partial analysis of 2300ppm Na, 500ppm K and 2700ppm Cl is considered representative of the fluid inclusion waters.

Sample 14091 (Wi 80)

Sample 14091 consists of large vug quartz crystals from the Main Reef (big slip) between the Premier and New Find sections. Because of the small amount of material (9g) the sample was not crushed under vacuum. The crushed sample was leached with the three different solutions.

Ca and Al contamination are low, whereas Mg and Li contamination are moderate. The extremely high total concentration of Cl, relative to Na, K and Ca, indicates Cl contamination has occurred.

The leaching patterns of Na and K follow the general patterns and may indicate that the concentrations of these ions are representative of the inclusion fluid. If so the inclusion fluids have a Na/K ratio of 4.

Sample 14094 (Wi89)

Sample 14094 consists of large vug quartz crystals from

the Welcome vein. The sample gave a low water yield, 9mg of water from 53g of quartz. The crushed sample was leached with the three different leaching solutions.

Al, Mg and Li contamination are high, whereas Ca contamination is low (reflecting the trace element composition of the quartz). The leaching patterns of both Na and K deviate from the general patterns, with Na being highest in the ammonium nitrate leach and K highest in the nitric acid leach.

The total concentration of Cl is insufficient for a correct charge balance with Na and K.

The total salinity of Na+K+Li is of a similar order to other samples but the possibility of Na contamination may be indicated by: the low water yield, high concentration of Al and Li, the unusual leaching pattern of Na, an overall abundance of Na+K over Cl, and the high Na/K ratio of 14 (the water leach and the combined leached have the same ratio).

Sample 14098 (Wi 94)

Sample 14098 consists of large vug quartz crystals from the Inverness Vein. Because of the small quantity of sample it was not crushed under vacuum. The crushed sample was leached with the three different solutions.

High levels of Ca, Al, and Li contamination have occurred. The total concentration of Cl is high relative to Na+K and contamination may have occurred in the water leach. The leaching pattern of Na follows the general trend but K is very high in the nitric acid leach relative to the water and ammonium nitrate leaches.

Using only the concentrations of Na and K from the water and ammonium nitrate leaches gives a Na/K ratio of 5.7 which may be representative of the inclusion fluids.

Calcites

Northern Colville Peninsula

Sample 13970 (DC 4)

Sample 13970 consists of calcite from a vein crossing a tributary of Doctors Creek, Paritu area. The sample was not

crushed under vacuum. The crushed sample was leached once with water.

As expected Ca and Mg contamination is high. The concentration of Li may be representative of the inclusion fluid. Cl is high in relation to Na+K and requires balancing with Ca if no Cl contamination has occurred. K may be a minimum value due to the absence of ammonium nitrate leach values.

In conclusion, if the sample is representative of the inclusion waters they have a Na/K ratio of less than 3.4 and a Na/Li ratio of 120.

Tokatea

Sample 13962 (RO 3)

Sample 13962 consists of calcite from the Royal Oak mine (7 level). The sample gave a moderate yield of water (13mg). The crushed sample was leached successively with water and ammonium nitrate.

Ca was not analysed but Mg contamination is high, Li may be representative of the inclusion waters. The leaching patterns of Na and K deviate from the general patterns but the total concentration is insufficient to balance the concentration of Cl indicating that only slight contamination could have occurred. The presence of a small amount of Ca may be necessary to balance the Cl.

In conclusion, the partial analysis is 720ppm Na, 380ppm K, 16ppm Li and 1700ppm Cl.

APPENDIX VTHERMOCHEMICAL CALCULATIONSINTRODUCTION

Thermodynamics may be used in the study of ore deposits to calculate various physical and chemical parameters that may characterise the conditions of mineralisation. The ultimate aim of this application is to establish the reasons for the presence of particular assemblages of minerals and the absence of others in any individual deposit.

NOTATION AND UNITS

a_i	Activity of ion i
a_i°	Effective radius of ion i
(aq)	Aqueous ionic or molecular species
A } B }	Constants of Debye - Hückel equation
eq.wt.% NaCl	
	Apparent salinity from fluid inclusion freezing temperature data (equivalent weight percent sodium chloride)
f_j	Fugacity of species j (bars)
f_j°	Fugacity of species j in its standard state
G	Gibbs free energy (J. mol^{-1})
(g)	Ionic or molecular species in the gaseous state
H	Enthalpy (J. mol^{-1})
I	Ionic strength
$\bar{I}$	True ionic strength
i	Ionic species
j	Ionic or molecular species
J	Joule
K	Kelvin temperature
K	Equilibrium constant
K_g	Henry's Law coefficient
(l)	Liquid molecular species
log	Logarithm to the base 10
m_j	Molality of species j (concentration in moles/kg)
M_j	Molarity of species j (concentration in moles/litre)
mol	Mole
P	Pressure (bars)

P_j	Partial pressure of species j (bars)
pH	Negative logarithm of the hydrogen ion activity
S	Entropy ($J.K^{-1}.mol^{-1}$)
(s)	Solid molecular species
$m \leq S$	Concentration of total sulphur in solution
T	Temperature in degrees Kelvin, $K = t + 273.15$
t	Temperature in degrees celsius ($^{\circ}C$)
X_j	Mole fraction of species j
Z_i	Charge of ion i
α	Degree of dissociation
γ_{st}	Stoichiometric mean ionic activity coefficient
γ_i	Activity coefficient of ion i
δ	Deviation, in per mil, of an isotopic ratio from the standard
Σ	Summation

EQUILIBRIUM

Introduction

Barton et al (1963) stressed the importance of evaluating the degree of attainment of equilibrium before application of mineral assemblage and mineral composition data to the interpretation of the physicochemical environment of mineralisation.

Barton et al (1977) considered the following four aspects: "(1) the degree of attainment of equilibrium between aqueous species; (2) the degree of attainment of equilibrium between the ore fluid and the minerals being deposited from it; (3) the degree to which the original state (equilibrium or otherwise) has been preserved, or to which it has been modified by postdepositional changes; and (4) the degree to which mineral phases can be considered to be in communication with the ore fluid (and through it with each other) at any given time."

(1) Equilibrium Between Aqueous Species

Barton et al (1963) and Barton et al (1977) stated that most reactions between aqueous species are rapid even at room temperature and equilibrium is quickly attained. With the exception of reactions between oxidised and reduced sulphur species these reactions can be considered almost instantaneous.

Figure V-1: Effects of disequilibrium between a hydrothermal solution and the vein (mineral) system. (From Barton et al., 1977).

(2) Equilibrium Between the Fluid and Precipitating Minerals

Reactions between crystals and aqueous solution are rapid relative to the time involved for ore - forming processes but much slower than reactions between aqueous species.

Fig. V-1 illustrates the effects of disequilibrium between crystals and the hydrothermal fluid. Although some supersaturation is required for nucleation, once this has been achieved Barton et al (1963) considered that it is possible for crystals to grow from almost imperceptibly supersaturated solutions (i.e. at equilibrium in Fig. V-1). The rate of crystal growth will probably be proportional to the degree of supersaturation.

Variations in crystal - supersaturated fluid disequilibrium are demonstrated by growth zoning in crystals. Some examples encountered in this study are; (a) growth zoning in quartz, generally defined by zones of fluid inclusions (Figs. 6-3 and 6-4) but in one example by inclusions of another mineral (Fig. 7-2), (b) growth zoning in sphalerite defined by colour bands (probably due to varying iron concentrations) or by chalcopyrite inclusions (Fig. 4-19) (c) growth zoning in pyrite defined by zones of inclusions, and (d) alternating zones of quartz and calcite in some crystals from Maratoto and Komata.

Occurrences of crystal - undersaturated fluid disequilibrium causes hydrothermal leaching, the partial or complete re-resolution of hydrothermal minerals by later hydrothermal solutions undersaturated with respect to those minerals. Hydrothermal leaching of calcite occurred in many of the veins within the study area as evidenced by the presence of quartz pseudomorphs after calcite. The quartz pseudomorphs originally consisted of an intergrowth of quartz and calcite, however at some time after deposition the calcite was leached out leaving the quartz with a platy or lamellar texture. Re-resolution of quartz also occurred in some deposits, for example some vug quartz crystals at Maratoto are etched and corroded.

(3) Preservation or Modification of Assemblages

The deposits studied have presumably been subject to continuous uplift since their formation and therefore were not subjected to regional metamorphism, deep burial or crushing. However, some early stages of mineralisation may be overprinted by later stages (e.g. Thames c.f. Merchant, 1978) and supergene processes may have removed many of the vein constituents and possibly redistributed some others (e.g. the occurrence of native silver and mustard gold is attributed to processes of secondary enrichment), in addition to forming the readily identified secondary replacements of primary sulphides and oxides (e.g. supergene covellite, chalcocite, azurite and limonite).

Similarly, there appears to have been considerable overprinting of early propylitic wall rock alteration assemblages by late "oxyacidic" solutions which formed intermediate argillic assemblages in the wall rocks and deposited kaolinite in the veins (c.f. Te Ahumata and Broken Hills).

Nevertheless the sulphide and oxide assemblages identified from unoxidised samples by petrographic studies are considered here to be representative of the assemblages prevailing at the end of mineralisation and provided that the paragenesis has been adequately defined the assemblages will represent assemblages of minerals compatible with each other and the hydrothermal fluid at the time of deposition.

(4) Mineral - Fluid - Mineral Interaction

Barton et al (1977) considered that there is insufficient information known about any deposit to adequately fulfil their fourth criterion because it requires the definition of all phases, components and variables of the specific equilibrium assemblage in question. "How can we completely define the chemical 'environment' in a chemically dynamic system?" (Barton et al, 1977 p7).

The closest approach to this last criterion has been achieved by a few sphalerite stratigraphic studies (e.g.

McLimans et al, 1980) in which individual zones in sphalerites have been defined and correlated in different parts of a deposit.

Discussion

The sulphur isotope data reported in Chapter 9 contains many examples which depart from isotopic equilibrium between seemingly cogenetic sulphide species. This evidence together with observed crystal zoning and crustified vein textures (e.g. Fig. 4-6) prove that the various assigned paragenetic stages are only groupings of broadly similar individual events in the evolution of the vein systems.

Barton et al (1963) differentiated between equilibrium in the sense of compatibility of phases and equilibrium in the sense of compatibility of mineral composition. The latter is required for the application of sulphur isotope data to geothermometry but provided the ranges in composition of the individual minerals are small, averaged compositions (e.g. mole % FeS in sphalerite) of individual minerals together with the generalised mineral assemblage data may be used to infer broad limits on the physicochemistry of mineral deposition.

This thesis, like most previous similar studies takes the broad generalised approach, assuming that the range of compositions in zoned crystals is small and that individual stages in the recognised parageneses represent equilibrium assemblages. In this way average values for temperature and selected chemical parameters can be defined for individual mineralisations.

Considering the limitations of the thermochemical data used to calculate the various parameters, further refinement of the analytical data and mineral phase information, with the exception of a detailed sphalerite stratigraphy study, would probably add little to the following interpretation.

An investigation of sphalerite stratigraphy of an individual deposit is not possible in the study area at present because of the absence of a suitable suite of adequately located samples of sphalerite from any of the deposits, however, if the present mineral exploration activity produces a

working mine in the future such a study may be feasible.

EVIDENCE FROM FLUID INCLUSIONS AND STABLE ISOTOPES

Measured values of temperature (from fluid inclusion and stable isotope data), average apparent salinity (from fluid inclusion-freezing temperature data) and concentrations of Na^+ , K^+ , Cl^- and CO_2 (from fluid inclusion chemical analyses) for some of the deposits are listed underlined in Table V-1.

Although the few values for concentration of individual species relate to late stage fluids they are used here to approximate the fluids during mineralisation. The validity of this approximation is supported by the fact that the total apparent salinity (from fluid inclusion-freezing temperatures) of fluids in fluid inclusions does not differ significantly between main and late stage material.

Values of NaCl molality underlined in Table V-1 have been averaged from the fluid inclusion apparent salinity and chemical analysis data to reduce the errors inherent in the different types of measurement. Apparent salinities calculated from freezing temperatures are probably maximum values of equivalent NaCl concentration because they have not been corrected for the presence of dissolved CO_2 , whereas equivalent NaCl concentrations calculated from the Na^+ , K^+ and Cl^- concentrations of fluid inclusion leach analyses are probably minimum values because other ions (e.g. Ca^{2+} , SO_4^{2-} etc) may be present in significant quantities.

Values for temperature, salinity, molality of NaCl, Na^+ and Cl^- not underlined in Table V-1 have been interpolated. For example, Na^+ , K^+ and Cl^- concentrations were calculated from measured or assigned salinity and temperature values by using Na^+/K^+ ratios calculated from the Na/K geothermometer of Ellis & Mahon (1977) and finally balancing Na^+ and K^+ concentrations with Cl^- to match the total salinity values. NaCl molality values were derived from the apparent salinity data.

Facing page

TABLE V-1: Some thermochemical parameters for selected mineralisations.

Values underlined were calculated from fluid inclusion and stable isotope data, whereas all other values were estimated (see text).

Note: $t_e^{\circ}\text{C}$ = temperature assigned to the mineralisation ($^{\circ}\text{C}$).

	t_e °C	Apparent salinity eq. wt % NaCl	m NaCl	Na/K wt. ratio	m Na ⁺	m K ⁺	m Cl ⁻	m CO ₂	I	α NaCl	$\bar{I}$	Log mK ⁺ (25°C)	Log mK ⁺ (t_e °C)	Log δ K ⁺ (for I)	Log δ K ⁺ (for $\bar{I}$)	Log aK ⁺ (25°C)	Log aK ⁺ (t_e °C)	pH of Kaolinite/Sericite	pH of Sericite/K-feldspar	δ Ca ²⁺	δ HCO ₃ ⁻	minimum pH for calcite stability	X CO ₂ (x10 ⁻²)	f CO ₂ (bars)	Log f CO ₂
MINERS HEAD	425	10	1.7	2.4	1.2	0.5	1.7		1.7	0.1	0.17	-0.3	-1.3	-1.74	-1.01	-2.04	-2.31	4.3	5.5						1.5
TE AHUMATA } Stage 1	240	1	0.17	6.4	0.147	0.023	0.17		0.17	0.9	0.15	-1.64	-1.68	-0.27	-0.25	-1.91	-1.93	4.7	6.1						1.5
TE AHUMATA } Stage 2a	220	1	0.17	7.5	0.150	0.020	0.17		0.17	0.9	0.15	-1.70	-1.74	-0.25	-0.24	-1.95	-1.98	4.8	6.2						1.5
TE AHUMATA } Stage 2b	230	1	0.17	6.9	0.148	0.022	0.17		0.17	0.9	0.15	-1.66	-1.70	-0.26	-0.25	-1.92	-1.95	4.9	6.2						1.5
PARITU } Coastal Section	425	7	1.2	2.4	0.85	0.35	1.2		1.2	0.1	0.12	-0.46	-1.46	-1.66	-1.13	-2.12	-2.59	4.3	5.6						1.5
PARITU } Cu-Pb-Zn Veins	325	1.6	0.27	3.7	0.213	0.057	0.27		0.27	0.7	0.19	-1.24	-1.40	-0.49	-0.45	-1.73	-1.85	4.1	5.6						1.5
KAURI - KAPANGA	220	1	0.17	7.5	0.150	0.020	0.17		0.17	0.9	0.15	-1.7	-1.74	-0.25	-0.24	-1.95	-1.98	4.9	6.2						1.5
TOKATEA } Base Metals	280	1.5	0.26	4.8	0.215	0.045	0.26		0.26	0.8	0.21	-1.35	-1.44	-0.37	-0.34	-1.72	-1.78	4.3	5.8						1.5
TOKATEA } Au - Ag	220	2.1	0.23	2.0	0.090	0.025	0.087	0.5	0.18	0.97	0.17	-1.60	-1.62	-0.25	-0.25	-1.85	-1.87	4.8	6.1	-0.75	-0.22	4.9	0.9	56	1.7
PETOTE STREAM	300	2.1	0.24	16.3	0.14	0.006	0.093	0.6	0.12	0.88	0.11	-2.26	-2.28	-0.32	-0.31	-2.58	-2.59	5.1	6.5	-0.96	-0.28	5.6	1.0	41	1.6
WHANGAPOUA } Stage 2	280	1.5	0.26	4.8	0.215	0.045	0.26		0.26	0.8	0.21	-1.35	-1.44	-0.37	-0.34	-1.72	-1.78	4.3	5.8						1.5
WHANGAPOUA } Stage 4	200	1	0.11	5.1	0.10	0.012	0.104	0.8	0.11	0.97	0.11	-1.94	-1.94	-0.20	-0.20	-2.14	-2.14	5.2	6.5	-0.67	-0.19	4.8	1.5	99	2.0
KUAOTUNU	250	1	0.17	6	0.146	0.024	0.17		0.17	0.9	0.15	-1.62	-1.67	-0.28	-0.27	-1.90	-1.94	4.6	6.1						1.5
BROKEN HILLS	240	1	0.17	6.4	0.147	0.023	0.17		0.17	0.9	0.15	-1.64	-1.68	-0.27	-0.25	-1.91	-1.93	4.7	6.1						1.5
TAPU - } Cu - Bi	400	2	0.34	2.6	0.246	0.094	0.34		0.34	0.2	0.07	-1.03	-1.73	-0.95	-0.57	-1.98	-2.30	4.2	5.6						1.5
THAMES } Pb - Zn	280	3.2	0.55	4.8	0.455	0.095	0.55		0.55	0.7	0.39	-1.02	-1.18	-0.46	-0.41	-1.48	-1.59	4.1	5.6						1.5
THAMES gold-pyrargyrite	230	2.6	0.44	6.9	0.384	0.056	0.44		0.44	0.8	0.35	-1.25	-1.35	-0.35	-0.32	-1.60	-1.67	4.4	5.9						1.5
NEAVESVILLE } Ajax	250	0.7	0.11	1.9	0.032	0.016	0.034	0.2	0.04	0.97	0.04	-1.79	-1.79	-0.16	-0.16	-1.95	-1.95	4.7	6.1	-0.54	-0.15	5.1	0.26	14	1.1
NEAVESVILLE } Bluffs	220	0.6	0.10	7.5	0.088	0.012	0.10		0.10	0.9	0.10	-1.92	-1.92	-0.20	-0.20	-2.12	-2.12	5.0	6.4				0.26	16	1.2
MARATOTO	280	1	0.13	4.1	0.124	0.019	0.034	0.2	0.09	0.95	0.09	-1.73	-1.74	-0.25	-0.25	-1.98	-1.99	4.6	6.1	-0.81	-0.23	5.5	0.38	16	1.2
WAITEKAURI	280	1.1	0.19	4.8	0.15	0.040	0.19		0.19	0.8	0.15	-1.40	-1.49	-0.33	-0.31	-1.73	-1.8	4.4	5.8						1.5
WAIHI } low levels	325	1.9	0.33	3.7	0.260	0.070	0.33		0.33	0.6	0.20	-1.15	-1.38	-0.52	-0.45	-1.67	-1.83	4.1	5.5	-1.32	-0.40	5.9	1.5	56	1.7
WAIHI } intermediate lev.	280	1.9	0.33	4.8	0.27	0.057	0.33		0.33	0.7	0.23	-1.25	-1.40	-0.39	-0.35	-1.63	-1.75	4.3	5.7				1.5	72	1.9
WAIHI } upper levels	220	1.9	0.33	7.5	0.291	0.039	0.33	0.8	0.33	0.9	0.30	-1.41	-1.45	-0.31	-0.30	-1.72	-1.75	4.6	6.0	-0.87	-0.27	4.9	1.5	93	2.0
KARANGAHAKE (low levels)	300	2.3	0.39	4.2	0.315	0.075	0.39		0.39	0.7	0.27	-1.12	-1.28	-0.46	-0.42	-1.58	-1.7	4.1	5.5						
TUI MINE } Stage 1	400	3	0.51	2.6	0.37	0.14	0.51		0.51	0.2	0.10	-0.85	-1.55	-1.06	-0.66	-1.91	-2.21	4.1	5.5				0.97	19	1.3
TUI MINE } Stage 2	300	3	0.38	5.2	0.23	0.026	0.226	0.5	0.24	0.80	0.19	-1.59	-1.68	-0.40	-0.37	-1.99	-2.05	4.5	6.0	-1.18	-0.34	5.6	0.97	42	1.6
WAIORONGOMAI	325	1.6	0.18	4.4	0.13	0.021	0.076	0.6	0.10	0.79	0.08	-1.69	-1.78	-0.36	-0.33	-2.05	-2.11	4.5	5.9	-1.04	-0.33	5.9	1.0	32	1.5

IONIC STRENGTH (AT ROOM TEMPERATURE)

Ionic strength, I , "is a quantitative measure of the interatomic effects of ions on the basis of the concentrations of, and the charges on, the ions" (p316 Vaughan & Craig, 1978). It is defined as follows:

$$I = \frac{1}{2} \sum n_i Z_i^2 \quad (V-1)$$

Where n_i is the molality and Z_i is the charge of the i th ion in the solution, the summation being taken over all ions, positive and negative.

The ionic strengths of analysed inclusion fluids at room temperature, assuming complete dissociation of ion pairs, are listed underlined in Table V-1. Ionic strength values not underlined in Table V-1 were calculated from the apparent salinity values (freezing temperature measurements) assuming a simple NaCl fluid composition.

ASSOCIATION OF IONS AT ELEVATED TEMPERATURE

At elevated temperatures ions in solution form ion pairs and complexes, reducing the ionic strength of the solution and the activity (see following section for discussion on activity) of the various ions. Therefore the true ionic strength ($\bar{I}$) at a specific elevated temperature may be related to the ionic strength at room temperature (I) by a correction for association. The expression used here is;

$$\bar{I} = I \alpha \quad (V-2)$$

Where α is the degree of dissociation* of the complex or ion pair.

Evaluation of α requires knowledge of the dissociation constant (K_d) and the stoichiometric mean ionic activity coefficient (γ_{st}) for the various ion pairs and complexes. Experimentally derived data for these parameters is sparse for the various species assumed to be present in the hydrothermal

FOOTNOTE: * α is sometimes expressed as the degree of association (c.f. Seward, 1981) in which case α association = 1 - α dissociation.

fluids. In fact for the temperatures and concentrations considered here, data are available for only NaCl. Therefore for the evaluation of high temperature association the system is considered to be represented by the reaction;

This approximation is probably not far from the real situation because Na^+ and Cl^- are the dominant ions found in fluid inclusion analyses and K^+ , the next most common ion, exhibits similar behaviour with Cl^- to Na^+ (c.f. Fig. 2 of Helgeson, 1969) at these temperatures and concentrations.

CALCULATION OF THE DEGREE OF DISSOCIATION

The underlined values of α NaCl, the degree of dissociation of the NaCl ion pair, presented in Table V-1 were calculated by the method described by Seward (1976). Three equations are required for the calculation:

$$[\text{Cl}^-]^2 + \frac{K_d}{\gamma_{\text{Cl}^-}} [\text{Cl}^-] - [\text{Cl}^-]_{\text{in}} \frac{K_d}{\gamma_{\text{Cl}^-}} = 0 \quad (\text{V-4})$$

(modified form of equation 23 of Seward, 1976)

$$\gamma_{\text{Cl}^-} = \frac{\gamma_{\text{st}}}{\alpha} \quad (\text{equation 24 of Seward, 1976}) \quad (\text{V-5})$$

$$\alpha = 1 - \frac{\gamma_{\text{st}}^2 [\text{Cl}^-]}{K_d \cdot \gamma_u} \quad (\text{equation 25 of Seward, 1976}) \quad (\text{V-6})$$

where $[\text{Cl}^-]$ = concentration of free Cl^- (unknown)

K_d = dissociation constant of NaCl (values from Fig. 6.7 of Seward, 1981)

$[\text{Cl}^-]_{\text{in}}$ = concentration of total Cl^- = measured concentration of Cl^- in fluid inclusion leach experiments

γ_{st} = stoichiometric mean activity coefficient of NaCl (values from Table 4 of Lui & Lindsay, 1972)

γ_u = activity coefficient of the NaCl ion pair (taken as unity)

Equation (V-4) was solved iteratively for $[\text{Cl}^-]$, initially

Figure V-2: The degree of dissociation (α) of NaCl solutions up to 300°C.
(Modified from Fig. 6.9 of Seward, 1981.)

by making $\gamma_{\text{Cl}^-} = \gamma_{\text{st}}$ and then by using new values of γ_{Cl^-} derived from equations (V-5) and (V-6), using each new value of $[\text{Cl}^-]$ from equation (V-4) until essentially constant values of $[\text{Cl}^-]$ were obtained. Between two and four cycles through the set of three equations were required to obtain each underlined value of α_{NaCl} presented in Table V-1.

Values of α_{NaCl} not underlined in Table V-1 were interpolated from Fig. V-2 for the assigned values of temperature and NaCl equivalent concentration.

It is apparent from the calculated and interpolated values of α_{NaCl} that for most of the mineralisations considered here ion association is not a very important factor and when the possible errors on the various parameters (e.g. temperature, salinity, etc) are considered, the association correction for mineralisations formed below 325°C could probably be ignored. However, to avoid problems in selection of a cut-off point, corrections for association are made here for all mineralisations considered.

ACTIVITY AND ACTIVITY COEFFICIENTS

Activity is a measure of the effective concentration of a reactant or product in a chemical reaction.

The activity (a_i) of a specific ion i is related to its concentration (expressed in molality units; m_i) by the activity coefficient (γ_i) as defined by;

$$a_i = \gamma_i \cdot m_i \quad (\text{V-7})$$

Activity coefficients may be derived experimentally or calculated by one of various equations based on the Debye - Hückel theory. Experimental derivation of activity coefficients at high temperatures and in dilute solutions is difficult and consequently few data are available for these situations.

Values for $\gamma_{\text{Ca}^{2+}}$, γ_{K^+} and $\gamma_{\text{HCO}_3^-}$ listed in Table V-1 were therefore calculated using the Debye - Huckel expression;

Figure V-3: Ion product and neutral pH of water at elevated temperatures.
(Plotted from data in Fisher & Barnes, 1972.)

$$-\log \gamma_i = \frac{A \cdot Z_i^2 \sqrt{I}}{1 + a_i^0 \cdot B \sqrt{I}} \quad (V-8)$$

Where Z_i is the charge of the i th ion and a_i^0 is its effective radius (values from Table 2.7 of Garrels & Christ, 1965), I is the ionic strength of the solution and A and B are constants characteristic of the solvent (considered here to be water) at the specified temperatures. Values for A and B , for temperatures up to and including 325°C , were taken from Table 1 of Helgeson (1967), however values for 400°C and 425°C were extrapolated graphically from Helgeson's data because the highest temperature listed for these constants is 350°C .

Extrapolated values for A and B used here are as follows:

A ; $400^\circ\text{C} = 3.0$, $425^\circ\text{C} = 4.0$ and B ; $400^\circ\text{C} = 0.475$ and $425^\circ\text{C} = 0.510$.

pH

pH is defined as the negative of the logarithm of the hydrogen ion activity;

$$\text{pH} = -\log a_{\text{H}^+} \quad (V-9)$$

Neutral pH is 7 at 25°C but changes with increasing temperature. Fisher & Barnes (1972) investigated the ion product of water, and hence neutral pH, at elevated temperatures (100 to 350°C). Their results are shown in Fig. V-3. Between 200°C and 350°C , a range bracketing most of the mineralisation temperatures of the deposits studied here, neutral pH is between 5.5 and 5.7.

The pH of the hydrothermal fluid can be estimated using the activity of potassium in solution and the wall rock alteration mineral assemblage. The stability relations between the diagnostic alteration minerals are illustrated in Fig. V-4 and defined by the following hydrolysis reactions:

Figure V-4: Mineral stability relations in the system $K_2O-Al_2O_3-SiO_2-H_2O-HCl$.
(From Fig.1 of Montoya & Hemley, 1975.)

The pH of the reactions can be expressed as follows:

$$\text{pH} = \log K - \log aK^+ \quad (\text{V-14})$$

Where $\log K$ is the equilibrium ratio aK^+/aH^+ read off Fig. V-4, for specific temperatures, and $\log aK^+$ is the activity of potassium in solution without correction for complexing and ion pairing effects at the elevated temperature because these are accounted for in the stability diagram (Montoya & Hemley, 1975).

pH values of the relevant hydrolysis reactions for the various deposits studied are presented in Table V-1.

CALCITE STABILITY AND pH

The pH above which calcite is stable can be calculated from the CO_2 content of the fluid using the following relationship:

$$(aH^+)^3 = \frac{(K_1)^2 (K_2) \gamma_{Ca^{2+}} \cdot mH_2CO_3 \text{ (ap.)}}{2 K_{cc} \cdot \gamma_{HCO_3^-}} \quad (\text{V-15})$$

Where K_1 , K_2 and K_{cc} are the equilibrium constants for the following reactions respectively:

$\gamma_{Ca^{2+}}$ is the activity coefficient for Ca^{2+} , $\gamma_{HCO_3^-}$ is the activity coefficient for HCO_3^- , and $mH_2CO_3 \text{ (ap.)}$ is equated to mCO_2 , analysed from the fluid inclusions.

The minimum pH values for calcite stability calculated from measured concentrations of CO_2 are presented in Table V-1. A value for high temperature mineralisation at Waihi ("Waihi

TABLE V-2: Values of fCO_2 calculated from the concentration of CO_2 in fluid inclusions (Table 7-9).

Sample number		Location	X_{CO_2}	t °C	K_g (m_{NaCl} =0.2)	fCO_2 bars	log fCO_2
V.U.W. NO:	Field No:						
13957	TK2 (2)	Tokatea, Tokatea Big Reef	0.004	240	5700	23	1.4
13958	B02	Tokatea, Buffalo Mine	0.008 *	250	5500	44	1.6
13962	R03	Tokatea, Royal Oak 7L	0.015	230	6000	90	2.0
13907	Hutt 2	Petote Stm.Area, Hutt Creek	0.014	280	4800	67	1.8
13980	AS 1	Petote Stm.Area, Aitken Stream	0.009 *	280	4800	43	1.6
13998	PS15	Petote Stm.Area, Chalcopyrite Lode	0.007	280	4800	34	1.5
13910	Wg 9	Whangapoua, Waingaro Stream	0.015	200	6600	99	2.0
13939+13941	N16 + N14	Neavesville, Ajax 2L	0.003 *	250	5500	17	1.2
13919	M2q	Maratoto, Camoola 3L	0.002	230	6000	12	1.1
13926	M10	Maratoto, Silver Queen 3L	0.008	280	4800	38	1.6
13928	M19	Maratoto, Camoola 3L	0.003 *	280	4800	14	1.2
14034	Wh4	Waihi, No.5 shaft mullock heap	0.015	230	6000	90	2.0
14037	Wh10	Waihi, Martha Vein upper levels	0.015 *	200	6600	99	2.0
14057	Tui13	Tui Mine, Champion 5L	0.008	290	4400	35	1.5
14061	Tui19	Tui Mine, Champion 5L	0.010 *	260	5200	52	1.7
14094	Wi89	Waiorongomai, Welcome Vein	0.010	260	5200	52	1.7

*¹ average of 2 values
*² average of 3 values

low levels") is also listed and was calculated for 325°C using the measured CO₂ concentration from the low temperature fluids.

FUGACITY

Introduction

The fugacity (f), of a gas is the 'effective' partial pressure of the gas and may be regarded as being the measured partial pressure corrected for deviation from perfect - gas behaviour. At small pressures ($\leq$ 1 bar) fugacity approximates partial pressure.

Fugacity is related to activity by the following expression:

$$a = \frac{f}{f^0} \quad \text{where } f^0 \text{ is the fugacity of the gas in its standard state.} \quad (\text{V-19})$$

Krauskopf (1972) pointed out that in most geological applications $a = f$ for gases.

Fugacity of CO₂

Fugacity of CO₂ from Fluid Inclusion Data

The fugacity of CO₂ can be calculated from the measured fluid inclusion concentration of CO₂ using Henry's Law, expressed as follows:

$$K_g = \frac{f_{\text{CO}_2}}{X_{\text{CO}_2}} \quad (\text{V-20})$$

Where K_g is the Henry's Law coefficient, f_{CO_2} the fugacity of CO₂ and X_{CO_2} the mole fraction of CO₂ in the fluid. Values of K_g for specific temperatures were read off Fig. 2 of Ellis & Goldring (1963).

f_{CO_2} values calculated from selected fluid inclusion analyses (c.f. Chapter 7) are listed in Table V-2. The fluids that these represent were generally later in the vein paragenesis than those responsible for the main mineralising events.

TABLE V-3: fCO_2 during deposition of epithermal deposits at Sunnyside, Colorado (Table V-3A) and Baguio District, Philippines (Table V-3B), based on fluid inclusion analyses by Casadevall & Ohmoto (1977) and Sawkins et al (1979) respectively.

Although Casadevall & Ohmoto (1977) calculated values of $\log fCO_2$ between -0.3 and +0.6, their data are recalculated here because of several mistakes in their paper which appear to have been incorporated into their calculations. For example they incorrectly stated (on p1302) that Ellis & Goldring's (1963) data indicate that K_g at 200°C is 4,700 whereas this value should be 6,700. Also the range of X_{CO_2} given in their text, 0.001 to 0.0001, does not agree with the values listed in their tables (approximately 0.01 to 0.0002).

TABLE V-3A: Sunnyside (Sample numbers, CO_2 analyses and temperatures from Casadevall and Ohmoto, 1977)

Sample No:	Stage	X_{CO_2} *1	t °c	K_g	fCO_2	$\log fCO_2$
9-20-9	2	0.00291	300	4300	13	+1.1
TC-15-73	3	0.0036 *2	290	4400	16	+1.2
2040	4	0.00025	300	4300	1.1	+0.0
9-18-5	5	0.00360	300	4300	15	+1.2
2090-1	5	0.00350	300	4300	15	+1.2
9-11-1	6	0.00071	230	6000	4.3	+0.6
2150	6	0.00017	230	6000	1.0	0.0

*1 Values from X condensables column in Table 6 of Casadevall & Ohmoto (1977) used to approximate X_{CO_2} (CO_2 makes up > 95% of the condensable gas fraction).

*2 listed as 0.00036 by Casadevall & Ohmoto but must be 0.0036 to agree with their stated mCO_2 value of 0.20 (also their Table 6)

TABLE V-3B: Baguio District (sample numbers, CO_2 analyses and temperatures from Sawkins et al, 1979)

Sample No:	X_{CO_2}	t*1 °c	t*2	K_g	fCO_2	$\log fCO_2$
76-B-21	0.0013		280	4700	6.2	+0.8
75-B-1	0.0023	280		4700	11	+1.0
75-B-22	0.0030	260		5300	16	+1.2
76-B-16	0.0022		280	4700	11	+1.0
76-B-22	0.0006	310		4000	2.5	+0.4
76-B-2	0.0074	280		4700	35	+1.5
76-B-20	0.0052		280	4700	24	+1.4

t*1 approximate temperature indicated by fluid inclusion filling temperatures for the specific sample.

t*2 temperature assigned to sample here (no temperatures listed by Sawkins et al)

$f\text{CO}_2$ values for main stage fluids, presented underlined in Table V-1 were extrapolated by averaging the CO_2 concentrations of individual analyses for each deposit and using values of Henry's Law coefficient for the higher temperatures.

The "main stage" $f\text{CO}_2$ values together with $f\text{CO}_2$ values for similar deposits, reported in the literature (listed in Table V-3), are plotted on a log $f\text{CO}_2$ versus temperature graph (Fig. V-5) in an attempt to define some relationship that may be used to predict $f\text{CO}_2$ values for mineralisations where no analyses are available.

A maximum value of $f\text{CO}_2$ can be predicted for most deposits because liquid CO_2 is not found in the fluid inclusions and CO_2 clathration was not observed during fluid inclusion freezing temperature experiments. These factors are discussed in Chapter 7 where it was concluded that they represent maximum CO_2 concentrations of 3 and 1.5 mole % respectively. The value of 3 mole % CO_2 , defined by the absence of liquid CO_2 is used here because freezing temperature experiments were not performed on all inclusions studied and therefore the absence of clathration may not be a universally applicable criteria.

Using a value of 3 mole % for the CO_2 concentration and the Henry's Law equation, values of maximum $f\text{CO}_2$ for fluid inclusions free of liquid CO_2 were determined for different temperatures and plotted as a line in Fig. V-5.

Giggenbach (1981) considered that in New Zealand geothermal systems (e.g. Wairakei, Kawerau and Broadlands) CO_2 pressure is related to temperature by the following semi - empirical formula:

$$\log P_{\text{CO}_2} = 15.26 - \frac{7850}{T} \quad (\text{where } T = ^\circ\text{K}) \quad (\text{V-21})$$

This relationship is illustrated in Fig. V-5.

Although the measured $f\text{CO}_2$ values from fluid inclusions plot in a random pattern there is some agreement with

Figure V-5: Plot of f_{CO_2} versus temperature. The f_{CO_2} values were calculated using equation (V-20) from CO₂ concentrations measured in fluid inclusions (Tables V-2 and V-3). Also plotted are a graphical form of Giggenbach's (1981) expression $PCO_2 = 15.26 - \frac{7850}{T}$, corrected to fugacity, and a line below which fluid inclusions would be expected to contain liquid CO₂ (observed in only one sample from the Hauraki Province, by Merchant 1978). A log f_{CO_2} value of +1.5 is selected for all deposits (at all temperatures considered) in which no measurements were made.

Giggenbach's curve between 280°C and 300°C, approximately the upper temperature range of most New Zealand geothermal systems. Below 280°C Giggenbach's equation underestimates the $f\text{CO}_2$ in the fossil hydrothermal fluids. Conversely above 320°C his curve crosses the line delineating the maximum $f\text{CO}_2$ limit for fluid inclusions free of liquid CO_2 (Fig. V-5) and therefore, with the exception of the single sample from the Garbo Mine reported by Merchant, overestimates $f\text{CO}_2$ for the high temperature fluid inclusions studied here and by Merchant.

Fluid inclusions from at least two high temperature mineralisations (Stage 1 mineralisation of Tui Mine and porphyry copper mineralisation at Paritu) have not been studied because of the absence of suitable material and therefore the hydrothermal fluids responsible for these deposits may have contained high concentrations of CO_2 . Giggenbach's formula predicts CO_2 partial pressures of approximately 3,000 and 10,000 bars respectively for these deposits, however considering that their maximum confining pressures are thought to be in the order of 400 (Tui Mine) and 700 bars (Miners Head) the values of $f\text{CO}_2$ will be of a similar magnitude or less.

Based on the available data presented in Fig. V-5 a value of +1.5 for $\log f\text{CO}_2$ would appear to be a reasonable approximation for the deposits where measured CO_2 concentrations are unavailable, with the provision that higher concentrations may have been present during early mineralisation at Tui Mine and in the porphyry copper mineralisation at Paritu.

Fugacity of CO_2 From Hydrothermal Alteration Mineral Assemblages

Browne & Ellis (1970) demonstrated that the stability of calcium minerals such as wairakite and epidote are related to the fugacity of CO_2 in solution. At high concentrations of CO_2 , calcite tends to be deposited at the expense of epidote or wairakite. Therefore the sequence of mineral assemblages: epidote + wairakite + calcite, wairakite + calcite and calcite represent increasing $f\text{CO}_2$ (c.f. Figs 3.8 and 3.9 of Ellis & Mahon, 1977). The presence of wairakite and epidote in an alteration assemblage may therefore be used to give a general indication of the CO_2 concentration in the hydrothermal fluid.

In the case of epidote this may be further refined to give a value of $f\text{CO}_2$, if the epidote composition (in terms of mole fraction pistacite) and temperature are known, by using the data of Bird & Helgeson (1981). Robson (1979) calculated CO_2 fugacities between 5.6 and 25 atmospheres ($\log f\text{CO}_2 = 0.7$ to 1.4 bars) in the temperature range of 250 to 320°C from his analyses of epidote in propylitic alteration of the Whangapoua area. Propylitic assemblages, formed between 250 and 320°C, in which epidote is absent were probably in equilibrium with a fluid containing higher fugacities of CO_2 .

Fugacity of S_2

Introduction

The fugacity of S_2 can be estimated from the iron (FeS) content of sphalerites in equilibrium with pyrite or pyrrhotite, from the iron (FeS) content of pyrrhotite, from the mole fraction of silver in electrum or by considering the mineral stability relations on $f\text{S}_2$ versus temperature diagrams. These different methods are discussed separately below.

$f\text{S}_2$ From Sphalerite Composition

For the estimation of $f\text{S}_2$ in the hydrothermal fluids, the iron content of sphalerite is conventionally expressed in mole % FeS;

$$\text{Mole \% FeS}^{\text{sp}} = \frac{\text{moles FeS}^{\text{sp}}}{\text{moles FeS}^{\text{sp}} + \text{moles ZnS}^{\text{sp}}} \times 100 \quad (\text{V-22})$$

Values of this parameter for the sphalerites analysed in this study are presented in Table V-4.

Fig. V-6 illustrates the effect of $f\text{S}_2$ and temperature on sphalerite compositions. Scott & Barnes (1971) noted that at any specific pressure sphalerite in equilibrium with pyrite and pyrrhotite (on the pyrite + pyrrhotite boundary of Fig. V-6) has a consistent composition at temperatures below 550°C (i.e. 20.7 ± 0.6 mole % FeS^{sp} at 1 bar pressure). The effect of pressure on sphalerite composition in the assemblage sphalerite + pyrite + pyrrhotite is shown in Fig. V-7.

TABLE V-4A

Sample Number		Location		Vein Stage	Wt % Fe	mole % FeS	sp °C	logfS ₂
V.U.W. No.	Field No.							
13965	MH 1	Miners Head	Mine		9.00	15.46	425	- 6.2
13908	GB 5	Te Ahumata	Barrier Reefs		1.16	2.02	240	-12.4
13971	DC12	Northern Colville Pen.	Doctors Creek		3.15	5.47	325	- 9.0
13974	SH11	"	Sorry Mary Stream		0.87	1.52	325	- 7.9
13959	TK 1	Tokatea	Tokatea Mine		2.39	4.15	280	-10.9
13982	AS 5	Petote Strm.area	Aitken Stream	1	1.72	2.99	300	- 9.6
13985	HC 3	"	Hutt Creek	1	0.84	1.46	"	- 9.0
13989	HC 4a	"	Hutt Creek	1	0.80	1.39	"	- 9.0
13991	PS 4	"	Chalcopyrite Lode	1	1.11	1.94	"	- 9.2
14000	PS21c	"	Galena Lode	1	1.29	2.25	"	- 9.4
14002	PS21h	"	Galena Lode	1	0.89	1.55	"	- 9.0
13937	M33	Maratoto	Camoola Vein	2b	0.31	0.55	280	- 9.1
285/37/6	M13	"	Silver Queen Vein	2c	0.58	1.01	"	- 9.7
285/37/7	M14	"	Silver Queen Vein	2c	0.31	0.54	"	- 9.1
285/37/8	M32	"	Silver Queen Vein	2c	0.33	0.57	"	- 9.2
(A.U. M18185)*		"	Camoola Vein	2b	0.28	0.49	"	- 9.0
(A.U. M18186)*		"	Camoola Vein	2b	0.22	0.38	"	- 8.8
14015	Wk6	Waitekauri	Jubilee Low level	2a	0.59	1.03	"	- 9.7
14020	Wk13	"	Jubilee Low level	2a	1.30	2.26	"	-10.4
14040	Wh29	Waihi	Martha Mine		11.47	19.63	325	-10.1
14046	Wh43	"	Martha Mine		6.33	10.92	"	- 9.6
14047	Wh44	"	Martha 7L		1.75	3.04	"	- 8.5
14048	Wh45	"	Martha Mine		1.03	1.79	"	- 8.0
14052	Wh50	"	Martha 10L		5.98	10.33	"	- 9.6
14023	TL17	Karanahake	Talisman Mine		2.39	4.15	300	- 9.9
14025	TL22(2)	"	Talisman Mine 14L		1.34	2.33	"	- 9.4
14025	TL22(6)	"	Talisman Mine 14L		1.54	2.68	"	- 9.5
14025	TL22(9)	"	Talisman Mine 14L		1.42	2.47	"	- 9.5
14057	Tui 14	Tui Mine	Champion 5L	2	1.23	2.14	300	- 9.3
14058	Tui 15	"	Ruakaka 3L	2	1.58	2.75	"	- 9.5
14059	Tui 17	"	Champion 5L	2	1.67	2.90	"	- 9.6
14060	Tui 18	"	Ruakaka 3L	2	1.21	2.11	"	- 9.3
14061	Tui 19	"	Champion 5L	2	1.43	2.49	"	- 9.5
13979	Wi 110	Waiorongomai	May Queen 3L	1	0.62	1.08	325	- 7.6
14072	Wi 21	"	No.1 Reef "Tramway"	1	0.76	1.32	"	- 7.8
14075	Wi 27	"	No.1 Reef "Waterfall"	1	1.23	2.14	"	- 8.2
14082	Wi 53	"	Bonanza	1	0.85	1.48	"	- 7.9
14086	Wi 58	"	Welcome Vein	1	1.43	2.49	"	- 8.3
14092	Wi 83	"	Colonist, Smithy level	1	0.44	0.77	"	- 7.3
14100	Wi 98	"	Colonist-Hero 1100' level	1	0.67	1.17	"	- 7.7

* Auckland University sample numbers

TABLE V-4: Log fS_2 values, for the assigned temperatures, calculated from the iron content in sphalerites. Log fS_2 values derived from sphalerite analyses made during this study are listed in Table V-4A, whereas Table V-4B lists log fS_2 values derived from sphalerite analyses reported in previous works.

TABLE V-4B

Location	Sample Number	Reference	Wt % Fe	Mole % FeS	t °C	log fS_2
Thames Cu-Bi Stage						
Monowai Reef	AU28956	Merchant	0.43	0.75	400	-4.40
Kaiser Reef	AU25302	(1978 p91)	0.53	0.92	400	-4.58
Thames Pb-Zn Stage		Merchant				
Monowai	AU28956	(1978 p115)	0.35	0.61	280	-9.2
Sylvia	AU25308	"	0.16	0.28	"	-8.5
Garbo Mine	AU28940	"	0.17	0.29	"	-8.6
Moanataiari	AU28955	"	0.60	1.04	"	-9.7
Australasian	AU28963	"	0.14	0.24	"	-8.4
Watchman	AU28933	"	0.04	0.07	"	-7.3
Monowai (3L)		"	0.22	0.38	"	-8.8
"		"	0.34	0.59	"	-9.2
Zeehan		"	0.35	0.61	"	-9.2
Sylvia		"	0.72	1.26	"	-9.8
Watchman		Couper (1975)	0.46	0.80	"	-9.5
Whangapoua Stage 2	PS31427	Robson (1979 p121)	0.64	1.12	"	-9.7
	PS31428?		0.78	1.29	"	-9.9

Figure V-6: Composition of sphalerite (mole % FeS^{sp}) in equilibrium with pyrite and pyrrhotite as a function of temperature and f_{S_2} . (From Czamanske, 1974.)

Figure V-7: Effect of pressure (bars) on sphalerite composition in the assemblage sphalerite + pyrrhotite. (From Scott & Barnes, 1971.)

Samples containing an assemblage of sphalerite + pyrite + pyrrhotite were encountered from only two areas during this study and they are represented by sample 13965 (15.5 mole % FeS^{sp}) from Miners Head and sample 14040 (19.6 mole % FeS^{sp}) from Waihi. The sphalerite of sample 14040 (Wh29) is in reasonable agreement with Scott & Barnes (1971) experimentally determined value of 20.7 ± 0.6 mole % FeS^{sp} for the sphalerite + pyrite + pyrrhotite assemblage, however even with a correction for a maximum pressure regime (2.5km cover and lithostatic pressure, equivalent to approximately 700 bars) sphalerite of sample 13965 (MH1) should contain 19 mole % FeS (Fig. V-7) considerably higher than the observed 15.5 mole % FeS . This discrepancy may reflect disequilibrium between the sphalerite + pyrite + pyrrhotite assemblage.

The compositions of sphalerites coexisting with pyrite but not pyrrhotite or bornite (i.e. plotting in the pyrite field of Fig. V-6) are related to the activity of S_2 by the following relationship from Barton & Skinner (1979):

$$\log X_{\text{FeS}^{\text{sp}}} = 7.16 - \frac{7730}{T} - \frac{\log a\text{S}_2}{2} \quad (\text{V-23})$$

$$\text{Because } X_{\text{FeS}^{\text{sp}}} = \frac{\text{mole } \%}{100} \quad (\text{V-24})$$

$$\begin{aligned} \text{Then } \log X_{\text{FeS}^{\text{sp}}} &= \log \text{mole } \% \text{FeS}^{\text{sp}} - \log 100 \\ &= \log \text{mole } \% \text{FeS}^{\text{sp}} - 2 \end{aligned} \quad (\text{V-25})$$

$$\begin{aligned} \text{Therefore } \log \text{mole } \% \text{FeS}^{\text{sp}} - 2 &= 7.16 - \frac{7730}{T} \\ &\quad - \frac{\log a\text{S}_2}{2} \end{aligned} \quad (\text{V-26})$$

$$\text{or } \frac{\log a\text{S}_2}{2} = 9.16 - \frac{7730}{T} - \log \text{mole } \% \text{FeS}^{\text{sp}} \quad (\text{V-27})$$

Finally, because $a\text{S}_2 = f\text{S}_2$ at low pressures:

$$\log f\text{S}_2 = 18.32 - \frac{15460}{T} - 2 \log \text{mole } \% \text{FeS}^{\text{sp}} \quad (\text{V-28})$$

Values of $\log f\text{S}_2$, calculated from the sphalerite compositions using equation (V-28), are presented in Table V-4.

Figure V-8: Composition of pyrrhotite (mole fraction FeS^{P0}) in the Fe-S system as a function of temperature and f_{S_2} . (From Toulmin & Barton, 1964.)

fS_2 From Pyrrhotite Composition

Toulmin & Barton (1964) experimentally determined the relationship between fS_2 and pyrrhotite composition as shown in Fig. V-8, derived from the following equation:

$$\log fS_2 = (70.03 - 85.83 X_{FeS_{po}}) \left(\frac{1000}{T} - 1 \right) + 39.30 \sqrt{1 - 0.9981 X_{FeS_{po}}} - 11.91 \quad (V-29)$$

where $X_{FeS_{po}}$ is the mole fraction of FeS (in this case mole fraction = twice the atom fraction of FeS) in pyrrhotite.

Pyrrhotites from two locations were analysed here, the results and calculated $\log fS_2$ values for the assigned depositional temperatures are presented in Table V-5.

The $\log fS_2$ value of -6.6 calculated from pyrrhotite in sample NH1 is in reasonable agreement with other data, however, the value of -7.9 derived from pyrrhotite of sample Wh29 is much too high and indicates that the pyrrhotite is iron deficient. At the assigned depositional temperature (325°C) the pyrite - pyrrhotite boundary occurs at $\log fS_2 = -10.0$. Under these conditions the mole fraction of FeS in pyrrhotite should be approximately 0.95 (c.f. Fig. V-8).

fS_2 From Electrum Composition

Barton & Toulmin (1964) experimentally determined the relations between temperature, fS_2 and electrum composition with the intention of providing an fS_2 indicator for laboratory experiments on sulphur systems. They found that above a certain fS_2 electrum tarnishes, due to the formation of argentite (acanthite) from the alloyed silver, via the reaction;

For a specific temperature, lower fugacities of S_2 are required to form a tarnish with increasing mole fractions of silver (Fig. V-9).

Their data have subsequently been used by a number of authors (particularly Japanese e.g. Hattori 1975 and Shikazono

TABLE V-5: Log fS_2 values, for the assigned temperatures, calculated from the compositions of pyrrhotites.

V.U.W. No.	13965	14040
Field No.	(MH1)	(Wh29)
Location	Miners Head	Martha Mine, Waihi
Wt. % Fe	59.70	58.79
Wt. % S	39.35	39.72
Atom fraction Fe	0.47	0.46
mole fraction FeS ($X_{FeS^{sp}}$)	0.94	0.92
Temperature of Deposition	425°C	325°C
log fS_2	-6.6	-7.9

Figure V-9: Smoothed tarnish curves for electrum compositions (mole fraction Ag^{el}). (From Barton & Toulmin, 1964.)

Figure V-10: Correction factors ($\Delta \log fS_2$) that equate Barton & Toulmin's (1964) equation [see equation (V-31)], relating electrum composition to fS_2 and temperature, to experimental data. The dashed lines are after Barton & Toulmin (1964), whereas the solid lines (used in this study) are after Barton (1980).

1978) to determine fS_2 in ore deposits from the composition of electrum. The assumption made is that the electrum is deposited in equilibrium with the hydrothermal solution $\pm$ argentite, as described by the equation above.

Barton & Toulmin's theoretical equation relating fS_2 to X_{Ag}^{el} and temperature is as follows:

$$\log fS_2 = \frac{1}{4.576 T} \left\{ -41980 + 16.52 T - 18.296 T \log X_{Ag}^{el} + 4 (1 - X_{Ag}^{el})^2 [5650 - 1600 (1 - X_{Ag}^{el}) - 1.375 T] \right\} \quad (V-31)$$

Corrections required to equate solutions of the above equation to Barton & Toulmin's (1964) experimental results are shown graphically in Fig. V-10.

Values of fS_2 calculated from gold and electrum analyses determined during this study are presented in Table V-6A.

Ramsay (1971), Moore (1976), Merchant (1978), Torckler (1978) and Erceg (1981) also reported electrum analyses from the province but did not use them to calculate sulphur fugacities. Therefore their analyses are listed in Table V-6B together with fS_2 values calculated here.

All of the electrum analyses referred to above were determined by the electron probe micro-analyser, however Fraser & Adams (1907) reported average electrum analyses and gold: silver ratios from several mines, determined by fire assay methods. These are listed in Table V-6C together with calculated values of fS_2 .

Log fS_2 corrections indicated from Fig. V-10 are significant for the gold analyses (Table V-6A) and have been applied, however corrections indicated for the electrum analyses are less than -0.1 and, considering the possible errors in the data are probably not significant and were not applied.

TABLE V-6: Log fS_2 values, for the assigned temperatures, calculated from the mole fraction of silver in electrum and gold.

Table V-6A, EPMA analyses made during this study.

Table V-6B, EPMA analyses reported in previous studies.

Table V-6C, fire assay and gold - silver ratios reported by Fraser & Adams (1907).

TABLE V-6A: (i) Electrum

Sample Number			Wt %		X _{el}	t	
V.U.W. No.	Field No.	Location	Au	Ag	Ag	°C	log fS_2
13961	TK 7	Tokatea, Tokatea Mine	60.4	38.6	0.54	220	-12.3
285/37/8	M 32	Maratoto Silver Queen	58.7	40.7	0.56	280	-10.7
13937	M 33	Maratoto Camoola	54.8	44.1	0.60	280	-11.0
14025(a)	TL22(2)	Karangahake Talisman 14L	74.2	26.3	0.39	300	- 8.6
" (b)	TL22(6)	" " "	70.5	25.6	0.40	300	- 8.7
" (c)	TL22(9)	" " "	71.2	25.1	0.39	300	- 8.6
14032	GJ 3	Waihi, Grand Junction	52.3	46.7	0.62	230	-11.1
14043	Wh35	Waihi, Martha Mine	65.8	33.9	0.48	280	-10.0
14046	Wh43	" "	68.2	31.4	0.46	280	- 9.7
14048	Wh45	" "	62.9	36.6	0.52	280	-10.3

(ii) Gold

V.U.W. No.	Field No.	Location	Wt %		X _{el}	t	log	Cor-	Correc-
			Au	Ag	Ag	°C	fS_2	rec-	ted
								(Fig	log fS_2
								V-10)	
13915	Tui 27(a)	Tui Mine Champion 5L Stage 1	87.8	11.8	0.20	400	-4.32	-0.34	-4.7
"	Tui 27(b)	"	88.8	8.6	0.15	400	-3.57	-0.50	-4.1
13909	Tui 30b	"	90.2	8.0	0.14	400	-3.38	-0.54	-3.9
14092	Wi 83	Waiorongomai	80.27	19.64	0.31	325	-7.09	-0.1	-7.2

	Reference	Au	Wt % Ag	X _{el} Ag	t °C	log fS ₂
TE AHUMATA	Ramsay &	55	45	0.60	220	-12.9
Sunbeam	Kobe (1974)					
Iona Quarry						
zoned core	"	47	53	0.67	220	-13.5
rim	"	84	16	0.26	220	-9.0
Iona	Erceg (1981)	51	49	0.63	220	-13.1
BROKEN HILLS	Moore (1976)	67	33	0.47	220	-11.7
Sievers Leader	"	"	"	"	240	-11.0
Breccia Pipe 2 level	"	64	36	0.51	220	-12.0
	"	"	"	"	240	-11.4
THAMES	Merchant					
Gold-pyrargyrite	(1978)	70	30	0.44	230	-11.0
NEAVESVILLE	Torckler					
Graces Open Cut	(1978)	70	30	0.44	220	-11.3

(ii) Gold

	Wt % Au	Wt % Ag	X _{el} Ag	t °C	log fS ₂	Correction (Fig V-10)	Corrected log fS ₂	
TAPU-THAMES								
Pb-Au stage of								
Sylvia-Watchman								
area (Merchant,	range	82	18	0.28	280	-7.7	< -0.1	-7.8
1973)		94	6	0.11	280	-4.7	-0.4	-5.1

TABLE V-6C:

Location	*1	*2	Au	Wt % Ag	X _{el} Ag	t °C	log fS ₂
Kauri Block Mines	113	A	74	26	0.39	220	-10.7
Coromandel							
Kapanga Mine	117	A	70	30	0.44	220	-11.3
Coromandel							
Royal Oak Mine	122	B	67	33	0.47	220	-11.7
Tokatea, Coromandel							
Opitonui Mine	130	A	50	50	0.65	220	-13.3
Whangapoua							
Waitaia Mine	135	B	72	28	0.42	250	-10.1
Kuaotunu	"	"	"	"	"	220	-11.0

*1 Page number in Fraser & Adams (1907)

*2 A, stated as electrum composition

B, ratio of gold to silver in ore, but no silver mineral noted.

fS_2 From Mineral Stability Relations on fS_2 Versus Temperature Diagrams

If the depositional temperature of a mineral assemblage is known, limits of fS_2 can be determined by comparison of the sulphidation reactions of the various minerals plotted on an fS_2 versus temperature diagram (c.f. Fig I-H-4). Most of the common sulphidation reactions are illustrated in Figs. 7-21, 7-22 and 7-23 of Barton & Skinner (1979). A linear $10^3 \cdot K^{-1}$ temperature scale is used so that the reactions plot as straight lines.

Most of the mineralisations studied here contain pyrite and chalcopyrite and therefore plot between the pyrite/pyrrhotite and chalcopyrite/bornite plus pyrite reactions (c.f. Fig. I-M-4). Other diagnostic reactions used to determine $\log fS_2$ are antimony/stibnite, silver/argentite, arsenopyrite/pyrite plus arsenic, arsenic/realgar and tetrahedrite/famatinite (Fig. I-H-4 and figures cited from Barton & Skinner 1979).

The occurrence of the silver/argentite reaction (c.f. Fig. 7.23 of Barton & Skinner 1979) at very low sulphur fugacities, lower than the pyrrhotite/pyrite reaction, demonstrates that native silver in mineral assemblages containing pyrite, is not primary but was deposited at some later stage, probably during supergene processes. Similarly, native antimony occurring with pyrite and other sulphides at Whangapoua (Fig. I-H-4) is considered to have originated during a later stage of mineralisation than the adjacent minerals.

Fugacity of O_2

Introduction

Oxygen fugacity may be estimated from mineral stability relations on fS_2 versus fO_2 and fO_2 versus pH diagrams. The construction of the latter requires knowledge of the concentration of total sulphur in solution ($m \leq S$) and therefore this parameter will be considered between discussion of the fS_2 versus fO_2 and fO_2 versus pH diagrams.

TABLE V-7: Thermodynamic data used to calculate the fS_2 versus temperature and fS_2 versus fO_2 diagrams. The free energy change is given in the form $G^\circ = \Delta H - T\Delta S^\circ$

Equation Number	Reaction	Free energy change (in joules for T in K)	Source*
(V-32)	$2Fe + S_2 = 2FeS$	$-300,500 + 105.10T$	(1)
(V-33)	$\frac{3}{2}Fe + O_2 = \frac{1}{2}Fe_3O_4$	$-551,030 + 154.52T$	(1)
(V-34)	$4Fe_3O_4 + O_2 = 6Fe_2O_3$	$-488,620 + 278.19T$	(1)
(V-35)	$3FeS + 2O_2 = Fe_3O_4 + \frac{3}{2}S_2$	$-651,315 + 151.38T$	(1)
(V-36)	$2FeS + S_2 = 2FeS_2$	$-280,466 + 279.78T$	(1)
(V-37)	$3FeS_2 + 2O_2 = Fe_3O_4 + 3S_2$	$-207,351 - 281.92T$	(1)
(V-38)	$2FeS_2 + \frac{3}{2}O_2 = Fe_2O_3 + 2S_2$	$-219,668 - 141.59T$	(1)
(V-39)	$5CuFeS_2 + S_2 = Cu_5FeS_4 + 4FeS_2$	$-211,869 + 240.45T$	(1)
(V-40)	$Fe_2O_3 + S_2 + \frac{5}{2}O_2 = 2FeSO_4$	$-1,151,000 + 615.5T$	(2)
(V-41)	$FeS_2 + 2O_2 = FeSO_4 + \frac{1}{2}S_2$	$-680,300 + 241.8T$	(2)
(V-42)	$S_2(v) = S_2(s)$	$-115,483 + 130.29T$	(1)
(V-43)	$Fe + CO_2 + \frac{1}{2}(O_2) = FeCO_3$	$-354,400 + 251.0T$	(2)
(V-44)	$FeS + CO_2 + \frac{1}{2}O_2 = FeCO_3 + \frac{1}{2}S_2$	$-193,930 + 177.0T$	(2)
(V-45)	$FeS_2 + CO_2 + \frac{1}{2}O_2 = FeCO_3 + S_2$	$-47,488 + 49.0T$	(2)
(V-46)	$Fe_3O_4 + 3CO_2 = 3FeCO_3 + \frac{1}{2}O_2$	$-31,380 + 414.0T$	(3)
(V-47)	$FeCO_3 + 3O_2 = 6Fe_2O_3 + 15CO_2$	$-363,100 - 1379 T$	(1+3)
(V-48)	$C + O_2 = CO_2$	$-394,133 - 0.84T$	(4)
(V-49)	$CaCO_3 + \frac{1}{2}S_2 + \frac{3}{2}O_2 = CaSO_4 + CO_2$	$-684,837 + 189.87T$	(4)
(V-50)	$MnS + CO_2 + \frac{1}{2}O_2 = MnCO_3 + \frac{1}{2}S_2$	$-222,798 + 195.98T$	(4)
(V-51)	$MnS + 2O_2 = MnSO_4$	$-851,860 + 172.4T$	(4)
(V-52)	$MnCO_3 + \frac{1}{2}S_2 + \frac{3}{2}O_2 = MnSO_4 + CO_2$	$-628,981 + 181.59T$	(4)
(V-53)	$2As + S_2 = 2AsS$	$-203,828 + 177.44T$	(1)
(V-54)	$\frac{4}{3}Sb + S_2 = \frac{2}{3}Sb_2S_3$	$-231,919 + 167.78T$	(1)
(V-55)	$4Ag + S_2 = 2Ag_2S$	$-175,644 + 69.12T$	(1)
(V-56)	$2FeAsS + S_2 = 2FeS_2 + 2As$	$-257,734 + 258.15T$	(1)
(V-57)	$\frac{2}{3}Cu_{12}Sb_4S_{13} + S_2 = \frac{8}{3}Cu_3SbS_4$	$-173,958 + 166.73T$	(1)

- * (1) Barton & Skinner (1979)
 (2) Holland (1959)
 (3) Holland (1965)
 (4) Kubaschewski & Alcock (1979)

fS_2 versus fO_2 Diagrams

The fS_2 versus fO_2 diagrams presented in Appendix I were constructed at various temperatures by the methods outlined in Vaughan & Craig (1978 pp256 and 257) using the data listed in Table V-7. The following explanatory notes detail specific aspects of their construction and discuss aspects of some specific mineral systems.

(i) Consistency of Data on Stability Relations of Iron Minerals

The thermodynamic data used in the construction of the fS_2 versus fO_2 diagrams were found to give generally consistent results with the exceptions of the pyrite - pyrrhotite - magnetite and pyrite - hematite - $FeSO_4$ triple points. In both cases the boundaries which meet to define the triple points did not intersect. The error was small in the former case but relatively large in the latter case.

To form an intersection for the pyrite - pyrrhotite - magnetite triple point the pyrite-pyrrhotite line was plotted as calculated but the pyrrhotite - magnetite and pyrite - magnetite lines were adjusted.

In the case of the pyrite - hematite - $FeSO_4$ triple point the data involving $FeSO_4$ was considered to be the least reliable and therefore only the hematite/ $FeSO_4$ and pyrite/ $FeSO_4$ boundaries were adjusted.

Intersection at the iron - pyrrhotite - magnetite and magnetite - hematite - pyrite triple points were satisfactory and no adjustments were required.

(ii) Chalcopyrite/Bornite Plus Pyrite Boundary

The data used for the construction of the chalcopyrite/bornite plus pyrite boundary (listed in Table 7.2 of Barton & Skinner 1979 but originally from Schneeberg 1973) is applicable only to temperatures of 230 - 532°C. Yund & Kellner (1966) considered that assemblages of bornite and pyrite are unstable

below 228°C (Barton & Skinner 1979 suggested that this lower limit should be 270°C).

Therefore the chalcopyrite/bornite plus pyrite reaction may not be applicable at temperatures below 270°C. The relevant reaction may instead be chalcopyrite/digenite plus pyrite.

However, assemblages of pyrite plus bornite "are quite common in many ore bodies, including Magma Mine, Arizona, where the elevated rock temperatures (at least as high as 50°C) have provided us with extraordinary long term experiments" (Craig & Scott, 1974 p CS-69).

In view of this conflicting evidence the chalcopyrite/bornite plus pyrite boundary is plotted on all fS_2 versus fO_2 diagrams presented in Appendix I. Because no other relevant data could be found, Schneeberg's 230 - 532°C data was also used for temperatures between 230°C and 200°C (the lowest temperature considered).

(iii) fCO_2

Where the fugacity of CO_2 is known it can be used to calculate the stability field of siderite (equations V-43 to V-47, Table V-7); graphite/ CO_2 (equation V-48, Table V-7) and calcite/anhydrite (equation V-49, Table V-7) boundaries.

Although French (1971) experimentally studied some aspects of siderite stability, his results were not conclusive, and therefore the most recent comprehensive data remains that listed by Holland (1959, 1965). However some authors consider that this data is inaccurate (c.f. Holland, 1965; French, 1971; Einaudi, 1977) and its application here gave inconsistent results: some mineral boundaries required considerable adjustment, from their calculated positions on the fS_2 versus fO_2 diagrams, to form intersections.

The siderite field, although probably only approximate, is shown in Fig. I-0-13 for the Maatoto deposit because of the

Figure V-11: Diagrammatic representation of the stability relations of some phases in the system As-S-O as a function of f_{S_2} and f_{O_2} at constant temperature. Native arsenic and possibly realgar are considered to be the only phases relevant to hypogene mineralisations in the Hauraki Province because of the high values of f_{S_2} and f_{O_2} required for the stability of orpiment and arsenolite respectively (note that both of these phases have been reported from the province as supergene minerals).

occurrence of siderite adjacent to the sulphide mineralisation, however it is not plotted in other diagrams because of the inconsistencies in the thermodynamic data and the apparent absence of siderite from most primary mineralisations. Nevertheless, it should be noted that the siderite field may replace a large part, or all, of the magnetite field in the low to moderate temperature (up to 280°C) systems with values of $f\text{CO}_2$ between 10 and 30 bars ($\log f\text{CO}_2 = 1$ to 1.5).

(iv) Manganese Minerals

Rhodochrosite occurs with sulphide mineralisation at Maratoto and therefore the stability of the various manganese minerals (rhodochrosite MnCO_3 , alabandite MnS , and MnSO_4) are plotted in Fig. I-0-12 using equations V-50, V-51 and V-52 of Table V-7.

(v) Arsenic System

Native arsenic occurs in the mineralisation around Coromandel (Kauri Block and Kapanga Mines) and Whangapoua, and therefore the stability of native arsenic is of interest. The mineral stability relations in the system $\text{As} - \text{S} - \text{O}$ are shown in Fig. V-11. Data for the arsenic/realgar reaction at elevated temperatures are listed in Table V-7, (equation V-53), however compatible data could not be found for the reactions involving arsenolite. The latter are considered to be irrelevant to the mineralisations studied due to their almost certain occurrence within the magnetite and hematite stability fields. Therefore only the arsenic/realgar reaction is considered important here.

Concentration of Total Sulphur in Solution

The concentration of total sulphur in solution ($m \leq \text{S}$) during ore deposition is considered by most workers to be in the range of 0.1 to 0.001 m (Barnes & Czamanske 1967, Ohmoto 1972). Table V-8 lists values of $m \leq \text{S}$ calculated for epithermal ore deposits by previous studies. Based on this work a general scheme of $m \leq \text{S}$ values for the different deposits of Great Barrier Island and the Coromandel Peninsula is presented in Table V-9.

TABLE V-8: Concentrations of total sulphur in solution assigned to some epithermal deposits by other works.

<u>Deposit</u>	<u>$m \leq S$</u>	<u>$\log m \leq S$</u>	<u>Reference</u>
Tui Mine	0.01 - 0.001	-2 to -3	Robinson (1974)
Vatukoula, Fiji	0.001	-3	Ahmad (1979)
Creede, Colorado	0.02	-1.7	Barton <u>et al</u> (1977)
Sunnyside, Colorado	0.05	-1.3	Casadevall & Ohmoto (1977)
Lake City, Colorado	0.01	-2	Slack (1980)
Finlandia, Peru	0.003	-2.5	Kamilli & Ohmoto (1977)
Yatani, Japan	0.01 - 0.001	-2 to -3	Hattori (1975)
Toyoha, Japan	0.01 - 0.001	-2 to -3	Shikazono (1975)

TABLE V-9: Concentration of total sulphur in solution during formation of some deposits in the Mairaki Gold - Silver Province. The estimated values represent a general scheme based on values calculated by other studies for similar deposits (e.g. Table V-8), whereas the calculated values were derived by comparison of mineral stability relations with contours of $\log a_{\text{S}}$ plotted on $f\text{S}_2$ versus $f\text{O}_2$ diagrams.

Location	Stage	t °C	Total sulphur in solution				Reference
			Estimated a_{S}	log a_{S}	Calculated a_{S}	log a_{S}	
Miners Head		425	0.05	-1.3			
Te Ahumata	1 (base metal)	240	0.005	-2.3			
	2a (Ag-Au)	220	0.001	-3.0			
	2b (stibnite)	230	0.001	-3.0			
	Paritu coastal section	425	0.05	-1.3			
Northern Colville Peninsula	Cu-Pb-Zn veins	325	0.01	-2.0	0.01	-2.0	I-C-4
Kuaotunu	3	250	0.005	-2.3	0.005	-2.3	I-D-4
Tokatea	Base metal	280	0.01	-2.0			
	Gold - silver	220	0.001	-3.0			
Kauri-Kapanga		220	0.001	-3.0			
Petote Stream	1	300	0.01	-2.0	0.01	-2.0	I-G-5
Whangapoua	2	280	0.01	-2.0			
	4 (stibnite)	200	0.001	-3.0			
Broken Hills	1 and 2	240	0.005	-2.3	0.001	-3.0	I-K-8
Tapu Thames	Cu - Bi	400	0.05	-1.3			
	Pb - Zn	280	0.01	-2.0			
Thames	Gold - pyrrargyrite	230	0.001	-3.0	0.001 (to 0.01?)	-3.0 (to -2.0?)	I-M-5
Neavesville	Ajax	250	0.005	-2.3	≈0.005	≈-2.3	I-N-6
	Bluffs section	220	0.001	-3.0	0.01	-2.0	I-N-8
Maratoto	2	280	0.01	-2.0			
Waitekauri	2	280	0.01	-2.0			
Waihi	Low levels	325	0.01	-2.0			
	Intermediate levels	280	0.01	-2.0			
	Upper levels	220	0.001	-3.0	≥0.001	≥-3.0	I-S-11
Karangahake	Low levels	300	0.01	-2.0			
Tui Mine	1	400	0.05	-1.3			
	2	300	0.01	-2.0	0.01	-2.0	I-U-12
Waiorongomai	1	325	0.01	-2.0	0.01	-2.0	I-V-4

TABLE V-10: Thermodynamic data used to calculate the f_{O_2} versus pH diagrams. The free energy change is given in the form $\Delta G^\circ = \Delta H - T \cdot \Delta S^\circ$

Equation Number	Reaction	Free energy change (in joules for T in K)	Source*
(V-58)	$2H_2S(aq) + O_2(g) = S_2(g) + 2H_2O(l)$	$-367,730 + 95.8T$	(1)
(V-59)	$\frac{1}{2}S_2(g) + \frac{3}{2}O_2(g) + H_2O(l) = SO_4^{2-}(aq) + 2H^+(aq)$	$-687,640 + 472.4T$	(1)
(V-60)	$HS^-(aq) + H^+(aq) = H_2S(aq)$	$-20,083 - 66.5T$	(1)
(V-61)	$H_2S(aq) + 2O_2(g) = HSO_4^-(aq) + H^+(aq)$	$-855,377 + 427.6T$	(1)
(V-62)	$HSO_4^-(aq) = SO_4^{2-}(aq) + H^+(aq)$	$-16,108 + 92.0T$	(1)
(V-63)	$HS^-(aq) + 2O_2(g) = SO_4^{2-}(aq) + H^+(aq)$	$-891,569 + 453.5T$	(1)
(V-64)	$H_2S(aq) + 2O_2(g) = 2H^+(aq) + SO_4^{2-}(aq)$	$-871,485 + 519.7T$	(1)
(V-65)	$2FeS(s) + 2HS^-(aq) + O_2(g) + 2H^+(aq) = 2FeS_2(s) + 2H_2O(l)$	$-688,364 + 242.7T$	(1+2)
(V-66)	$2FeS(s) + H_2S(aq) + O_2(g) = 2FeS_2(s) + H_2O(l)$	$-648,198 + 375.7T$	(1+2)
(V-67)	$6FeS(s) + O_2(g) + 6H_2O(l) = 2Fe_3O_4(s) + 6HS^-(aq) + 6H^+(aq)$	$-78,935 + 414.6T$	(1+2)
(V-68)	$Fe_3O_4(s) + 6HS^-(aq) + 6H^+(aq) + O_2(g) = 3FeS_2(s) + 6H_2O(l)$	$-1,016,344 + 170.3T$	(1+2)
(V-69)	$3FeS_2(s) + 6H_2O(l) + 11O_2(g) = Fe_3O_4(s) + 6SO_4^{2-}(aq) + 12H^+(aq)$	$-4,333,068 + 2,548T$	(1+2)
(V-70)	$2FeS_2(s) + 4H_2O(l) + 15/2 O_2(g) = Fe_2O_3(s) + 4SO_4^{2-}(aq) + 8H^+(aq)$	$-2,970,146 + 1,745.6T$	(1+2)
(V-71)	$2FeS_2(s) + 4H_2O(l) + 15/2 O_2(g) = Fe_2O_3(s) + 4H^+(aq) + 4HSO_4^-(aq)$	$-2,905,717 + 1,377.4T$	(1+2)
(V-72)	$5CuFeS_2(s) + 2H_2S(aq) + O_2(g) = Cu_5FeS_4(s) + 4FeS_2(s) + 2H_2O(l)$	$-579,601 + 336.4T$	(1+2)
(V-73)	$5CuFeS_2(s) + 2HS^-(aq) + O_2(g) + 2H^+(aq) = Cu_5FeS_4(s) + 4FeS_2(s) + 2H_2O(l)$	$-619,768 + 203.3T$	(1+2)
(V-74)	$Cu_5FeS_4(s) + 4FeS_2(s) + 2H_2O(l) + 3O_2(g) = 5CuFeS_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq)$	$-1,163,370 + 702.9T$	(1+2)
(V-75)	$3/2 O_2(g) + H_2O(l) + \frac{1}{2}S_2(g) = H^+(aq) + HSO_4^-(aq)$	$-671,532 + 379.9T$	(1)
(V-76)	$2HS^-(aq) + O_2(g) + 2H^+(aq) = S_2(g) + 2H_2O(l)$	$-407,898 - 37.2T$	(1)
(V-77)	$CaCO_3(s) + H_2S(aq) + 2O_2(g) = CaSO_4(s) + CO_2(g) + H_2O(l)$	$-868,703 + 238.1T$	(1+3)
(V-78)	$CaSO_4(s) + CO_2(g) + H_2O(l) = CaCO_3(s) + SO_4^{2-}(aq) + 2H^+(aq)$	$-2,782 + 281.7T$	(1+3)
(V-79)	$MnS(s) + CO_2(g) + H_2O(l) = HS^-(aq) + MnCO_3(s) + H^+(aq)$	$-18,849 + 214.6T$	(1+3)
(V-80)	$MnS(s) + CO_2(g) + 2O_2(g) + H_2O(l) = MnCO_3(s) + SO_4^{2-}(aq) + 2H^+(aq)$	$-910,397 + 667.3T$	(1+3)
(V-81)	$MnS(s) + CO_2(g) + H_2O(l) + 2O_2(g) = MnCO_3(s) + H^+(aq) + HSO_4^-(aq)$	$-894,309 + 575.5T$	(1+3)
(V-82)	$Ba^{2+}(aq) + H_2S(aq) + 2O_2(g) = BaSO_4(s) + 2H^+(aq)$	$-897,175 + 420.1T$	(1)
(V-83)	$Ba^{2+}(aq) + HS^-(aq) + O_2(g) = BaSO_4(s) + H^+(aq)$	$-917,258 + 354.0T$	(1)
(V-84)	$Ba^{2+}(aq) + HSO_4^-(aq) = BaSO_4(s) + H^+(aq)$	$-41,798 - 7.5T$	(1)

- * (1) Helgeson (1969)
 (2) Barton & Skinner (1979)
 (3) Kubaschewski & Alcock (1979)

The estimated values of $m \leq S$ may be checked by comparison of the mineral stability relations with contours of $m \leq S$ plotted on fS_2 versus fO_2 diagrams. Contours of $m \leq S$ were calculated, for specific values of temperature and pH, by the method outlined by Raymahashay & Holland (1969). The method consists of the following four steps:

(a) Contours of H_2S (independent of pH) and SO_4^{2-} (pH dependent) were plotted on the fS_2 versus fO_2 diagrams using equations V-58 and V-59 of Table V-10 respectively.

(b) Concentrations of H_2S , HS^- , SO_4^{2-} and HSO_4^- were calculated at the pyrite-pyrrhotite-magnetite and pyrite-magnetite-hematite triple points by substituting the fS_2 and fO_2 coordinates of these points in equations V-58, V-59, V-60 and V-61 of Table V-10 respectively.

(c) The individual concentrations of H_2S , HS^- , SO_4^{2-} and HSO_4^- were summed to give the $m \leq S$ at each triple point.

(d) Contours of $m \leq S$ were drawn parallel to the H_2S and SO_4^{2-} contours using the triple point $m \leq S$ values as reference for contour value and spacing.

$m \leq S$ contours were calculated for only a few representative fS_2 versus fO_2 diagrams at different temperatures (e.g. Figs I-C-4, I-D-4, I-G-5, I-K-8, I-M-5, I-N-6, I-N-8, I-S-11, I-U-12, and I-V-4) because of the involved nature of the calculations and the fact that those calculated were generally consistent with the estimated values of $m \leq S$ (Table V-9).

fO_2 versus pH Diagrams

The fO_2 versus pH diagrams presented in Appendix I were constructed by the methods outlined in Vaughan & Craig (1978 pp 327 - 330) from the data listed in Table V-10. The stability of the aqueous sulphur species (HSO_4^- , SO_4^{2-} , H_2S and HS^-) were calculated first, followed by the boundaries of the various iron phases (pyrrhotite, pyrite, magnetite, hematite and $FeSO_4$). These types of diagrams are only relevant up to temperatures between 350 and 400°C. At higher temperatures, SO_2 and H_2S are the dominant sulphur species (c.f. Figs 10-1 and I-A-6).

The aqueous sulphur species and mineral stability fields

Figure V-12: Contours of $f_{\text{H}_2\text{S}}$ in equilibrium with the predominant aqueous sulphur species at $\Sigma S = 0.1M$ and 25°C . (modified from Fig.5 of Barnes & Kullerud, 1961.)

of the fO_2 versus pH diagrams represent fields of predominance and are not necessarily exclusive of species in adjacent fields, particularly near the boundaries. On any specific boundary the concentration of the species represented on either side of the boundary is 1:1 and with progression into one field the concentration of the predominant species increases at the expense of the other species (Fig. V-12).

The following explanatory notes detail specific aspects in the construction of the diagrams:

(i) Effect of Variation in the Concentration of Total Sulphur in Solution

With the exception of the boundaries involving liquid sulphur (liquid sulphur/ HSO_4^- and liquid sulphur/ H_2S), positions of the boundaries between the various aqueous sulphur species are independent of variations in the concentration of total sulphur in solution. In contrast the positions of the boundaries between the iron minerals are dependant on the concentration of total sulphur in solution. With increasing concentrations of total sulphur the chalcopyrite/bornite plus pyrite and pyrite/pyrrhotite boundaries expand outward increasing the stability range of the pyrite and pyrrhotite fields at the expense of magnetite and hematite.

(ii) Chalcopyrite/Bornite plus Pyrite Boundary

The comments discussed under this heading in the fS_2 versus fO_2 diagram section apply equally here.

(iii) $\log fS_2$ Contours

Where required, contours of $\log fS_2$ were constructed by the method outlined by Vaughan & Craig (1978 pp 329 - 330) using equations V-58, V-59, V-75 and V-76 (Table V-10).

(iv) fCO_2

Where fCO_2 is known several potentially limiting boundaries

can be defined. The CO_2 /graphite boundary is dependant only on $f\text{O}_2$ and therefore its position is defined as for the $f\text{S}_2$ versus $f\text{O}_2$ diagrams. The anhydrite/calcite boundary, however, is dependant on both $f\text{O}_2$ and $f\text{S}_2$. Its position was calculated using equations V-77 and V-78 (Table V-10). The pH of the calcite soluble/insoluble boundary is dealt with in the earlier section of this Appendix titled "calcite stability and pH".

(v) Manganese Minerals

The rhodochrosite/alabandite boundary was calculated using equations V-79, V-80 and V-81 (Table V-10).

(vi) Barite Soluble/Insoluble Boundary

The barite soluble/insoluble boundary was calculated using equations V-82, V-83 and V-84 (Table V-10). A value of 0.0001M for the concentration of Ba^{2+} in solution is indicated by other studies (e.g. Robinson, 1974) and therefore this value was used here.

(vii) $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ Contours

Contours of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ (and HS^-) can be plotted on $f\text{O}_2$ versus pH diagrams for a given value of $\delta^{34}\text{S}_{\text{S}}$.

The contours were constructed for some diagrams in this thesis by proportioning out $\delta^{34}\text{S}_{\text{S}}$ to $\delta^{34}\text{S}_{\text{H}_2\text{S}}$, $\delta^{34}\text{S}_{\text{HS}^-}$, $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$, and $\delta^{34}\text{S}_{\text{HSO}_4^-}$ - using fractionation factors from Ohmoto (1972) and assigning the values to contours of x% sulphide - y% sulphate calculated from equations V-61, V-63 and V-64 of Table V-10.

This approach is not as rigorous as that suggested by Ohmoto (1972) and Ohmoto & Rye (1979), in which the concentration of a large number of sulphur species is evaluated (using activity coefficients) at various points in the $f\text{O}_2$ versus pH diagram, however considering the errors involved in the construction of the $f\text{O}_2$ versus pH diagram and the calculation of the parameters of the individual mineralisations (temperature, $f\text{S}_2$, pH etc) the method described here is considered adequate.

TABLE V-11: Thermodynamic data used to calculate the $f\text{Te}_2$ versus $f\text{S}_2$ diagrams. The free energy change is given in the form $\Delta G^\circ = \Delta H - T\Delta S^\circ$. All data are from Table 7-2 of Barton & Skinner (1979).

Equation Number	Reaction	Free energy change (in joules for T in K)
(V-85)	$\text{Te}_{2(\text{v})} = 2\text{Te}(\text{s})$	$-156,620 + 149.66T$
(V-86)	$\text{Au} + \text{Te}_2 = \text{AuTe}_2$	$-175,820 + 155.44T$
(V-87)	$4\text{Ag} + \text{Te}_2 = 2\text{Ag}_2\text{Te}$	$-209,564 + 67.36T$
(V-88)	$2\text{Hg} + \text{Te}_2 = 2\text{HgTe}$	$-240,781 + 173.26T$
(V-89)	$2\text{Pb} + \text{Te} = 2\text{PbTe}$	$-296,085 + 164.26T$
(V-90)	$2\text{Hg} + \text{S} = 2\text{HgS}$	$-239,074 + 215.5T$
(V-91)	$2\text{HgTe} + \text{S}_2 = 2\text{HgS} + \text{Te}$	$-19,213 + 39.3T$

Figure V-13: The stability of ferberite (FeWO_4) as a function of $f\text{O}_2$ and $f\text{S}_2$ at 577°C and 1 kbar. MH = $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$, NNO = Ni/NiO , FMQ = $\text{Fe}_2\text{SiO}_4/\text{Fe}_3\text{O}_4 + \text{SiO}_2$ and WM = $\text{FeO}/\text{Fe}_3\text{O}_4$. (From Hsu, 1976.)

Fugacity of Te_2

$f\text{Te}_2$ was estimated for a few mineralisations by plotting the mineral stability relations on $f\text{Te}_2$ versus $f\text{S}_2$ diagrams (Figs 11-5, I-L-8, I-O-15 and I-V-6). The diagrams were constructed using the equations listed in Table V-11 following a similar procedure to that employed in the construction of the $f\text{S}_2$ versus $f\text{O}_2$ diagrams.

SPECIFIC MINERAL SYSTEMS

Tungsten Minerals

Skinner (1967) identified disseminated wolframite in the igneous and hornfels rocks of the coastal section south of Paritu, and Weigel (1978) noted its occurrence in the early mineralisation at Tui Mine. Neither occurrence was confirmed during this study and the composition of these minerals in relation to the wolframite solid solution series ferberite (FeWO_4) - huebnerite (MnWO_4) is unknown. Scheelite (CaWO_4), the other major naturally occurring tungsten mineral has not been found in the province.

The stability relations of a number of tungsten minerals have recently been investigated by Stemprock (1971), Hsu & Galli (1973) and Hsu (1976, 1977, 1981). Figs V-13, V-14 and V-15 illustrate the stability relations of ferberite, huebnerite, scheelite and tungstenite (WS_2) at 577°C and 1000 bars pressure. Although the tungsten mineralisation at Paritu and Tui Mine is believed to have occurred at temperatures around 425°C , Hsu's high temperature and pressure diagrams are used here because thermodynamic data, without considerable extrapolation, are not available for temperatures between 25°C and 577°C .

The stability relations of ferberite at 300°C shown in Fig. V-16 calculated by Kolonin et al (1975) by extrapolation of 25°C data, are incompatible with the experimental data of Hsu (1976). For example Kolonin et al's diagram precludes assemblages of ferberite with magnetite or hematite which have been produced under experimental conditions (Stemprock, 1971; Hsu, 1976). This case demonstrates the dangers of extra-

Figure V-16: The stability fields of tungsten and iron minerals as a function of $\log P_{O_2}$ ($\approx f_{O_2}$) and pH at 300°C. (From Kolonin *et al.*, 1975.)

polating thermodynamic data over large temperature ranges.

Tungstenite is rare in nature, requiring conditions of very low fO_2 and high fS_2 (Stemprock, 1971; Hsu, 1977) to be stable (Fig. V-13, V-14 and V-15). Scheelite is stable over a wide range of fO_2 and fS_2 conditions (Fig. V-15), whereas ferberite and hubnerite have a more restricted occurrence, having limited fields of stability with pyrite and very limited stability fields with pyrrhotite in comparison with scheelite (c.f. Figs V-13 and V-14). Both scheelite and wolframite are stable under a wide range of conditions with magnetite and hematite. The assemblage ferberite plus hematite is replaced by ferric tungstate (Fe_2WO_6) and WO_3 at high oxygen fugacities above $540^\circ C$ (Hsu, 1976).

The wolframite at Paritu occurs with pyrite but is replaced by pyrrhotite (Skinner, 1967). Therefore wolframite deposition occurred within the pyrite stability field probably not far from the pyrite/pyrrhotite boundary so that only a small change in fS_2 is required to make pyrrhotite stable at a later stage. The wolframite/ WS_2 boundary in the pyrite field of Figs V-13 and V-14 restricts wolframite stability in the pyrite field close to the pyrite/magnetite boundary and therefore the Paritu tungsten mineralisation must plot near the pyrrhotite - pyrite - magnetite triple point in Fig. I-C-3.

The occurrence of wolframite at Tui Mine has not been described beyond Weigel's (1978) mention of its presence as an early phase, therefore its relation to other minerals is not known.

Tui Mine Stage 1 mineralisation consists of pyrite, chalcopyrite, hematite, minor bismuthinite, electrum, rare tetradymite and possibly bornite although not all coexisting together. Pyrrhotite has not been recorded. The Stage 1 assemblage plots on or near the hematite/pyrite boundary in Figs V-13 and V-14. Similar conditions for wolframite deposition are compatible with the ferberite and huebnerite stability diagrams.

The absence of scheelite from the tungsten mineralisation at Paritu and Tui Mine may be attributed to a low activity of calcium in the hydrothermal solutions.

Seleniferous and Selenide Minerals

Introduction

Because selenium has similar chemical and physical properties to sulphur it may isomorphously substitute for sulphur in sulphide minerals. Such substitution is the main form of occurrence of selenium in medium and high temperature ore deposits: selenide minerals generally occur only in deposits formed at low temperature and under relatively oxidising conditions (Tischendorf & Ungethüm, 1964; D'yachkova & Khodakovskiy, 1968).

The proportion of Se/S in sulphide minerals is considered to be related to the ratio of dissolved reduced selenium species/dissolved reduced sulphur species in the parent hydrothermal fluid. Recent studies have suggested that this ratio is not only dependent on the ratio of total dissolved selenium to total dissolved sulphur ($\Sigma \text{Se}/\Sigma \text{S}$) in solution but may also be influenced by the oxidation state, pH and temperature of the solution. Therefore the occurrence of seleniferous or selenide minerals in a mineral assemblage may be used to indicate the oxidation state of the hydrothermal fluid.

Thermochemical Studies

Tischendorf & Ungethüm (1964) suggested that for a given temperature and ratio of $\Sigma \text{Se}/\Sigma \text{S}$ in solution, the ratio of $\text{Se}^{2-}/\text{S}^{2-}$ in solution increases with increasing oxidation potential and decreasing pH. D'yachkova & Khodakovskiy (1968) supported their hypothesis and added that the $\text{Se}^{2-}/\text{S}^{2-}$ ratio also increased with decreasing temperature.

Shikazono (1978) applied these relationships to several Japanese ore deposits using the Se content of acanthites to help determine the $f\text{O}_2$ and pH conditions of mineralisation. Yamamoto (1976) took the method a step further by comparing

Figure V-17: Predominant aqueous selenium and sulphur species as a function of fO_2 and pH, at 300°C , $\log m_{\text{S}} = -2$ and $\log m_{\text{Se}} = -7$. The selenium species boundaries were redrawn from Fig. 1c of Yamamoto (1976). The oxidised/reduced aqueous selenium species boundary occurs at a higher fO_2 than the oxidised/reduced aqueous sulphur species boundary and therefore the ratio of reduced selenium species/reduced sulphur species in solution increases with increasing fO_2 above the oxidised/reduced sulphur species boundary. The effect is believed to indicate that the precipitation of seleniferous and selenide minerals is most likely to occur in oxidising environments.

Se/S ratios of different sulphide minerals (pyrite, pyrrhotite, sphalerite, chalcopyrite and bornite) with the ratios of their sulphur isotopes.

However, these studies assumed that S^{2-} is the important sulphur species in solution, whereas Ellis & Giggenbach (1971) demonstrated that under most natural conditions the concentration of S^{2-} in hydrothermal solutions is insignificant, invalidating much of the thermochemical data presented by the authors cited previously.

Nevertheless, their general conclusions, that the deposition of seleniferous or selenide minerals is favoured by oxidising conditions and low temperature, is probably correct because the oxidised/reduced aqueous selenium species boundary occurs at a higher fO_2 than the oxidised/reduced aqueous sulphur species boundary (Fig. V-17). Therefore the ratio of reduced selenium species/reduced sulphur species in solution increases with increasing fO_2 above the oxidised/reduced sulphur species boundary. The separation of the two boundaries is believed to increase with decreasing temperature, therefore increasing the effect.

A rigorous appraisal of this effect is not possible because of the probable inaccuracy of the available thermodynamic data for aqueous selenium species (the data has not been significantly revised since D'yachkova & Khodakovskiy, 1968).

Application

The relationship of Se to temperature in deposits of the Hauraki Gold - Silver Province seems to follow that suggested by D'yachkova & Khodakovskiy (1968): in moderate to high temperature environments Se isomorphously substitutes for S in tetradyrite (Monowai, Tapu - Thames; Merchant, 1978), tellurobismutite (Sylvia, Tapu - Thames, Merchant, 1978) and acanthite (Maratoto and Waihi; c.f. Table 5-2), whereas selenide (plus seleniferous) minerals occur in the low temperature deposits at Te Ahumata (aguilarite, naumannite, seleniferous agyrodite and seleniferous galena; Ramsay, 1971) and Broken Hills (aguilarite, naumannite, aguilarite -

naumannite intergrowths, acanthite - aguilarite intergrowths and some complex gold - silver arsenic sulphoselenide minerals; Moore, 1976).

Fig. V-17 illustrates that the presence of seleniferous and selenide minerals in an assemblage may reflect a relatively high sulphate/sulphide ratio in the parent hydrothermal fluid. This appears to be the case at Broken Hills (Fig. I-K-9) and Maratoto (Fig. I-O-13) but not Te Ahumata (Fig. I-B-6) Tapu - Thames (I-L-7) and Waihi (I-S-10). The $\sum \text{Se} / \sum \text{S}$ ratio of the hydrothermal fluid may have been the controlling parameter in the latter systems.

APPENDIX VIORE PETROGRAPHY OF SAMPLES FROM WAIHISAMPLE 13901 (Wh36), MARTHA MINE (UNLOCATED)

Sample 13901 is finely banded as follows (in order of deposition):

1. 1mm band of quartz.
2. 0.3mm band of quartz with subordinate galena (av. 0.08mm, max. 0.3mm) the latter filling spaces between subhedral quartz. A single aggregate (0.3mm dia.) of a sphalerite (av. 0.02mm, max. 0.05mm), pyrite (0.05mm) and galena (av. 0.01mm, max. 0.05mm) intergrowth occurs surrounded by quartz. Very rare grains of electrum (less than 0.01mm) occur in quartz.
3. 1mm band of quartz and a discontinuous string of subhedral pyrite grains (av. 0.2mm, max. 0.5mm). The pyrite contains inclusions of galena and some grains that occur adjacent to galena of the previous band are embayed by galena.
4. 0.3 - 0.5mm band of quartz.
5. 1mm wide quartz band containing a subordinate pyrite - galena intergrowth. Pyrite and galena (both av. 0.1mm max. 0.3mm) have mutual boundary relations and fill spaces between subhedral quartz.
6. 0.3mm band of quartz.
7. 1mm band of mainly quartz but with isolated grains of pyrite, sphalerite and galena - acanthite composite grains all averaging approximately 0.1mm.
8. 0.2 - 0.8mm wide ribbon-like band of almost continuous pyrite grains. The quartz on both sides is subhedral towards the pyrite. Galena and acanthite occur as inclusions in pyrite and rarely as grains (up to 0.1mm) scattered along both sides of the pyrite band.
9. 0.5mm band of quartz.
10. 3mm band of a complex intergrowth between pyrite (av. 0.1mm, max. 0.3mm) and equigranular (av. 0.05mm) quartz, sphalerite galena - acanthite composite grains and very rare electrum (max. 0.03mm). Pyrite contains abundant inclusions of galena - acanthite and electrum. The quantity of pyrite varies in different parts of the band.

11. 0.03mm ribbon-like band of chalcopyrite.
12. 3x7mm lens of quartz with subhedral to anhedral pyrite (av. 0.2mm, max. 0.4mm) and lesser galena (av. 0.1mm, max. 0.3mm), sphalerite (av. 0.05mm, max. 0.3mm) and chalcopyrite (av. 0.05mm, max. 0.1mm). Galena, sphalerite and chalcopyrite occur mainly at the margins of and embay the pyrite grains. Pyrite contains inclusions of galena.
13. The remaining part of the section (up to 10mm) contains galena - acanthite composite grains (av. 0.1mm, max. 0.3mm), pyrite (av. 0.1mm, max. 0.4mm), sphalerite (av. 0.1mm, max. 0.6mm) and chalcopyrite (av. 0.1mm, max. 0.3mm) generally as isolated grains or aggregates of two or three grains filling spaces between subhedral to euhedral quartz. There is a general coarsening of grain size away from band 12. The sulphides make up less than 50% of the band and their proportions vary; galena - acanthite being dominant near band 12 but pyrite becoming dominant several millimetres away from band 12. Sphalerite and chalcopyrite are locally abundant at the outside edge of band 13 (the edge of the specimen). Boundaries between adjacent sulphides in composite grains appear mutual. Sphalerite contains abundant tiny blebs, and a few larger areas, of chalcopyrite. Pyrite contains abundant inclusions of galena - acanthite (generally 10% but up to 30% of the pyrite grain). Some pyrite grains adjacent to and embayed by sphalerite also contain abundant inclusions of sphalerite.

SAMPLE 13902 (Wh37), MARTHA MINE (UNLOCATED)

Individual grains of anhedral to subhedral pyrite (av. 0.1 mm, max. 0.4mm; approximately 20% of section), anhedral chalcopyrite (av. 0.1mm, max. 0.4mm; approximately 2% of section), anhedral galena (av. 0.1mm, max. 0.2mm; approximately 1% of section) and groups of small scattered rounded grains of sphalerite (av. 0.03mm, max. 0.1mm; approximately 5% of section) occur filling spaces between subhedral to anhedral grains of quartz (av. 0.1mm, max. 0.4mm; approximately 72% of section). The sphalerite may represent remnants left after replacement (resorption) by quartz.

SAMPLE 13903 (Wh48), MARTHA MINE (UNLOCATED)

Bands (approximately 3mm wide) of quartz with scattered grains of subhedral pyrite (av. 0.2mm max. 0.5mm) alternate with bands (1 - 4mm wide) of quartz with scattered subhedral pyrite (av. 0.1mm, max. 0.5mm) and aggregates (up to 1mm in diameter) of sphalerite, galena, pyrite, chalcopryrite and very rare electrum. The sphalerite is subhedral to anhedral to surrounding quartz and contains abundant but extremely small (approximately 1 micrometre or less) blebs of chalcopryrite. Larger inclusions (0.01mm), veinlets and grains (less than 0.1mm) of chalcopryrite occur rarely in sphalerite. Chalcopryrite also occurs as rare solitary ovoid grains (av. 0.04, max. 0.1mm) in quartz. Galena (av. 0.03mm, max. 0.4mm) generally occurs intergrown with sphalerite or as ovoid inclusions and cores in pyrite, but rarely as solitary grains in quartz. Sphalerite has mutual embayment relations with adjacent grains of pyrite although rare veins of pyrite penetrate sphalerite. Rare electrum generally occurs as isolated grains (0.02mm or less) in quartz although one inclusion was noted in galena. The sulphides make up less than half of the sulphide bands.

SAMPLE 13978 (Wh27), MARTHA MINE (UNLOCATED)

Subhedral to euhedral grains of sphalerite (av. 2mm, max. 5mm) are separated and replaced by interstitial areas of quartz, galena (av. 0.2mm, max. 0.5mm) and minor pyrite (av. 0.1mm, max. 0.2mm). The sphalerite grains contain abundant tiny blebs of chalcopryrite (Fig. 4-19) and larger inclusions of galena, pyrite, chalcopryrite and pyrrhotite arranged in dendritic - "streaky" (Fig. 4-25) and poikilitic (Fig. 4-26) textures. The poikilitic textures are interpreted as cross-sections of the streaky textures. The pyrite, chalcopryrite and pyrrhotite are generally ovoid shaped inclusions (0.01 - 0.02mm in diameter) in both the streaky and poikilitic textures, whereas the galena occurs as long ribbons up to 0.05mm wide and 0.5mm long in the streaky textures. The two types of textures consist of either galena or a combination of galena with chalcopryrite, pyrrhotite or pyrrhotite plus pyrite. In some grains containing poikilitic galena plus chalcopryrite it is difficult to distinguish the chalcopryrite of the poikilitic texture from that of the usual chalcopryrite in sphalerite exsolution, epitaxial growth or

replacement. Chalcopyrite may make up substantial proportions of the sphalerite grains in these cases.

The sphalerite, plus contained inclusions, generally makes up approximately 90% of the section; however in one mount this material is cross-cut by a 2 - 4mm wide vein of anhedral galena (=the matrix, grain size approximately 1mm?), subhedral pyrite (av. 0.3mm, max. 0.5mm) and subhedral to anhedral quartz. The pyrite is commonly embayed by galena.

In summary, the textures are interpreted as representing a sequence of sphalerite invaded and replaced by various combinations of galena + quartz $\pm$ pyrite $\pm$ chalcopyrite $\pm$ pyrrhotite, in turn followed by galena + pyrite + quartz.

SAMPLE 14032 (GJ3), GRAND JUNCTION MINE (UNLOCATED)

A 2 - 3mm band, in otherwise barren quartz, contains scattered grains of pyrite (av. 0.2mm, max. 0.4mm) filling spaces between subhedral grains of quartz. Sphalerite (av. 0.06mm, max. 0.1mm), galena - acanthite composite grains (av. 0.03mm, max. 0.1mm) and electrum (av. 0.01mm) occur as solitary grains filling spaces between subhedral quartz (av. 0.1mm) or intergrown with each other in small aggregates (up to 0.2mm in diameter) or intergrown with the larger pyrite grains (exhibiting mutual boundary relations with each other and pyrite). The pyrite grains, both when solitary in quartz or intergrown with aggregates of other sulphides, contain abundant (typically 10% of the pyrite grain) inclusions of galena (-acanthite?) and electrum (both typically 0.01mm) and less common inclusions of sphalerite. Except for minute blebs in sphalerite, chalcopyrite is very rare. Electrum occurs solitary in quartz or associated with any of the sulphides but most commonly with galena as inclusions in pyrite. The content of the mineralised band is approximately 60% quartz, 23% pyrite, 8% sphalerite, 8% galena (including subordinate acanthite) and less than 1% chalcopyrite and electrum.

SAMPLE 14039 (Wh28), MARTHA MINE (UNLOCATED)

In polished section, specimen 14039 consists of large masses of sphalerite with occasional small intergranular areas (0.2 - 0.5mm) of interstitial chalcopyrite, quartz and galena. Thin

(typically 0.01mm, but up to 1mm in the case of quartz) veinlets of chalcopyrite and quartz with sparse individual grains of subhedral pyrite (av. 0.08mm, max. 0.2mm) and anhedral galena (av. 0.1mm, max. 0.3mm) penetrate and fill cracks in the sphalerite masses. The sphalerite contains abundant tiny inclusions of chalcopyrite which delineate grain boundaries, indicating an average grain size of 0.2mm for the sphalerite.

At one edge of the polished mount a 2 x 1mm mass of galena containing subhedral pyrite (av. 0.03mm, max. 0.08mm) and anhedral chalcopyrite (av. 0.03mm, max. 0.06mm) interfingers with the sphalerite.

SAMPLE 14040 (Wh29), MARTHA MINE (UNLOCATED)

The two polished mounts examined of sample 14040 are very similar to sample 13978. In one, subhedral to euhedral grains of sphalerite (av. 1.5mm, max. 4mm) occur separated by quartz, the latter making up only about 20% of the mount. Small (av. 0.1mm, max. 0.2mm) subhedral to euhedral grains of pyrite commonly occur at the margins of the sphalerite grains. Galena also occurs as marginal grains (av. 0.1mm, max. 0.3mm) to sphalerite but more commonly as poikilitic and dendritic - streaky inclusions within sphalerite, in association with pyrrhotite, pyrite or chalcopyrite (the latter grains generally 0.01 to 0.02mm in diameter). However, this polished mount of 14040 differs from 13978 in that there appears to be a complete transition from the dendritic - streaky and poikilitic galena to large (0.1 - 0.5mm) grains of galena in the sphalerite and in adjoining quartz gangue. The quartz also contains isolated subhedral grains of pyrite (av. 0.08mm, max. 0.2mm). Finally a 1mm wide band of quartz cross-cuts and includes some fragments of the earlier material.

In the second polished mount of sample 14040 the grains of galena (av. 0.15mm, max. 0.6mm) and pyrite (av. 0.05mm, max. 0.2mm) are much more abundant, the poikilitic and dendritic - streaky galena ⁺ pyrite ⁺ pyrrhotite (chalcopyrite does not appear to be associated with these textures in this mount) less common, and the mount is characterised by a greater degree of brecciation and infilling by later barren quartz. The pyrite

grains are subhedral, contain abundant inclusions of, and are very corroded (e.g. embayed) by, galena. The quantity of chalcopyrite blebs in sphalerite is quite variable, ranging from abundant in some grains to almost absent in others. Like the other mount of this sample, at one edge the sphalerite predominant material is invaded by a large area (6 x 3mm) of galena containing anhedral sphalerite (av. 0.15mm, max. 0.3mm), anhedral quartz (av. 0.08mm, max. 0.20mm), subhedral embayed pyrite (av. 0.04mm, max. 0.1mm) and small blebs of chalcopyrite (max. 0.03mm), isolated in the galena.

SAMPLE 14041 (Wh30), MARTHA MINE (UNLOCATED)

Sample 14041 contains predominantly galena (approximately 55%) and chalcopyrite (approximately 20%) with minor sphalerite (5%) and pyrite (5%) cross-cut by a 0.2 - 1.5mm wide band of quartz (5%) and euhedral pyrite (av. 0.03mm, max. 0.2mm; approximately 5% of the section). In the former material, large masses of chalcopyrite (approximately 2-3mm) contain clusters of anhedral to euhedral pyrite pseudomorphing marcasite balls originally averaging 0.5mm in diameter. The chalcopyrite masses are surrounded by areas containing predominantly anhedral rounded grains of galena (av. 0.4mm, max. 1mm) with interstitial chalcopyrite (matrix), sphalerite (av. 0.1mm, max. 0.2mm), quartz (av. 0.06mm, max. 0.2mm) and pyrite (av. 0.1mm, max. 0.4mm) the latter euhedral to chalcopyrite but embayed by and containing inclusions of galena and sphalerite.

Supergene covellite replaces margins of chalcopyrite.

SAMPLE 14043 (Wh35), VICTORIA VEIN, ADIT LEVEL

Sample 14043 contains bands (0.5 - 5mm) of virtually barren quartz alternating with bands (0.5 - 2mm) containing scattered individual grains of acanthite (av. 0.05mm, max. 1.0mm) and electrum (av. 0.1mm, max. 0.2mm). The mineralised bands contain up to 30% acanthite but less than 1% electrum.

SAMPLE 14046 (Wh43), MARTHA MINE (UNLOCATED)

Sample 14046 is banded as follows (in order of deposition):

1. 2mm band of quartz containing rare isolated grains (0.05mm) of subhedral pyrite and sphalerite.
2. 2mm band of quartz with scattered subhedral pyrite (av.

- 0.1mm, max. 0.3mm; 25-30% of band) and blebs (av. 0.02mm, max. 0.05mm) of sphalerite (5%) and galena (2%). Pyrite contains abundant inclusions of sphalerite and galena (av. 0.01mm each) and a few inclusions of electrum (0.005mm).
3. 2mm band of sphalerite (av. 1mm, max. 2mm) containing abundant inclusions of galena in poikilitic (Fig. 4-22) and dendritic - "streaky" textures.
 4. 0 - 0.4mm band of pyrite (av. 0.2mm, max. 0.3mm) subhedral to following quartz but interfingers with sphalerite of band 3 (Fig. 4-22). The pyrite contains abundant inclusions of galena.
 5. 3mm band (remainder of mount) of quartz with scattered grains of subhedral - euhedral pyrite (av. 0.3mm, max. 0.8mm) which, in contrast to pyrite of band 4, contain very few inclusions of galena. The pyrite grains are generally fractured.

SAMPLE 14047 (Wh44), MARTHA VEIN, 7 LEVEL

Three phases of mineralisation, represented by different bands, occur in specimen 14047. Two are observed in polished section, whereas the third was noted in hand specimen.

An early phase of euhedral pyrite grains (av. 0.2mm, max. 0.5mm) in clusters surrounded by chalcopryite is brecciated and the 2 - 3mm fragments are surrounded by quartz.

The second phase consists of sphalerite (av. 1mm, masses up to 2.5mm) and quartz with lesser galena (av. 0.4mm, max. 0.8mm), chalcopryite (av. 0.2mm, max. 0.8mm), pyrite (av. 0.1mm, max. 0.2mm) and electrum. The sphalerite is subhedral and contains variable quantities of tiny chalcopryite inclusions and larger inclusions of chalcopryite and galena. Galena occurs as grains adjacent and intergrown with sphalerite and also separately in quartz. Chalcopryite occurs as thin rims and blebs at the junction of sphalerite and galena and also as larger masses intergrown with galena, sphalerite and quartz. Subhedral pyrite occurs solitary in quartz or with sphalerite, galena and chalcopryite, often embayed by these sulphides. It contains abundant inclusions of galena. Electrum occurs as small blebs (0.005mm) in galena, larger areas (av. 0.01mm, max. 0.03mm)

intergrown with galena, solitary in quartz, and in one instance as two 0.02mm inclusions in sphalerite.

The third phase, recognised in hand specimen, consists of medium grained quartz (2mm) with interstitial fine grained (0.5mm) pyrite and chalcopyrite.

SAMPLE 14048 (Wh45), UNLOCATED

Sample 14048 is banded as follows (in order of deposition):

1. 5 - 8mm band of quartz, subhedral pyrite (av. 0.3mm, max. 0.7mm; 25% of band) and chalcopyrite (av. 0.2mm, max. 0.5mm; 5% of band), the latter filling spaces between subhedral - euhedral quartz.
2. 1 - 2mm band of sphalerite (av. 0.1mm, max. 0.5mm; 40%), chalcopyrite (av. 0.1mm, max. 0.3mm; 15%), acanthite - galena composite grains (av. 0.05mm, max. 1.0mm; 3%) and electrum (av. 0.02mm, max. 0.2mm; 1%) intergrown with each other and quartz. Quartz is subhedral - euhedral towards the sulphides, particularly chalcopyrite.
3. 2mm band of subhedral - anhedral rounded pyrite grains (av. 0.3mm, max. 0.6mm; varying from 50% to a continuous chain). Pyrite is intergrown with, and contains abundant inclusions of, electrum (av. 0.05mm, max. 0.12mm); some pyrite grains containing up to 20% electrum. Pyrite also contains less common and smaller (0.01mm) inclusions of galena. Band 3 is not parallel with the other bands and appears to partly cross-cut band 4.
4. 2 - 6mm band of near equigranular quartz (av. 0.1mm, max. 0.3mm; 40%), sphalerite (av. 0.1mm, max. 0.4mm; 30%), galena - acanthite composite grains (av. 0.05mm, max. 0.3mm; 15%), pyrite (av. 0.1mm, max. 0.5mm; 10%), chalcopyrite (av. 0.1mm, max. 0.3mm; 5%) and electrum (av. 0.02mm, max. 0.15mm; less than 1%). The quantity of pyrite and chalcopyrite relative to sphalerite and galena - acanthite varies from one part of the band to another and areas locally dominated by pyrite or chalcopyrite occur. Boundary relations between the different sulphides are mutual but quartz is generally subhedral to the sulphides. Electrum occurs intergrown with all other phases.
5. 7mm band of quartz with scattered grains of pyrite (av. 0.1mm,

max. 0.5mm; 10%), sphalerite (av. 0.06mm, max. 0.2mm; 1%) and chalcopryite (av. 0.05mm, max. 0.3mm; less than 1%). Pyrite is subhedral but sphalerite and chalcopryite fill spaces between subhedral quartz.

6. Quartz crystals projecting up to 0.5mm into vugs.

SAMPLE 14049 (Wh42) MARTHA VEIN "AT DEPTH"

Sample 14049 consists mostly of quartz with approximately 30% pyrite (av. 0.1mm, max. 0.4mm), 8 - 10% sphalerite (av. 0.2mm, max. 0.8mm) and 1 - 2% galena (av. 0.05mm, max. 0.2mm). Pyrite occurs as individual grains or clusters of a few grains scattered in the quartz gangue. The smaller grains of sphalerite occur as cores within large pyrite grains or pyrite clusters, whereas the larger grains occur in quartz but have grains of pyrite distributed discontinuously around their rims. Pyrite is euhedral in quartz but sphalerite is subhedral within or when adjoining pyrite. Galena also occurs as cores and inclusions in pyrite, intergrown with sphalerite or separately. It very rarely occurs as isolated grains in quartz. Chalcopryite occurs only in sphalerite as tiny blebs which are extremely small and generally uncommon.

SAMPLE 14050 (Wh47) MARTHA VEIN, 10 LEVEL

Sample 14050 exhibits cockade structure, consisting of breccia fragments coated by a 1 to 2mm band of semi-continuous chalcopryite enclosing subhedral to anhedral quartz (av. 0.1mm, max. 0.2mm) and euhedral pyrite (av. 0.05mm, max. 0.15mm).

SAMPLE 14051 (Wh49), UNLOCATED

Large masses of sphalerite (up to 6mm in diameter) have marginal grains of subhedral pyrite (av. 0.1mm, max. 0.8mm), anhedral galena (av. 0.2mm, max. 1.0mm) and anhedral chalcopryite (av. 0.08mm, max. 0.4mm). Tiny blebs of chalcopryite are uncommonly present in the sphalerite, however chalcopryite and, to a lesser extent, pyrite penetrate sphalerite along thin veinlets (typically 0.01mm and generally less than 0.06mm wide). This material is brecciated and followed by subhedral quartz (av. 0.1mm, max. 0.3mm) subhedral pyrite (av. 0.1mm, max. 0.4mm) and anhedral chalcopryite (av. 0.1mm, max. 0.4mm) and, later, by more abundant filling of subhedral to euhedral second

Figure VI-1: Replacement of sphalerite (light gray) and galena (white) by quartz (dark gray) in sample 14052 from the Martha Vein, 10 level, Waihi. Some sphalerite grains exhibit a lamellar texture with quartz. The small black areas are pits. 50X.

Figure VI-2: Replacement of galena (white) sphalerite (grey) by quartz (dark grey) in sample 14052 from the Martha Vein 10 level, Waihi. The galena exhibits a dendritic texture in quartz. 50X.

generation quartz (av. 0.4mm, max. 1.0mm).

The proportion of the various minerals (regardless of stage) is approximately 45% sphalerite, 35% quartz, 10% pyrite, 8% galena and 2% chalcopyrite.

SAMPLE 14052 (Wh50), MARTHA VEIN, 10 LEVEL

A 2mm wide band containing grains of subhedral pyrite (av. 0.3mm, max. 0.5mm) scattered in quartz (approximately 70% gangue, 30% pyrite) occurs adjacent to a 12mm band containing approximately 50% quartz, 30% sphalerite, 16% galena, 2% pyrite, 1% chalcopyrite and collectively 1% tetrahedrite, acanthite and electrum. In the latter band the sulphides appear to be replaced by quartz, as demonstrated by lamellar texture of sphalerite (Figs. 4 - 23 and VI-1) and dendritic - vermicular texture of galena (Fig. VI-2) in quartz. Sphalerite masses and laths occur up to 2mm long and contain abundant tiny inclusions of chalcopyrite, sometimes in preferential orientations, and inclusions of tetrahedrite (av. 0.01mm, max. 0.03mm). Galena occurs as interconnecting atolls, ribbons etc. Occupying areas up to 2mm in which isolated grains of galena are typically 0.1 to 0.2mm long.

In addition to the abundant blebs in sphalerite, chalcopyrite also occurs as grains (av. 0.05mm, max. 0.12mm) generally intergrown with galena. Similarly acanthite (av. 0.02mm, max. 0.05mm) and electrum (av. 0.02mm, max. 0.04mm) also generally occur intergrown with galena although acanthite also occurs as solitary grains in quartz. Subhedral to euhedral pyrite (av. 0.1mm, max. 0.5mm) is embayed by and contains inclusions of galena (and rarely sphalerite) indicating replacement of pyrite by the other sulphides. Galena may also replace sphalerite in some parts of the band.

In summary a sequence of; pyrite, sphalerite + tetrahedrite, galena + chalcopyrite + acanthite + electrum, and quartz, is indicated.

APPENDIX VIIORE PETROGRAPHY OF SAMPLES
FROM KARANGAHAKESAMPLE 14023 (TL17), TALISMAN MINE (UNLOCATED)

In sample 14023 (TL17) medium grained (but mainly as masses up to 5mm) galena, sphalerite and chalcopyrite occur approximately in equal proportions with lesser quantities of quartz and pyrite. Galena is generally subhedral to sphalerite and some sphalerite grains penetrate adjacent galena as rare veins. Chalcopyrite from the large masses fill fractures in adjacent sphalerite grains and also penetrate and include galena. This is particularly marked in a later phase of chalcopyrite introduced by late quartz. Anhedral pyrite from this stage also penetrates galena from the margins of the quartz vein, the galena being subhedral to the pyrite. Small inclusions of galena occur in chalcopyrite and vice versa. Tiny inclusions of chalcopyrite occur in sphalerite (exsolution, replacement or epitaxial growth). Rare pyrite (one grain 0.4mm) occurs in sphalerite with sphalerite being subhedral to the pyrite.

Spherules (av. 0.8mm, max. 2.0mm dia) of pyrite (after marcasite?) and quartz occur in chalcopyrite. In the largest example the quartz has penetrated the chalcopyrite along a narrow vein. The pyrite consists of small grains (av. 0.05mm, max. 0.1mm), subhedral near the margins of the spherules and fibrous toward the centres. Euhedral grains (av. 0.2mm, max. 0.4mm) of pyrite also occur in chalcopyrite.

These relationships are interpreted as indicating near simultaneous deposition of galena and sphalerite (perhaps with some galena before sphalerite) followed by chalcopyrite and pyrite, the latter pair probably in two stages.

SAMPLE 14024 (TL21), TALISMAN MINE (UNLOCATED)

Sample 14024 (TL21) contains a sequence of thin quartz and sulphide bands, ending in vug quartz crystals (up to 2mm long) overgrown by large crystals of gypsum.

The sequence is continuous (uninterrupted by brecciation etc) beginning with a 1mm band of quartz containing scattered grains of euhedral fine grained pyrite (av. 0.1mm, max. 0.3mm) lining very altered country rock.

An 0.5mm band follows containing individual grains of galena (av. 0.2mm, max. 0.5mm) surrounded by euhedral quartz. A further 0.5mm band of quartz contains sphalerite (av. 0.3mm, max. 0.5mm), galena (av. 0.1mm, max. 0.3mm) and minor pyrite and chalcopyrite (both av. 0.1mm, max. 0.3mm) generally as aggregates of a few grains scattered in quartz. The sphalerite is anhedral, margined and penetrated by adjacent galena and contains a few large inclusions of galena and abundant tiny inclusions of chalcopyrite. The galena contains a few small grains of chalcopyrite (max. 0.05mm), embays pyrite and occurs as inclusions in pyrite (replacement of py by gn). Both 0.5mm bands contain approximately 40% sulphides and are recognisable in hand specimen as a composite black band contrasting with the adjacent clear and milky quartz.

A further 0.5mm band of quartz contains a few individual euhedral grains of pyrite (av. 0.2mm max. 0.5mm). These bands are separated from another sulphide band by three 1mm bands of barren quartz. The last sulphide band (2-3mm) is mostly quartz with subhedral pyrite (av. 0.3mm, max. 1.0mm). The pyrite contains inclusions of sphalerite and galena and is embayed by these minerals when they occur as adjacent grains (replacement of py). Sphalerite (av. 0.2mm, max. 0.8mm) and galena (av. 0.1mm, max. 0.4mm) also occur as individual grains or as aggregates of two or three grains in euhedral or subhedral quartz. Chalcopyrite (av. 0.05mm) occurs as rare individual grains in quartz. Vug quartz with crystals up to 2mm long follows and is coated by large (30mm long) crystals of gypsum.

SAMPLE 14025 (TL22), TALISMAN 14 LEVEL

Sample 14025 (TL22) from 14 level is crustified, consisting of sulphide bands separated by bands of milky quartz and carbonate. (Fig. 4-6). In polished section sphalerite and galena predominate although chalcopyrite is locally abundant. Pyrite and electrum are present in lesser quantities.

Several different textures occur, the particular texture developed depending on the proportion of the various sulphides. Sphalerite and galena generally occur in complex intergrowths (Figs. 4-27 and 4-28) which surround and penetrate larger masses of chalcopyrite (max. 3mm) and sphalerite (masses up to 4mm). In a few examples quartz accompanies sphalerite and galena in the complex textures but generally it occurs as distinct grains surrounded by the sphalerite-galena intergrowth, accompanying the larger grains of chalcopyrite and sphalerite or invading them.

Large masses of chalcopyrite (max. 5mm) occur in some bands. They contain euhedral grains of pyrite and inclusions of galena, electrum and pyrite. Chalcopyrite generally penetrates fractures in adjacent sphalerite masses.

Sphalerite contains abundant tiny inclusions of chalcopyrite (exsolution or epitaxial growth) and in a few bands large masses of sphalerite contain inclusions of galena, galena and chalcopyrite or galena, chalcopyrite and electrum arranged in poikilitic (Fig. 4-29), dendritic - "streaky" (Fig. 4-30) and myrmekitic textures.

Pyrite occurs as small grains in chalcopyrite or galena and larger grains (max. 1mm) in quartz. One pyrite after marcasite ball occurs in a large mass of chalcopyrite of p.s. 14025₇ (TL22₇). When contacting galena, pyrite is embayed and contains abundant inclusions of galena.

Electrum occurs as abundant tiny grains in many bands of the specimen. It mainly occurs with quartz invading earlier sulphides (Fig. 4-31) but also as intergrowths with galena in the complex galena-sphalerite intergrowths. Inclusions of electrum in chalcopyrite and sphalerite are common in some bands.

Carbonate occurs as small aggregates in some quartz bands but also as a 5mm thick band which replaces the sulphides (particularly marked with galena and chalcopyrite along its margins.)

SAMPLE 14026 (TL24), TALISMAN 13 LEVEL

Sample 14026 (TL24) contains two bands of scattered subhedral pyrite grains (av. 0.5mm, max. 2mm) in quartz with rare chalcopyrite (av. 0.05mm), separated by 2 - 4mm of barren quartz from a central 2mm band of fine grained pyrite (av. 0.1mm, max. 0.8mm) with very minor sphalerite (av. 0.1mm, max. 0.07mm), galena (av. 0.05mm, max. 0.4mm) and chalcopyrite (av. 0.05mm). Pyrite is subhedral to anhedral and together with chalcopyrite, sphalerite and galena occurs as individual grains or aggregates of a few grains interstitial to quartz. Examples of mutual intergrowth occur between all four sulphides indicating coprecipitation. The sulphides make up approximately 30% of the central band which is easily distinguished in hand specimen because of its black quartz (chalcedony) in contrast to adjacent milky quartz.

SAMPLE 14027 (TL25), TALISMAN 13 LEVEL

Sample 14027 (TL25) contains three sulphide bands, each 2 to 3mm thick, separated by barren quartz. An early band, containing scattered individual grains of sphalerite (av. 0.05mm, max. 0.1mm) in quartz, coats the country rock. Rare electrum (one grain 0.01mm seen in p.s. TL25) occurs in quartz of this stage. This is followed by a band of pyrite (av. 0.2mm, max. 0.5mm), sphalerite (av. 0.05mm, max. 0.1mm) and rare galena (av. 0.03mm, max. 0.1mm) and a band of sphalerite (av. 0.05mm, max. 0.7mm), chalcopyrite (av. 0.05mm, max. 0.1mm), pyrite (av. 0.2mm, max. 0.5mm) and galena (av. 0.03mm, max. 0.1mm). In the latter bands pyrite is anhedral to euhedral and contains a few inclusions of sphalerite and abundant inclusions of galena. Galena grains usually occur with sphalerite. The sulphides occur scattered in quartz and generally make up only 20% of the bands but in places, the sphalerite and quartz band contains up to 40% sphalerite.

Supergene chalcocite and covellite rim chalcopyrite and chalcocite rims sphalerite.

APPENDIX VIIIACCESS AND ORE PETROGRAPHY OF
VEINS IN THE WAIORONGOMAI AREAINTRODUCTION

The locations of the major veins and workings in the Waiorongomai area are shown in Fig. VIII-1.

PREMIER - COLONIST SECTIONIntroduction

The workings on the Hero, Colonist, Premier and Vulcan veins, at the northern end of the Waiorongomai Valley, are the largest underground workings in the area (Figs. VIII-1 and VIII-2). The mine plans (Fig. VIII-2) show the extent of workings and the location of referenced samples.

Of the workings west of the tramway only Colonist Smithy level was found to be accessible. The entrance to Mcleans 1100' level has been covered by a slip and therefore material from this level was collected from the mullock heap. Both the entrance and mullock heap of the 1404' level are buried under another slip. The other levels were not located.

North of the tramway, 1480' level is covered by a slip but Premier No.4, Vulcan No.4A, Vulcan No.2 (eastern drive) and Mcleods 1786' level are accessible via their portals. The portal to Vulcan No.2 western drive is collapsed but the drive is accessible (although very wet) behind the portal, where the roof has collapsed, and via a cross cut from No.2 eastern drive. Similarly the portal of Vulcan No.3 (1630') level is collapsed but further around the hill part of the level has been opened because of roof collapse. The levels mentioned as accessible via their portals are generally open over their entire length although Vulcan No.2 (eastern drive) is impassible beyond the crosscut to the western drive due to stopping from below.

Figure VIII-1: Locations of the major veins and workings in the Wairongomai area (based on old mine plans and the diagrams in Henderson & Bartrum, 1913).

- A = Mcleans 1100' Level (sample 14100)
- B = May Queen 2 Level (sample 14078)
- C = May Queen 3 Level (samples 14079, 14080 and 14081)
- D = No. 1 Reef Diamond Creek waterfall (samples 14072 through to 14075)
- E = Main Vein, adit above pack track (sample 14090)
- F = Main Vein Diamond Creek waterfall (samples 14087, 14088 and 14089)

Figure VIII-2: Plan of the Colonist (Hero and Colonist Veins) and Premier (Premier and Vulcan Veins) Sections, also known as Hardy's Mines, redrawn from old mine plans. See Fig. VIII-1 for location.

Figure VIII-3: Brecciated medium to coarse grained sulphide mineralisation (predominantly sphalerite and galena) from Colonist Smithy Level. The sample (14077) is 15cm wide.

Colonist Smithy Level

The location of Colonist Smithy level is shown in Fig. VIII-2. A fall prevents access beyond a big stope open to the surface. A number of quartz veins (up to 120mm wide) are exposed in the southern wall of a side "room". They contain several stages of brecciation and quartz deposition. Thin bands (up to 5mm) containing rare fine to medium grained sulphides, generally a combination of sphalerite and galena or pyrite and chalcopyrite, occur in the sequence of quartz bands, coating breccia fragments of country rock and along the vein margins. The centres of the veins are generally vuggy with quartz crystals up to 12mm long.

In contrast samples found on the floor of the stope contain abundant medium to coarse grained sulphides (Fig. VIII-3). A 100mm wide specimen (14077) rich in sulphides is coated with fine vug quartz crystals on one side indicating that the original vein was at least 200mm wide if symmetrical. The sample records a history of several phases of brecciation and mineral deposition. The main sulphide stage contains fragments of wall rock and an early fine grained sulphide and quartz stage.

In polished section (14076b) the early material contains euhedral pyrite (av. 0.1mm, max. 0.3mm) minor chalcopyrite (av. 0.2mm, max. 0.5mm) and rare sphalerite (av. 0.2mm, max. 0.5mm) as individual grains scattered in quartz. The main sulphide stage is itself brecciated (fragments 60 x 40mm) and filled with later quartz veinlets (av. 5mm, but up to 30mm in 14092a) that crisscross the specimens. Some of these quartz veinlets developed vugs with quartz crystals up to 5mm long. In hand specimens of the rich sulphide material sphalerite predominates and occurs in masses up to 10mm in diameter. Chalcopyrite and galena are locally abundant and also occur in large masses, up to 20mm and 8mm respectively. Pyrite is not seen in hand specimen. In polished section most of the larger sulphide minerals are fractured and filled with quartz (p.s. 14076a, 14076b, 14077a and 14077b), however two samples (p.s. 14092a and 14092b) show only minor fracturing. Sphalerite appears to have crystallised early in the sequence

and is penetrated by later chalcopyrite and galena (p.s. 14077a and 14092b). Pyrite is rare in the medium to coarse grained mineralisation but occurs as euhedral grains (av. 0.2mm, max. 0.3mm) in chalcopyrite of p.s. 14076b. Hessite and electrum occur as small inclusions of various shapes in galena (p.s. 14077, 14092a and 14092b).

Sample 14092a shows that in some parts of the vein the sequence of deposition of the main sulphide stage is more complicated. The sample is cut by a 10mm thick base metal vein which is zoned as follows:

Zone 1. Chalcopyrite (av. 0.3mm, max. 2.0mm) and sphalerite (av. 0.5mm, max. 1.0mm) are developed interstitially to an early euhedral quartz phase along the vein margins. The larger masses of chalcopyrite contain some euhedral grains of pyrite (av. 0.2mm, max. 0.1mm) with quartz. Chalcopyrite contains a few inclusions of sphalerite, sphalerite contains very small blebs of chalcopyrite, whereas pyrite contains small inclusions of chalcopyrite and galena arranged zonally. The sulphides occur scattered in euhedral quartz (30% sulphides).

3mm into the vein, galena (av. 0.3mm, max. 0.5mm) and chalcopyrite (av. 0.3mm, max. 0.5mm) occur scattered between subhedral quartz in a band approximately 1mm wide. They interfinger, contain inclusions of each other and appear to have precipitated together. The galena embays earlier pyrite and occurs as inclusions in the pyrite (indicating replacement of py by gn). Earlier sphalerite is subhedral to galena and chalcopyrite, its fractures filled by chalcopyrite. Galena contains inclusions (0.04mm) of hessite.

Zone 2. Galena (av. 2.0mm, max. 4mm) lines the above zone and interfingers with later massive sphalerite. Some chalcopyrite (av. 0.2mm, max. 0.4mm) occurs in galena especially at narrow points in the string of grains, defining grain boundaries. Very rare (3 in p.s. 14092) inclusions (0.02mm) of electrum and a few elliptical inclusions (0.02mm) of hessite occur in galena. Grains of galena (av. 0.5mm, max.

1.0mm) continue into the massive sphalerite at the end of the "fingers" but for at least 2mm sphalerite is practically the only phase (tiny inclusions of chalcopryrite and thin veinlets of quartz being the only exceptions).

At approximately 8mm in from the beginning of zone 2, chalcopryrite (av. 1mm but masses up to 4mm), pyrite (av. 0.3mm, max. 0.7mm) and galena (av. 0.5mm, max. 1mm) reappear. Chalcopryrite and galena interfinger and appear to have coprecipitated. Although boundaries with sphalerite appear mutual, chalcopryrite fills fractures in the sphalerite. Galena contains rare inclusions of hessite. In this material sphalerite still predominants, followed in order of abundance by chalcopryrite, galena and lastly pyrite. Pyrite occurs as subhedral grains in quartz and contains small inclusions of chalcopryrite and a few inclusions of galena. It has subhedral to euhedral boundaries with galena and chalcopryrite, but is embayed by quartz.

McLeans 1100' Level

Samples (100mm dia.) of mineralisation from the mullock heap of the 1100' level are composed of massive medium grained sphalerite and galena cross cut by veins of barren coarsely crystalline quartz. In polished section (14100a and 14100b)

It embays (replaces?) and occurs as inclusions in pyrite, but has mutual boundary relations with chalcopyrite.

Pyrite occurs mostly in galena, less in sphalerite and rarely in quartz (euhedral in this case).

At least two generations of quartz occur in p.s. 14100a. One accompanies the sulphides, euhedral to their margins and filling their fractures. A second occurs as a 1mm vein cross-cutting the specimen.

Supergene covellite and a translucent mineral (cerussite or anglesite?) replace galena to the extent of 20 to 30%.

Premier No.4, Vulcan No.4A and Vulcan No.2 Levels

Of the accessible levels north of the tramway only Vulcan No.2 (eastern drive) has been extensively stoped (although Vulcan No.3 level is stoped up to No.2 level). In 1532' No.4 level a 2m wide quartz vein is exposed in the cross cut to a winze (Fig. VIII-2). The vein contains fragments of wall rock cemented by sulphides and several stages of quartz. The sulphides, medium to fine grained (av. 1mm) galena, sphalerite, chalcopyrite and pyrite are present in small quantities.

Apart from the single exposure described above, pyrite was the only sulphide found in the massive quartz veins of Premier No.4, Vulcan No.4A and Vulcan No.2 (eastern and western drives). Calcite may have been present in Vulcan No.2 level as blocks of platy quartz (quartz pseudomorphs after calcite) are abundant on the mullock heap and slip below the portal of the eastern drive. Henderson & Bartrum (1913) noted that calcite was present in the lowest adit of the Premier (5 level?) but absent above this level. They also stated that the gold to silver ratio in the upper levels of the premier was 1:4 but rose to 1:2.5 in the lowest stoped level.

Figure VIII-4: Plan of the New Find workings, redrawn from old mine plans.
For location see Fig. VIII-1.

MAIN VEIN

Main Vein, Diamond Creek Waterfall

The pack track crosses Diamond Creek at the head of a high waterfall. At this locality two sets of veinlets considered to be part of the Main Vein cross the stream and coalesce on the southern side. The eastern veinlet dips 42° at 090° (strike due north), whereas the western veinlet strikes at 330° (dip not discernable).

The veinlets are up to 30mm thick (14089). A thin band (av. 1mm, up to 2mm) of fine grained sphalerite and galena lines the vein margins (14087 and 14089) and occurs as stringers in the adjacent wall rocks. Medium grained comby quartz fills the veinlets and crystals up to 7mm are developed in central vugs. Fine to medium grained (up to 2mm in 14088) pyrite and chalcopyrite occur as a thin band part way into the vein (14087 and 14088) or as aggregates of grains in the central quartz zone (14087 and 14089).

New Find Section of Main Vein

To the south of the Premier and Vulcan sections, the Main Vein and its adjoining branch veins have been worked in the New Find Section (Figs. VIII-1 and VIII-4). The workings are exposed at the surface as a 2m wide cleft in the rocks (Fig. VIII-5) which is several tens of metres deep (probably up to 60m) in places. Ore from the cleft was probably stoped from below and taken out via the New Find Low Level (1503'), Arizona No.2 Level and an unnamed adit at the southern end of the section (Fig. VIII-4).

A shaft (at least 30m deep) from Arizona No.2 Level opens to the surface by a track below the brow of the eastern side of the cleft. A short tunnel connects this area to the cleft and continues into the rock on the other side for about 3m.

Down on the hillside a tramway connects Arizona No.2 Level (entrance collapsed) to an iron shoot (for passing ore down to a hopper on the tramway below) and two adits at the

Figure VIII-5: Cleft excavated in the New Find section. The cleft is greater than 60m deep (the old plans suggest 90m) in front of the rock bridge on which the figure is standing.

southern end of the New Find workings. Both southern adits are accessible but a stope in the northern one has collapsed opening the roof to the surface, but making further passage impossible. The southern adit contains a thin quartz vein but no visible mineralisation.

MAY QUEEN

May Queen 1 level

The May Queen workings are located in Diamond Gully south of the May Queen Incline (Fig. VIII-1). From the top of the May Queen incline the tramway branches north and south. The southern branch follows on a level contour of the hill and after 35m passes an adit (considered here as May Queen No.1 Level) driven 3m into the side of the hill. An 0.8m quartz vein is exposed along the northern side of the adit, on the roof of the portal and on the ground outside, crossing under the tramway. The vein strikes 335° and consists of a number of cross cutting comby, coarsely crystalline quartz veins with some vugs. A track up by the northern side of the adit leads to a 5m open cut situated a little above the adit. The exposure is very weathered and little can be seen of the vein.

May Queen 2 level

A small hole in the ground (approximately 1.5m by 0.8m) outside the southern side of the 1 level adit opens out to a lower level situated at some considerable depth. The entrance to the lower level (considered here as May Queen 2 level) is covered by a slip but some samples of vein material were collected from the mullock heap.

The vein material generally consists of quartz cemented wall rock breccias with medium grained sphalerite and galena lining the fragments and coarse comby, sometimes vuggy, quartz (crystals typically 20mm long) filling the remainder of the vein. However some blocks exhibit cockade structure, consisting of breccia fragments surrounded by concentric rings of sulphides and quartz (Fig.4-7).

The breccia fragments contain disseminated fine grained

pyrite. Large masses of sphalerite (up to 15 x 25mm) occur developed from the banded sulphides in cavities and contain galena (av. 0.5mm, max 1.0mm), chalcopryrite (av. 0.2mm, max. 1.0mm) and pyrite (av. 0.05mm). Galena appears to be interstitial to sphalerite. Chalcopryrite occurs as grains in sphalerite or as small grains or inclusions at the edge of galena. Small inclusions of chalcopryrite occur in sphalerite and tend to be more concentrated near fractures and grain edges possibly resulting from a replacement rather than exsolution origin. A few euhedral pyrite crystals occur in or adjacent to pyrite. Quartz occurs in fractures or as small areas, however the sphalerite masses are approximately 98% sulphide.

The banded mineralisation in sample 14078b is in the following order:

1. The innermost concentric ring surrounding the breccia fragments is a band, approximately 3 to 4mm thick, predominantly composed of sphalerite (av. 2mm, max. 4mm) but also containing chalcopryrite (av. 1mm but masses up to 4mm), galena (av. 1mm, max. 3mm) and pyrite (av. 0.2mm, max. 0.7mm) occasionally separated by quartz (the band contains approximately 70% sulphides). Sphalerite contains only a few tiny inclusions of chalcopryrite (exsolution, replacement or epitaxial growth). Pyrite is subhedral to euhedral and occurs in or adjacent to chalcopryrite. Grains of chalcopryrite, sphalerite and galena have mutual boundary relations.

Two generations of pyrite occur and differ in size. The larger grains are euhedral and contain small inclusions of chalcopryrite, sphalerite and quartz and larger inclusions of galena. The smaller pyrite grains occur with quartz as "aggregates" (av. 0.1mm) in chalcopryrite. Pyrite may be replaced by quartz to give this aggregate texture.

2. 2mm band of quartz containing approximately 10% chalcopryrite (av. 0.2mm), and 40% galena. Grain boundaries indicate that the galena, chalcopryrite and quartz precipitated together.

3. Chalcopyrite (av. 0.5mm, max. 1.0mm) and subhedral pyrite (av. 0.2mm, max. 0.4mm) occur preceding, with and postdating a 0.5mm to 1mm white band of quartz prominent in hand specimen. The white band merges into galena of band 2 but does not itself contain any galena. Quartz is the major constituent of the zone. Chalcopyrite contains a few pyrite balls (av. 0.1mm dia.) and small elliptical inclusions of galena. Pyrite has abundant inclusions of chalcopyrite and galena.

After 1mm of this zone, sphalerite (av. 0.5mm, max. 2mm) appears. The sphalerite is embayed by quartz and contains abundant tiny inclusions of chalcopyrite. Galena (av. 0.5mm, max. 1mm) also occurs associated with, but in lesser quantities than sphalerite. Galena and sphalerite are embayed by euhedral quartz. Band 3 is generally 2mm wide but up to 3mm locally and contains approximately 50% sulphides.

4. 0.5mm band of unmineralised quartz.

5. 5mm band containing predominantly masses of chalcopyrite (up to 4mm long) surrounding subhedral to euhedral pyrite. Large masses of galena also occur (up to 2mm long) surrounding euhedral crystals of quartz. They have mutual boundary relations with chalcopyrite and sphalerite. Sphalerite (av. 0.5mm, max. 1.0mm) is a minor constituent of this band. It occurs as grains surrounding and embayed by euhedral quartz and contains abundant small inclusions of chalcopyrite. It also occurs as small grains in chalcopyrite. Chalcopyrite also contains small elliptical inclusions of galena (av. 0.01mm). The band contains 50-60% sulphides.

6. A 3-5mm band of chalcopyrite (av. 0.5mm, max. 1.0mm), lesser pyrite (av. 0.1mm, max. 0.3mm) and quartz averages approximately 30% sulphides. Chalcopyrite contains rare pyrite? balls and tiny elliptical inclusions of galena. Chalcopyrite is embayed by euhedral quartz. Chalcopyrite and pyrite generally occur as individual grains separated by quartz. The margins of chalcopyrite grains are serrated due to alteration to goethite and covellite.

Band 6 is invaded by a 1mm thick quartz plus pyrite (av. 0.1mm, max. 0.3mm) vein. The pyrite is subhedral to euhedral and occurs in quartz making up approximately 50% of the material. It contains abundant tiny inclusions of chalcopyrite.

In hand specimen the areas between the banded mineralisation are filled with quartz, medium to coarse grained chalcopyrite and fine grained pyrite, possibly a development of band 6 described above. Vugs containing quartz crystals up to 10mm long are developed.

Galena is variably altered to a translucent mineral (cerussite or anglesite?) and covellite.

May Queen 3 Level

Further down the hill the occurrence of No. 3 Level is marked by another mullock heap. The adit was located but found to be collapsed a short distance in from the portal. The tunnel follows a 50mm wide quartz vein (exposed along the roof for a short distance before reaching the fall). Another adit on the same level, 8m to the south-east, is also collapsed just inside the portal. Blocks from the mullock heap indicate that the vein is a quartz cemented wall rock breccia. Several stages of brecciation and deposition can be identified.

Samples 14079, 14080 and 13979 contain early unbrecciated mineralisation. A series of bands of quartz and sulphides coat the wall rock which contains disseminated pyrite. In polished section 13979 these bands are:

1. 2 to 3mm band of pyrite (av. 0.2mm, max. 0.8mm) with minor chalcopyrite (av. 0.3mm, max. 0.8mm), and rare sphalerite (av. 0.3mm, max. 0.5mm) and galena (one grain 0.5mm), broken up with white clay (sericite?) in places expanding the band to 15mm locally. Pyrite makes up approximately 50% of the band and occurs as aggregates of a few grains or strings of interlocking grains. The pyrite contains abundant tiny inclusions of chalcopyrite and larger inclusions of galena orientated along growth zones. A few grains contain large

inclusions of sphalerite and others quartz. Quartz surrounding chalcopryite is euhedral to the chalcopryite. Sphalerite contains tiny inclusions of exsolved? chalcopryite.

2. 5 to 8mm band of predominately sphalerite (massive), with quartz, galena (av. 0.5mm, max. 1.0mm) and chalcopryite (av. 0.5mm, max. 1.5mm) occurring along the inner margin of the band (most embaying the sphalerite mass) or as inclusions in the sphalerite. Inclusions of galena are subhedral to sphalerite. Rare tetrahedrite occurs in chalcopryite adjacent to sphalerite and with chalcopryite filling fractures and voids in sphalerite. The sphalerite mass is fractured (in-filled with quartz) into approximately 1mm fragments.

3. Along the outer margin of the sphalerite band, galena (av. 0.8mm, masses up to 2.5mm), chalcopryite (av. 0.4mm, masses up to 1mm), pyrite (av. 0.1mm, max. 0.2mm) and quartz occur in a 1 to 3mm band in the approximate proportions; 40% quartz, 35% galena, 23% chalcopryite and 2% pyrite. Quartz is euhedral to the galena and chalcopryite, but pyrite is subhedral to quartz. Chalcopryite contains inclusions of sphalerite, pyrite and tiny blebs of galena. Rare tetrahedrite (max. 0.2mm) occurs as inclusions in chalcopryite, at the margins of chalcopryite and sphalerite and with chalcopryite filling fractures in sphalerite.

4. A 5 to 10mm band of quartz (65%) contains scattered aggregates of pyrite (av. 0.3mm, max 0.8mm) and chalcopryite (av. 0.5mm, max. 1.0mm but masses up to 2mm) in approximately equal proportions. Pyrite is subhedral and contains tiny inclusions of chalcopryite and galena arranged zonally and rare larger inclusions of sphalerite (max. 0.02mm). Quartz is euhedral to sphalerite. Chalcopryite contains inclusions (av. 0.03mm, max. 0.2mm) of galena and sphalerite. Pyrite and chalcopryite generally occur separately but when together pyrite is euhedral towards chalcopryite. Some chalcopryite contains abundant small grains of euhedral pyrite (av. 0.03mm).

In hand specimens 14079 and 14080 band 4 is followed by a 5mm band of medium grained sphalerite and galena and subsequently by more quartz, pyrite and chalcopryite.

Several periods of brecciation and quartz deposition followed the banded mineralisation resulting in a vein breccia of sulphide fragments (typically 20mm but up to 60mm across) bounded by comby quartz veinlets (up to 35mm wide, 13900). Vugs with quartz crystals up to 5mm long are developed. This breccia appears to be the dominant vein material.

Some sulphide deposition followed an initial stage of brecciation, as evidenced by a large grain of chalcopyrite (8mm) surrounded, penetrated by, and containing inclusions of, euhedral pyrite (av. 0.4mm, max. 1.5mm) and galena (av. 1.0mm, max. 2.0mm) in p.s. 14080a. Galena adjacent to the chalcopyrite is graphically intergrown with quartz in a coarse texture. However, most of the later quartz is unmineralised.

NUMBER 1 REEF

No. 1 Reef, Tramway

235m along the tramway south of May Queen No.1 (and 12m south of the "New Find" hopper) a 1m wide vein is exposed in the western bank. It consists of approximately seven quartz stringers (max. width 12mm) dipping 65 - 90° at 235 (strike 325°) transecting an earlier quartz and sulphide cemented wall rock breccia vein of undetermined width (but less than 1m), dip and strike.

The latter vein contains breccia of silicified wall rocks (fragments av. 30mm but are up to 70mm) cemented with sulphides and quartz (veinlets up to 12mm). The fragments contain approximately 10% disseminated sulphides (p.s. 14072), mainly pyrite (av. 0.02mm, max. 0.1mm) but minor sphalerite (av. 0.05mm, max 0.2mm) and very rare galena (same size as sphalerite) also occur. Pyrite grains are euhedral and contain inclusions of galena arranged zonally.

The sulphide veinlets contain a zoned medium grained sphalerite, galena and quartz stage (approximately 60 - 80% sulphides) followed by barren vug quartz and cross cut by latter veinlets of barren quartz (the quartz stringers noted initially).

Figure VIII-6: Dendritic galena (white) in quartz (dark grey-black). The grey mineral is sphalerite. Sample 14072 from No.1 vein. 50X. See also Fig. 4-24.

Individual grains or small aggregates of subhedral pyrite (av. 0.2mm, max. 0.3mm) occur at approximately 1mm intervals separated by quartz along the margins of the braccia fragments. Sphalerite occurs veinward of the pyrite and embays its margins. An intergrowth of galena and sphalerite ranges from margining and interfingering to small veinlets of galena along fractures in the sphalerite suggesting replacement of sphalerite by galena. The proportion of galena to sphalerite varies. In one part of p.s. 14072 galena makes up 10 to 20% of the cross-section as opposed to 50 to 60% sphalerite, whereas over much of the sample a zonation is developed away from a breccia fragment. For the first 2mm galena is a minor phase (10 - 20%), however from 2 - 4mm away from the fragment it equals sphalerite in quantity and from 4mm onwards it predominates, the total width of the sulphide stage being 9mm. Some areas of the sulphide veinlet contain only galena and quartz. The latter occur in a herringbone dendritic-skeletal texture (Figs. VII-6 and 4-24).

Euhedral pyrite (av. 0.05mm) occurs very rarely and generally in quartz. Chalcopyrite occurs as small elliptical inclusions in galena and sphalerite and as small blebs (av. 0.03mm, max 0.1mm) with galena along the margins or veining. In the areas where sphalerite remains the dominant mineral throughout the vein cross section, chalcopyrite inclusions are largest, most abundant and arranged in various patterns indicating replacement or epitaxial growth (Fig. 4-20). In some grains chalcopyrite makes up 20% of the sphalerite grain.

The sulphides are succeeded by vuggy quartz at the vein centre. Some small grains of euhedral pyrite (av. 0.05mm) and anhedral chalcopyrite (av. 0.05mm, max. 0.3mm) occur at the margin of the sulphide band.

In summary pyrite appears to be the first sulphide precipitated, followed and replaced by sphalerite. Galena, chalcopyrite and quartz follow, replacing the sphalerite, and the quartz continues into vugs.

Figure VIII-7: Cut side of specimen 14073 from No.1 vein exhibiting banded sulphides followed by quartz (at first with minor sulphides) with comb structure. The sample (9cm wide x 8cm high) represents part (approximately 70% of the width) of an asymmetrical vein (the sulphides were poorly developed along the other vein margin).

No. 1 Reef, Diamond Creek Waterfall

A 2m wide vein (strike 350° , dip $40 - 50^{\circ}$ west) crosses Diamond Creek at the head of a waterfall. The vein is considered to be a continuation of No. 1 Reef and is designated No. 1 Reef Waterfall in Fig. VIII-1. It contains two parallel unmineralised 30-50mm vuggy quartz veins, one defining the footwall and separated from the other by 0.3m of country rock, followed by 0.15m of country rock and a 2.5m zone of 50 to 150mm wavy, cross cutting, comby quartz veins. The latter contain coarsely crystalline quartz (crystals up to 30mm long) and veins on the footwall side of this zone are mineralised, e.g. sample 14073 shown in Fig. VIII-7. The mineralised veins are banded, not always symmetrically, with bands of sulphides and quartz lining the walls and coarse comby, rarely vuggy, quartz filling the cavities. Fragments of wall rock are rare. Although slightly variable between veins a general sequence after 14073 (Fig. VIII-7) is as follows:

1. Fine grained pyrite disseminated in the wall rocks.
2. 3mm band of fine grained sphalerite and pyrite occurring as individual grains or aggregates of several grains scattered in quartz. Polished section (14075₂) contains sphalerite (av. 0.4mm, max. 1mm) and pyrite (av. 0.2mm, max. 0.3mm) in equal quantities and rare chalcopryrite (av. 0.1mm). Sphalerite contains inclusions of chalcopryrite probably from replacement or epitaxial growth. Pyrite is euhedral and contains a few inclusions of galena, chalcopryrite, sphalerite and quartz. In a few examples where it occurs with sphalerite it embays the latter possibly replacing it. Clusters of ascicular crystals (individuals 0.15mm long by 0.01mm wide) of pyrite occur in quartz. Galena occurs only as inclusions in other minerals.
3. 5mm band (but up to 30mm in other samples e.g. 14075) of white fine grained to microcrystalline quartz with small vugs sometimes developed. Fine grained pyrite occurs scattered sparsely in the white quartz.
4. 1mm band of fine grained pyrite and sphalerite in quartz. Polished section (14075₂) contains sphalerite (av. 0.2mm, max.

0.4mm) and pyrite (av. 0.1mm, max. 0.3mm) with minor galena (av. 0.1mm, max. 0.3mm) and chalcopryite (av. 0.05mm, max. 0.1mm) as single grains or aggregates of two or three grains scattered in quartz. Sphalerite contains inclusions of galena arranged along cleavage planes. Boundaries between sphalerite, galena and chalcopryite appear to be mutual. Pyrite is subhedral to euhedral and contains inclusions of the other sulphides but it may also be contemporaneous. One grain of electrum (0.03mm dia.) occurs solitary in quartz of this stage.

5. 1mm band of white very fine grained or microcrystalline quartz.

6. 5 to 7mm band of medium grained galena (av. 1.5mm, max. 3mm) and sphalerite (av. 2.0mm, max. 3mm but masses up to 10mm long) with minor chalcopryite and pyrite. The proportion of galena and sphalerite vary between different samples so that the band may almost entirely consist of galena or sphalerite. The band is segregated into two in p.s. 14075₂. The band nearest the wall of the vein is 2mm wide and contains sphalerite (av. 0.5mm, max. 2mm) and pyrite (av. 0.3mm, max 0.5mm) with lesser chalcopryite (av. 0.2mm, max. 0.3mm) and galena (av. 0.3mm, max. 1.0mm). The sulphides occur as aggregates of five or six grains separated by quartz. Sphalerite contains inclusions of chalcopryite generally arranged regularly along zones due to replacement or epitaxial growth. Pyrite is subhedral to quartz and chalcopryite but anhedral to sphalerite, exhibiting an intergrowth texture probably formed by coprecipitation. Pyrite contains inclusions of sphalerite, galena, and chalcopryite. Sphalerite is subhedral in contacts with chalcopryite. Galena has mutual boundary relations with chalcopryite.

2mm of medium grained quartz crystals separates the first sulphide sub-band from the second which consists of grains of galena and sphalerite (both av. 1.5mm, max. 3mm) separated by small quantities of quartz. Galena predominates over sphalerite but the two minerals have mutual boundary relations. Chalcopryite occurs as inclusions in sphalerite and rarely as grains (av. 0.3mm, max. 1mm) in aggregates with

sphalerite and galena (adjacent grains fill fractures in sphalerite) but more commonly as individual grains (av. 0.05mm, max. 0.1mm) or with pyrite and sphalerite (both av. 0.05mm, max. 0.1mm) in quartz interstitial to the medium grained galena and sphalerite.

7. 15mm band of coarse grained quartz (crystals up to 7mm long) with grains of pyrite, chalcopryite, sphalerite and galena occurring between the crystals.

8. Coarse barren comby quartz fills the centre of the vein with vugs sometimes developed.

BONANZA

At a bend in the pack track the location of the Bonanza Mine is marked by the sound of water falling down a hole, on the uphill side of the track, into a stope below (Fig. VIII-1). On the downhill side and approximately 10m below the track the adit entrance is covered by a slip but samples of vein material were collected from the mullock heap. This material was probably taken from the Bonanza vein although it may have come from the Three Fools vein (Fig. VIII-1) because, on the mine plans, both veins appear to have been intersected.

The vein is a quartz and sulphide cemented wall rock breccia(14083). Breccia fragments (up to 40 x 30mm) contain disseminated subhedral to euhedral pyrite (av. 0.1mm, max. 0.4mm). They are coated by banded sulphides which are described below from two polished sections (bands 1 to 3 from 14083a and bands 4 to 9 from 14083b) and in order of deposition around the fragments.

1. Breccia fragments are coated by a 0.8 to 2mm quartz band containing subhedral to euhedral pyrite (av. 0.2mm, max. 0.4mm), sphalerite (av. 0.3mm, max. 0.5mm), minor chalcopryite (av. 0.1mm, max. 0.3mm) and rare galena (av. 0.05mm, max. 0.1mm). Quartz embays all other phases and an interstitial relationship to quartz is particularly noted in the case of chalcopryite. Pyrite contains inclusions of quartz, chalcopryite, galena and occasionally sphalerite and develops subhedral to anhedral

boundaries to grains of these minerals. The sulphides appear to have precipitated together and occur as individual grains or aggregates of a few grains in quartz. The sulphides make up approximately 30% of the band.

2. 0.8mm band of barren quartz.

3. A band up to 5mm (in hand specimen) contains a string of sphalerite (av. 1.5mm, max. 4mm) grains separated by later galena (av. 0.3mm, max. 1mm), subhedral pyrite (av. 0.1mm, max. 0.5mm), chalcopryite (av. 0.3mm, max. 1.0mm) and quartz. These minerals also occur as inclusions (galena; av. 0.2mm, max. 0.6mm and pyrite; av. 0.1mm, max. 0.3mm) in the sphalerite masses. Chalcopryite blebs are arranged zonally in sphalerite indicating replacement of sphalerite by chalcopryite or epitaxial growth. Larger inclusions of chalcopryite (av. 0.1mm) also occur. The band contains approximately 60% sphalerite, 20% quartz, 8% chalcopryite, 8% pyrite and 4% galena.

4. 2 to 4mm band of interlocking anhedral pyrite (av. 0.3mm, max. 0.8mm) with subhedral quartz, minor sphalerite and very minor chalcopryite and galena. The chalcopryite (av. 0.2mm, max. 0.6mm) and galena (av. 0.2mm, max. 0.3mm) occur interstitial to euhedral quartz. Sphalerite (av. 0.3mm, max. 0.6mm) generally occurs in the pyrite masses at grain boundaries or on the pyrite margins with quartz, probably replacing the pyrite. The pyrite contains tiny inclusions of sphalerite and larger inclusions of galena (av. 0.05mm). The band is approximately 70% pyrite, 20% quartz, 7% sphalerite, 1% galena and 1% chalcopryite.

5. 3mm band of chalcopryite (av. 1mm, masses up to 4mm), galena (av. 1mm, max. 3mm), sphalerite (av. 1mm) and quartz. Chalcopryite surrounds most of the sphalerite and may replace it. Chalcopryite occurs as abundant tiny inclusions in sphalerite. It also may be later than galena which has subhedral boundaries to chalcopryite and occurs as inclusions in chalcopryite. In summary galena and sphalerite precipitated together followed by chalcopryite. The band contains approximately 30% chalcopryite, 20% galena, 10% sphalerite and 40% quartz.

6. Subhedral pyrite (av. 0.5mm, max. 0.8mm) occurs in clusters separated by subhedral quartz with interstitial chalcopyrite (av. 0.4mm, masses up to 2mm). Some pyrite grains are partially coated by rims of chalcopyrite. Sphalerite occurs as rare inclusions (av. 0.03mm) in chalcopyrite, and pyrite contains small inclusions of chalcopyrite (av. 0.005mm) and rarely galena (av. 0.01mm). The band is approximately 50% pyrite, 40% quartz and 10% chalcopyrite. In hand specimen the band can be seen to develop lobe structures into the vein so that it varies from 5 to 10mm thick.

7. 1mm band of barren quartz.

8. 4 to 10mm band (variable because one margin is straight and the other follows the lobate structure of band 6) of massive sphalerite. A few inclusions of galena (av. 0.1mm, max. 0.3mm) occur and are arranged along grain boundaries. Thin fractures (0.05mm approx) in sphalerite are filled with later galena, chalcopyrite and quartz. Chalcopyrite (av. 0.5mm, masses up to 1.5mm), euhedral pyrite (av. 0.2mm, max; 0.4mm) and galena (av. 0.1mm, max. 0.3mm) also fill embayments (largest 3mm long by 1.5mm wide) in sphalerite from band 7. Galena and chalcopyrite have mutual boundary relations. Pyrite contains small inclusions of chalcopyrite and galena. Chalcopyrite contains small inclusions of galena.

9. A quartz band with minor pyrite develops into vugs.

In some parts of the vein the earlier banded sulphides have been brecciated and infilled with quartz containing individual grains or aggregates of pyrite (av. 0.2mm, max. 0.8mm), minor chalcopyrite (av. 0.2mm, max. 1.0mm) and rare sphalerite (av. 0.1mm, max. 0.5mm) and galena (av. 0.1mm, max. 0.5mm) as shown in sample 14082. This is in turn cut by quartz plus abundant individual grains of euhedral pyrite (av. 0.04mm, max. 0.1mm) and later barren quartz developing vugs. These episodes may correlate with band 9 of 14083.

INVERNESS, LOYALTY AND WELCOME VEINS

Location

The locations of the Inverness, Loyalty and Welcome veins

Figure VIII-8: Plan of workings in the area of the Welcome and Inverness Veins, redrawn from old mine plans. See Fig. VIII-1 for location.

are shown in Figs. VIII-1 and VIII-8. They are described separately below.

Inverness

A 50mm quartz vein striking 180° is exposed on the walls approximately 8m in from the portal of the Vermont Drive (Fig. VIII-8). Several small open cut trenches were found between the Vermont and the northern adit (unnamed) which is collapsed approximately 22m in from the portal. A tramway (tracks still preserved outside the northern adit) originally connected the two adits but parts have been covered by a rock slide and others, slipped away. Quartz boulders lying outside the northern adit contain large vuggy quartz crystals (14098).

Loyalty

The workings on the Loyalty Vein are shown in Fig. VIII-8. The Phoenix Drive and Loyalty Low Level Drive were not located. The Loyalty Upper Level has collapsed just inside the portal but the vein is exposed at this point. It strikes at 200° , is at least 1m wide and consists of comby and vuggy quartz (14094, 14095, 14096 and 14097).

Although some plans differentiate the Loyalty and Welcome as separate veins (e.g. map 10 of Henderson & Bartrum 1913) some of the larger scale mine location maps combine them as the Welcome vein.

Welcome, Southern Adit (Hills or Ferguson's Drive)

Near its southern end, the upper pack track passes the portal of an adit (Hill's or Ferguson's Drive) driven into the hill beside the track. The adit is approximately 45m long and intersects two veins as shown in Fig. VIII-9. These veins are considered to be part of the Welcome vein.

The vein nearest the end of the tunnel dips 66° at 115° (strike 025°) and is approximately 60mm wide. It consists of comb quartz developing central vugs with quartz crystals up to 14mm long. In places it breaks into thin stringers. Pyrite is the only sulphide present and occurs disseminated in the wall rocks.

Figure VIII-9: Plan of the southern adit (Hill's or Fergusson's Drive?) intersecting the Welcome Vein, as seen by the writer. For location see Figs. VIII-1 and VIII-8.

The vein nearest the portal dips 22° at 130° (strike 040°) and is approximately 0.3m wide. This vein contains mainly medium to coarse grained quartz surrounding small breccia fragments of wall rock. Vugs are developed with quartz crystal up to 10mm long. Rare grains of sulphide (galena, sphalerite, chalcopryrite and pyrite, up to 1mm) occur with the coarse quartz but a band (up to 10mm thick) of sulphides is present along the footwall of the vein. The sulphide band is composed mainly of sphalerite but chalcopryrite, galena and pyrite are also present.

Material richer in sulphides is found on the ground just outside the portal. Wall rock fragments generally 5 to 10mm diameter are cemented by quartz and sulphides. This material is further brecciated into fragments approximately 20mm square and separated by criss-crossing veinlets of quartz 5 to 15mm thick.

In polished section 14085, the early breccia fragments contain abundant disseminated fine grained subhedral pyrite (av. 0.05mm, max. 0.1mm). These are coated by a thin band (0.3 to 2mm) of quartz containing subhedral pyrite (av. 0.2mm, max. 0.4mm) and very minor chalcopryrite (av. 0.05mm, max. 0.1mm). A band up to 4mm thick of massive sphalerite follows but at intervals is separated from the earlier material by individual grains of galena (av. 0.3mm, max. 1.0mm). Tiny inclusions of chalcopryrite in sphalerite are arranged zonally and along grain boundaries indicating replacement of sphalerite by chalcopryrite or epitaxial growth. The sphalerite is followed by quartz with chalcopryrite (av. 1.0mm, max 3.0mm) and euhedral pyrite (av. 0.5mm, max. 0.8mm). The chalcopryrite replaces the sphalerite.

MOA VEIN

A branch of the Moa vein is intersected by an adit located below the tramway (Fig. VIII-1). It consists of a 3m wide zone of quartz veins with no visible mineralisation. A sample (Fig. 4-9) reputedly from the Moa vein, and therefore probably from this mine, was donated by Mr R. Ansin and consists of quartz crystals (15mm long) covered by plates (up to 6mm across) of later barite.

APPENDIX IXLOCATION AND BRIEF DESCRIPTION OF SAMPLESINTRODUCTORY NOTESMethod of Listing

Referenced samples lodged in the rock collection of the Geology Department, Victoria University of Wellington, are listed here in two groups; the first with numbers beginning 285/37/- and the second containing numbers 13900 to 14100. Samples within each group are listed in order of increasing sample number.

Samples not Listed

M18185 and M18186 are Geology Department, University of Auckland, numbers and are not listed in the following sections. The samples were collected from the Camoola Vein of the Maratoto Mine by Mr J.V. Main and the reader is referred to Main (1971) for their specific locations.

Field Numbers

Alpha-numeric numbers listed within brackets after V.U.W. numbers are the writers field numbers.

Grid References

Grid references are from the 1:50,000 metric topographic maps N.Z.M.S. 259 and N.Z.M.S. 260 (S10, T10, T11, T12 and T13). Grid references for sheets S10, T10 and T11 (unpublished at the time of completion of this thesis) were converted from grid references for N.Z.M.S. 1 sheets using the Geological Survey's computer program.

Samples located "near" specific grid references originate from within 1km of the stated grid reference.

SAMPLES

285/37/2 (M12), near T13/560 280, Maratoto, Silver Queen Vein: Stage 2a qtz and Stage 2c fine grained qtz, sp, gn, hs, cp and py.

285/37/6 (M13), near T13/560 280, Maratoto, Silver Queen Vein: Stage 2a qtz, Stage 2b fine grained qtz, gn, hs, sp and py, and Stage 2c qtz with fine grain sp, gn, hs, cp and py.

285/37/7 (M14), near T13/560 280, Maratoto, Camoola Vein: Stage 2b fine grained qtz, sp, gn, py, cp, ac and hs. Supergene cc.

285/37/8 (M32), near T13/560 280, Maratoto, Camoola Vein: Stage 2b fine grained qtz, sp, gn, cp, py, ac and el.

13900 (W143), T13/537 034, Waiorongomai, May Queen 3 level (Fig. VIII-1), mullock heap: Stage 1 medium grained qtz, sp, gn, cp and py, and Stage 2 qtz with comb structure.

13901 (Wh36), near T13/620 200, Waihi, Martha vein: qtz and fine grained py, gn, sp, cp, ac and el. Sample courtesy of Mr J. Barbarich.

13902 (Wh37), near T13/620 200, Waihi, "Martha lode at moderate depth": qtz with fine grained py, sp, cp and gn. Geological survey sample No:7941.

13903 (Wh48), T13/620 200, Waihi, unlocated: qtz with fine grained py, sp, gn, cp and el. Mines Division display specimen.

13904 (N37), T12/495 439, Neavesville, Graces Adit: silicified black shale with fine grained py.

13905 (N36), T12/495 439, Neavesville, Graces Adit: silicified black shale with fine grained py.

13906 (Km31), T13/535 247, Komata Mine, mullock heap outside 8 level: qtz, calcite and fine grained py.

13907 (Hutt 2), T10/361 903, Patote Stream area, Hutt Creek, float: vug qtz with crystals up to 10mm long.

13908 (GB5), 259/672 723, Te Ahumata, Barrier Reefs Region, mullock heap outside 125m adit: fine grained qtz, py, mc, sp, gn, cp, pg, el, pb, apy and kaolinite. Sample courtesy of Mr W.R.H. Ramsay.

13909 (Tui30), near T13/521 053 (5 level portal), Tui Mine, Champion Vein 5 level, M stope: Stage 1 qtz, cp, py, hematite, bismuthinite, gold and tetradymite and Stage 2 qtz, sp, gn, cp and py. Supergene goethite. Sample courtesy of Dr H.W. Kobe.

13910 (Wg9), near T11/400 892, Whangapoua, Waingaro Stream, float: Stage 4 qtz, py and sb.

13911 (Wg10), near T11/400 892, Whangapoua, Waingaro Stream, float: Stage 4 qtz, py and sb.

13912 (N40), T12/499 445, Neavesville, Ajax 2 level, mullock heap: comb and vug qtz, crystals up to 40mm long.

13913 (Wh24), T13/617 201, Waihi, 2 level, small quartz stringers between 30 and 50cm away from main vein (Martha?): vug qtz, crystals up to 4mm long.

13914 (W1100), T13/535 038, Waiorongomai, Colonist Smithy level (Fig.VIII-2), vein exposed in southwestern corner of stope: Stage 1 medium grained qtz, sp, gn, cp and py, and Stage 2 qtz with vug crystals up to 8mm long.

13915 (Tui 27), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, M stope: Stage 1 qtz, cp, py, hematite, bismuthinite, gold and tetradymite. Supergene goethite. Sample courtesy of Dr H.W. Kobe.

13916 (CNS), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level, north stope: Stage 2c fine grained qtz, sp, gn, ac, cp and py, and Stage 2d qtz. Sample courtesy of Dr B.W. Robinson.

13917 (M1), near T13/560 280, Maratoto Mine, Silver Queen Vein, 5 level: Stage 2c qtz and calcite. Sample courtesy Dr B.W. Robinson.

- 13918 (M2 calcite), near T13/560 280, Maratoto Mine, Camoola Vein, south: Stage 1 calcite. Sample courtesy Dr B.W. Robinson.
- 13919 (M2 quartz), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level, extension of south drive: Stage 3 vug Qtz with crystals up to 40mm long. Sample courtesy Dr B.W. Robinson.
- 13920 (M3), near T13/560 280, Maratoto Mine, Silver Queen Vein, 5 level: Stage 2a Qtz and Stage 2c fine grained Qtz, sp, gn, hs and cp. Sample courtesy of Mr E. Coppard.
- 13921 (M4), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level, south stope, extreme end of workings: Stage 2a Qtz and calcite. Sample courtesy of Dr B.W. Robinson.
- 13922 (M5), near T13/560 280, Maratoto Mine, Silver Queen Vein: Stage 3 vug Qtz, crystals up to 70mm long, and py. Sample courtesy of Dr B.W. Robinson.
- 13923 (M6), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level, southern workings: Stage 3 Qtz and calcite with vug Qtz crystals up to 5mm long. Sample courtesy of Dr B.W. Robinson.
- 13924 (M8b), near T13/560 280, Maratoto Mine, Camoola Vein, southern workings: Stage 2a banded Qtz and calcite. Sample courtesy of Dr B.W. Robinson.
- 13925 (M9), near T13/560 280, Maratoto Mine, Silver Queen Vein: Stage 2a Qtz and Stage 2c fine grained Qtz, sp, gn, hs, cp and py.
- 13926 (M10), near T13/560 280, Maratoto Mine, Silver Queen Vein, 3 level: Stage 3 Qtz with vug crystals up to 10mm long.
- 13927 (M11), near T13/560 280, Maratoto Mine, Silver Queen Vein, 3 level: Stage 2c fine grained Qtz, sp, gn, hs, cp and py, and Stage 2c Qtz.
- 13928 (M19), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level: Stage 3 Qtz with vug crystals up to 10mm long.
- 13929 (M28), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level: Stage 1 calcite. Sample courtesy of Dr B.W. Robinson.
- 13930 (M8a), near T13/560 280, Maratoto Mine, Camoola Vein: Stage 3 Qtz and calcite with vug Qtz crystals up to 4mm long.
- 13931 (M23), near T13/560 280, Maratoto Mine, Silver Queen Vein: Stage 2a Qtz and Stage 2c fine grained Qtz, sp, gn, hs, cp and py. Sample courtesy of Mr C. Davis.
- 13932 (M24), near T13/560 280, Maratoto Mine, Silver Queen Vein, 3 level: Stage 2a Qtz and Stage 2c fine grained Qtz, sp, gn, hs, cp and py. Sample courtesy of Mr C. Davis.
- 13933 (M35), near T13/560 280, Maratoto Mine, Camoola Vein, southern workings: calcite. Sample courtesy of Dr B.W. Robinson.
- 13934 (M7), near T13/560 280, Maratoto Mine, Camoola Vein, southern workings: calcite. Sample courtesy of Dr B.W. Robinson.
- 13935 (M22), near T13/560 280, Maratoto Mine, Camoola Vein, 3 level: Stage 3 quartz and calcite with vug Qtz crystals up to 20mm long.
- 13936 (M27), near T13/560 280, Maratoto Mine, Silver Queen Vein, shaft sunk to 5 level: Stage 2a Qtz and Stage 2c fine grained Qtz, sp, gn, hs, cp and py. Sample courtesy of Dr S.D.C. Rabone.
- 13937 (M33), near T13/560 280, Maratoto Mine, Camoola Vein: Stage 2b fine grained Qtz, calcite, sp, gn, ac, cp, py and el. Supergene cv and cc. Sample courtesy of Mr E. Coppard.
- 13938 (N44), T12/499 433, Neavesville, Ajax 1 level, mullock heap: vug Qtz, crystals up to 30mm long.
- 13939 (N16), T12/499 445, Neavesville, Ajax 2 level, mullock heap: Vug and comb Qtz with crystals up to 40mm long.
- 13940 (N26), T12/496 429, Neavesville, Champion Mines, Adit 4 (see map 3 of Torckler, 1978), shaft at end of adit: Qtz.
- 13941 (N14), T12/499 445, Neavesville, Ajax 2 level: vug and comb Qtz, crystals up to 35mm long.

- 13942 (N42), T12/499 443, Neavesville, Ajax 1 level, 85m in from portal, northern wall: qtz with vug crystals up to 40mm long.
- 13943 (N39), T12/498 440, Neavesville, Birds Opencut: Vug qtz, crystals up to 20mm long.
- 13944 (N47), T12/495 439, Neavesville, Graces Opencut: vug qtz crystals. Sample courtesy of Mr L. Torckler.
- 13945 (N28), T12/495 439, Neavesville, Graces Adit: vug qtz, crystals up to 15mm long.
- 13946 (N46), T12/498 438, Neavesville, Golden Arrow Opencut: vug qtz, crystals up to 15mm long.
- 13947 (Km15), T13/540 246, Komata Mine, 8 level (Fig. I-Q-2): qtz and calcite.
- 13948 (Km18), T13/540 246, Komata Mine, 8 level (Fig. I-Q-2): qtz and calcite.
- 13949 (Km10), T13/545 245, Komata Mine, 8 level (Fig. I-Q-2): qtz with vug crystals up to 18mm long.
- 13950 (TR9), T12/542 517, Broken Hills Mine, 2 level (Fig. I-K-5): vug qtz, crystals up to 10mm long.
- 13951 (TR6), T12/542 517, Broken Hills Mine, 2 level (Fig. I-K-5): vug qtz, crystals up to 10mm long.
- 13952 (GB10), 259/673 707, Te Ahumata, Sunbeam Region, mullock heap beside shaft of the high level workings: Stage 1 qtz and py.
- 13953 (GB9), 259/670 707, Te Ahumata, Sunbeam Region, mullock heap outside southern adit of low level workings: Stage 1 qtz, py and sp.
- 13954 (GB12), 259/677 721, Te Ahumata, Barrier Reefs Region, mullock heap outside adit below high level track: Stage 2b qtz and sb. Vug qtz crystals up to 10mm long.
- 13955 (R01), T10/352 953, Tokatea (Coromandel), Royal Oak Mine, 7 level: qtz and calcite.
- 13956 (R07), T10/352 953, Tokatea (Coromandel), Royal Oak Mine: qtz with vug crystals up to 15mm long. Auckland Museum sample No. MC:3989.
- 13957 (TK2), T10/349 946, Tokatea (Coromandel), Tokatea Big Reef, outcrop near Tokatea Saddle: qtz (amethystine) with comb structure, crystals up to 30mm long.
- 13958 (B02), T10/352 927, Tokatea (Coromandel), Buffalo Mine, mullock heap: qtz (amethystine) with comb structure, crystals up to 50mm long.
- 13959 (TK1), near T10/349 946, Tokatea (Coromandel), unlocated: medium to fine grained qtz, sp, gn, cp and py. University of Auckland (Geol. Dept) sample No:MC416.
- 13960 (TK6), near T10/349 946, Tokatea (Coromandel), unlocated: medium to coarse grained qtz, cp, sp, gn and py. Geological Survey sample No:7934.
- 13961 (TK7), near T10/349 946, Tokatea (Coromandel), "Tokatea Reef": fine grained qtz, hs, sp and el. Geological Survey sample No. 7970.
- 13962 (R03), T10/352 953, Tokatea (Coromandel), Royal Oak Mine, 7 level: qtz and calcite.
- 13963 (GB2), 259/670 725, Te Ahumata, Barrier Reefs Region, 89.7m adit: Stage 2b qtz, sb and py. Sample courtesy of Mr W.R.H. Ramsay. Equivalent to University of Auckland (Geol. Dept.) sample No.19863.
- 13964 (GB3), 259/668 707, Te Ahumata, Sunbeam Region, "surface exposure of 0.25m wide reef striking E/W and dipping steeply to the north": Stage 2a qtz, py, pg and argyrodite. Supergene native Ag and ac. Sample courtesy of Mr W.R.H. Ramsay. Equivalent to University of Auckland (Geol. Dept.) Sample No. 19854.
- 13965 (MH1), 259/600 904, Miners Head, west wall of stope opposite shaft (Fig. I-A-1): qtz, cp, py, sp, po, gn and argentine pentlandite.
- 13966 (MH2), 259/600 904, Miners Head, west wall of stope opposite shaft (Fig. I-A-1): qtz.
- 13967 (M34), near T13/560 280, Maratoto Mine, Camoola Vein: Stage 2b fine grained qtz, calcite, sp, gn, py, cp, ac and el. Supergene cc. Sample courtesy of Dr B.W. Robinson.
- 13968 (TG1), T10/312 144, Northern Colville Peninsula, Tangiaro Stream, hanging wall of vein in top adit eastern side of stream: hydrothermally altered country rock with fine grained py.

- 13969 (GB4), 259/673 707, Te Ahumata, Sunbeam Region, "Sunbeam adit": Stage 2a gn, cp, sp, pg, py, mc, argyrodite, el and pb. Sample courtesy of Mr W.R.H. Ramsay. Equivalent to University of Auckland (Geol. Dept. Sample No. 19852).
- 13970 (DC4), S10/271 168, Northern Colville Peninsula, Doctors Creek, float: calcite, coarse grained (max. 12mm).
- 13971 (DC12), S10/271 168, Northern Colville Peninsula, Doctors Creek: medium to coarse grained qtz, gn, sp, cp and py, vug qtz crystals up to 6mm long.
- 13972 (SM4), S10/239 124, Northern Colville Peninsula, Sorry Mary Stream: medium to coarse grained qtz, sp, gn, cp and py, vug qtz crystals up to 5mm long.
- 13973 (SM7), S10/239 124, Northern Colville Peninsula, Sorry Mary Stream: medium to coarse grained qtz, sp, gn, cp and py.
- 13974 (SM11), S10/239 124, Northern Colville Peninsula, Sorry Mary Stream: medium to coarse grained qtz, sp, gn, cp and py, vug qtz crystals up to 6mm long.
- 13975 (SM12), S10/239 124, Northern Colville Peninsula, Sorry Mary Stream: medium to coarse grained qtz, sp, gn, cp and py, vug qtz crystals up to 3mm long.
- 13976 (SM14), S10/239 124, Northern Colville Peninsula, Sorry Mary Stream: medium to coarse grained qtz, sp, gn, cp and py, vug qtz crystals up to 5mm long.
- 13977 (Wt4), T10/558 915, Kuaotunu, Waitaia Mine, 4 level, country rock 1m from vein: hydrothermally altered greywacke with fine grained py.
- 13978 (Wh27), near T13/620 200, Waihi, "Martha Lode": medium to fine grained qtz, sp, gn, cp, py and po. Auckland Museum sample number MC6875.
- 13979 (W1110), T13/537 034, Waiorongomai, May Queen, 3 level (Fig.VIII-1), mullock heap: Stage 1 medium grained qtz, sp, gn, cp, py and thd, and Stage 2 qtz.
- 13980 (AS1), T10/360 908, Petote Stream area (Coromandel), Aitken Stream: Stage 2 qtz, vug crystals up to 20mm long.
- 13981 (AS2), T10/360 908, Petote Stream (Coromandel), Aitken Stream: Stage 1 medium to coarse grained qtz, gn, sp, py and cp, and Stage 2 qtz and py with vug qtz crystals up to 8mm long.
- 13982 (AS5), T10/360 908, Petote Stream area (Coromandel), Aitken Stream: Stage 1 medium to coarse grained qtz, gn, sp, py and cp, and Stage 2 qtz and py with vug qtz crystals up to 6mm long.
- 13983 (HC2), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 2 vug qtz, crystals up to 30mm long.
- 13984 (HC3), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 2 vug qtz, crystals up to 10mm long.
- 13985 (HC3a), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 1 medium to coarse grained qtz, sp, gn, cp and py.
- 13986 (HC3b), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 1 medium to coarse grained qtz, sp, gn, cp and py.
- 13987 (HC3c), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 1 medium to coarse grained qtz, sp, gn, cp and py.
- 13988 (HC3d), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 1 medium to coarse grained qtz, sp, gn, cp and py.
- 13989 (HC4), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 1 medium to coarse grained qtz, sp, gn, cp and py.
- 13990 (HC4₂), T10/361 903, Petote Stream area (Coromandel), Hutt Creek: Stage 1 medium to coarse grained qtz, sp, gn, cp and py.
- 13991 (PS4), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 qtz, cp, py, sp and gn (medium to coarse grained), Stage 2 qtz, cp and py (medium to coarse grained, vug qtz crystals up to 10mm long) and Stage 3 calcite (max. 4mm).

- 13992 (PS5), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 qtz, cp, py, sp and gn (medium to coarse grained), Stage 2 qtz, cp and py (coarse grained, vug qtz crystals up to 10mm long) and Stage 3 calcite.
- 13993 (PS7), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 2 qtz (vug crystals up to 12mm long) coarse grained py and cp, and Stage 3 calcite (max. 5mm).
- 13994 (PS9), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 medium to coarse grained qtz, cp, py, sp and gn, and Stage 2 qtz.
- 13995 (PS10), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 medium to coarse grained qtz, sp, gn, py and cp, and Stage 2 vug qtz with crystals up to 10mm long.
- 13996 (PS14a), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 medium to coarse grained qtz, sp, gn, py and cp, Stage 2 qtz, py and cp (coarse grained vug quartz crystals up to 7mm long).
- 13997 (PS14), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 medium to coarse grained qtz, sp, gn, py and cp, and Stage 2 qtz, with coarse grained py and cp.
- 13998 (PS15), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Chalcopyrite Lode: Stage 1 coarse grained qtz, sp, gn, py and cp, Stage 2 qtz, py and cp (coarse grained, vug qtz crystals up to 10 mm long) and Stage 3 calcite.
- 13999 (W170), T13/535 040, Waiorongomai, Vulcan 2 level (Fig.VIII-2): Stage 2 qtz and py, vug qtz crystals up to 14mm long.
- 14000 (PS21c), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Galena Lode: Stage 1 medium to coarse grained qtz, gn, sp, py and cp, and Stage 2 qtz with vug crystals up to 6mm long.
- 14001 (PS21g), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Galena Lode: Stage 1 coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz with vug crystals up to 7mm long.
- 14002 (PS21h), T11/363 899, Petote Stream Area (Coromandel), Petote Stream, Galena Lode: Stage 1 medium grained qtz, sp, gn, cp and py.
- 14003 (PS21f), T11/363 899, Petote Stream Area (Coromandel), Petote Stream, Galena Lode: Stage 1 medium grained qtz, sp, gn, cp and py.
- 14004 (Wt15), T10/558 915, Kuaotunu, Waitaia Mine, 4 level mullock heap: qtz and fine grained py and mc.
- 14005 (PS24), T11/363 899, Petote Stream area (Coromandel), Petote Stream, Galena Lode: Stage 2 vug qtz crystals.
- 14006 (PS26), T10/359 901, Petote Stream area (Coromandel), vein crossing access track on hill, southern side of Petote Stream: Stage 2 qtz with vug crystals up to 15mm long.
- 14007 (K3), T10/558 915, Kuaotunu, Waitaia Mine, 4 level mullock heap: qtz.
- 14008 (K4), T10/558 915, Kuaotunu, Waitaia Mine, 4 level mullock heap: qtz.
- 14009 (GL1), Near T10/549 940, Kuaotunu, Golden Link Mine: qtz with vug crystals up to 4mm long. Auckland Museum sample No. 368.
- 14010 (WK1), T13/553 215, Waitekauri, Jubilee low level, mullock heap: Stage 2 medium grained qtz, gn, sp, cp and py, and Stage 3 qtz with vug crystals up to 4mm long. Sample courtesy of Dr R.J. Merchant.
- 14011 (WK2), T13/553 215, Waitekauri, Jubilee low level, mullock heap: Stage 2 medium to fine grained qtz, sp, py, cp and gn, and Stage 3 qtz with vug crystals up to 5mm long. Sample courtesy of Dr R.J. Merchant.
- 14012 (WK3), T13/553 215, Waitekauri, Jubilee low level, mullock heap: Stage 2 medium to fine grained qtz, sp, cp, py and gn, and Stage 3 qtz with crystals up to 10mm long. Sample courtesy of Dr R.J. Merchant.

- 14013 (WK4), T13/450 205, Waitekauri, Maoriland Vein (c.f. Rabone, 1971, p86, bottom three lines): vug qtz crystals up to 50mm long. Sample courtesy of Dr S.D.C. Rabone.
- 14014 (WK5), T13/548 215, Waitekauri, Jubilee low level at junction of crosscut and drive: vug qtz crystals up to 25mm long. Sample courtesy of Dr S.D.C. Rabone.
- 14015 (WK6), T13/547 212, Waitekauri, Jubilee low level: Stage 2 qtz and fine grained cp, sp, py and gn. Sample courtesy of Dr S.D.C. Rabone.
- 14016 (WK7), T13/553 215, Waitekauri, Jubilee low level mullock heap: Stage 2 medium grained qtz, sp, cp, py and gn, and Stage 3 qtz with vug crystals up to 4mm long. Sample courtesy of Dr R.J. Merchant.
- 14017 (WK9), near T13/210 545, Waitekauri, Jubilee Mine 2 level: Stage 2 medium grained qtz, cp and py. University of Auckland (Geol. Dept) sample No. MC460 (Russell Collection:272).
- 14018 (WK11), T13/547 212, Waitekauri, Jubilee low level, 790m in from portal: Stage 2 fine grained qtz, py, cp, sp and gn, and Stage 3 qtz, py and cp with vug qtz crystals up to 3mm long. Sample courtesy of Dr S.D.C. Rabone. Equivalent to University of Auckland (Geol. Dept) sample No.18619.
- 14019 (WK12), T13/553 215, Waitekauri, Jubilee low level mullock heap: Stage 2 fine grained qtz, sp, cp, gn and py. Sample courtesy of Dr S.D.C. Rabone. Equivalent to University of Auckland (Geol. Dept) sample No.18606.
- 14020 (WK13), T13/553 215, Waitekauri, Jubilee low level mullock heap: Stage 2 medium grained qtz, sp, cp, gn and py, and Stage 3 qtz with vug crystals up to 4mm. Supergene cv. Sample courtesy of Dr S.D.C. Rabone. Equivalent to University of Auckland (Geol. Dept) sample No.18600.
- 14021 (TL2), T13/514 156, Karangahake, Talisman Mine, 11 level, approximately 60m in from portal: chalcedonic, comb and vug qtz. Vug qtz crystals up to 5mm long.
- 14022 (TL8), T513/513 155, Karangahake, Talisman Mine, 8 level, Maria Vein: chalcedonic qtz with rare vugs containing qtz crystals up to 5mm long.
- 14023 (TL17), near T13/513 151, Karangahake, Talisman Mine, unlocated: qtz, gn, sp, cp and py. University of Auckland (Geol. Dept) sample No. MC:853.
- 14024 (TL21), near T13/513 151, Karangahake, Talisman Mine, Maria Vein: qtz, gypsum, sp, gn, cp and py. Geological survey sample No:8437.
- 14025 (TL22), near T13/513 151, Karangahake, Talisman Mine, 14 level, Maria Vein: qtz, calcite, sp, gn, cp, py and el. Geological Survey display sample.
- 14026 (TL24), near T13/513 151, Karangahake, Talisman Mine, 13 level, Bonanza section of Maria Vein at sea level: (20 oz. 6dwt 16gr. Au and 98 oz. 4dwt. 22gr. Ag per ton) qtz, py, cp, sp and gn. Auckland Museum specimen, no number.
- 14027 (TL25), near T13/513 151, Karangahake, Talisman Mine, 13 level, Bonanza section of Maria Vein 3m below sea level: (9 oz. 17dwt. 15gr. Au and 52 oz. 5dwt. 8gr. Ag per ton) qtz, sp, py, cp, gn and el. Auckland Museum specimen, no number.
- 14028 (Wt18), T10/558 915, Kuaotunu, Waitaia Mine, 5 level mullock heap: qtz and medium to fine grained py and marcasite.
- 14029 (MM2), near T13/513 151, Karangahake, Talisman Mine, Marmion Extended Lode: qtz with vug crystals up to 4mm long. Auckland Museum sample No. 527.
- 14030 (GJ1), near T13/625 205, Waihi, Grand Junction Mine, unlocated: qtz and calcite. Auckland Museum sample no. MC:6833.
- 14031 (GJ2), near T13/625 205, Waihi, Grand Junction Mine, unlocated: calcite. Auckland Museum sample no. MC:6913.
- 14032 (GJ3), near T13/625 205, Waihi, Grand Junction Mine, unlocated: fine grained qtz, py, sp, gn, cp, ac and el with later vug qtz (crystals up to 8mm long) and pg. Auckland Museum sample no. MC:6793.
- 14033 (GJ4), near T13/625 205, Waihi, Grand Junction Mine, unlocated: fine grained qtz, gn, sp, py and cp. Mines Division display specimen.

- 14034 (Wh5), T13/622 199, Waihi, No.5 shaft, mullock heap: chalcedonic, comb and vug qtz. Vug qtz crystals up to 5mm long.
- 14035 (Wh4), T13/622 199, Waihi, No.5 shaft, mullock heap: chalcedonic, comb and vug qtz.
- 14036 (Wh8), near T13/618 202, Waihi, at bottom of winze from opencut to a drive on the Martha Vein, qtz stringer parallel to Martha: chalcedonic and vug qtz. Vug qtz crystals up to 10mm long.
- 14037 (Wh10), T13/618 201, Waihi, 3 level (Martha Hill), stope in Martha Vein: chalcedonic and vug qtz. Vug crystals up to 10mm long.
- 14038 (Wh15), near T13/618 202, Waihi, at bottom of winze from opencut to a drive on the Martha Vein, qtz stringers parallel to Martha Vein: vug qtz, crystals up to 6mm long.
- 14039 (Wh28), near T13/620 200, Waihi, Martha Vein, unlocated: medium to fine grained qtz, sp, gn, cp and py. Auckland Museum sample No. MC:6855.
- 14040 (Wh29), near T13/620 200, Waihi, Martha Mine, unlocated: medium to fine grained qtz, sp, gn, py, cp and po, later comb (crystals up to 10mm) and vug (crystals up to 3mm) qtz. Auckland Museum sample No. MC:6979.
- 14041 (Wh30), near T13/620 200, Waihi, Martha Mine, unlocated: medium to fine grained qtz, gn, cp, py and sp. Auckland Museum sample No. MC:6855.
- 14042 (Wh32), near T13/620 200, Waihi, Martha Mine, unlocated: qtz (amethystine) with comb structure, crystals up to 30mm long. Auckland Museum sample No. MC:6949.
- 14043 (Wh35), near T13/620 200, Waihi, Victoria Vein, adit level: fine grained qtz, sp, gn, py, cp, ac and el. Auckland Museum sample No. 294.
- 14044 (Wh40), near T13/620 200, Waihi, Martha Vein east, 5 level: calcite. Geological Survey sample No. 2776.
- 14045 (Wh41), near T13/620 200, Waihi, Empire Vein, 12 level: qtz (amethystine) with comb structure, crystals up to 10mm long. Geological Survey sample No. 8060.
- 14046 (Wh43), near T13/620 200, Waihi, Martha Mine, unlocated: fine grained qtz, sp, gn, py, cp and el. Geological Survey sample No. 7810.
- 14047 (Wh44), near T13/620 200, Waihi, Martha Vein, 7 level: fine grained qtz, sp, gn, py, cp and el. Geological Survey sample No. 7988.
- 14048 (Wh45), near T13/620 200, Waihi, unlocated: fine grained qtz, sp, gn, cp, py, ac and el. Auckland Museum specimen, no number.
- 14049 (Wh42), near T13/620 200, Waihi, Martha Vein, "at depth": fine grained qtz, sp, gn, py and cp. Geological Survey No. 7935.
- 14050 (Wh47), near T13/620 200, Waihi, Martha Vein, 10 level: medium grained qtz, cp and py. Sample courtesy of Mr J. Barbarich.
- 14051 (Wh49), near T13/620 200, Waihi, unlocated: qtz, sp, py, cp and gn. Mines Division display specimen.
- 14052 (Wh50), near T13/620 200, Waihi, Martha Vein, 10 level: medium to fine grained qtz, sp, gn, cp, py, ac, thd and el. Mines Division display specimen.
- 14053 (Tui3), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level: Stage 2 medium to coarse grained qtz, sp, gn, cp and py.
- 14054 (Tui6), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level: Stage 3 qtz. Sample courtesy of Mrs R. Handley.
- 14055 (Tui12), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level: Stage 2 coarse grained qtz, sp, gn, py and cp. Sample courtesy of Dr B.W. Robinson.
- 14056 (Tui13), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level: Stage 2 medium grained sp, gn, py and cp, and comb qtz (crystals up to 10mm long).
- 14057 (Tui14), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, Stope L1: Stage 2 medium to coarse grained qtz, sp, gn, cp and py. Sample courtesy of Dr B.W. Robinson.
- 14058 (Tui15), near T13/521 053 (5 level portal), Tui Mine, Ruakaka Vein, 3 level, 20m north of stope 18: Stage 2 coarse grained sp, gn, py, cp and thd. Sample courtesy of Dr B.W. Robinson.

- 14059 (Tui17), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, end of workings (1973): Stage 2 medium grained qtz, sp, gn, py and cp, and Stage 3 comb qtz (crystals up to 12mm long) and kaolinite. Sample courtesy of Dr B.W. Robinson.
- 14060 (Tui18), near T13/521 053 (5 level portal), Tui Mine, Ruakaka Vein, 3 level, 20m north of Stope 18: Stage 2 coarse grained sp, gn, py, cp and qtz with vug crystals up to 10mm long.
- 14061 (Tui19), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, DD crosscut: Stage 2 coarse grained sp, gn, py, cp and qtz, and Stage 3 comb qtz with crystals up to 15mm long. Sample courtesy of Dr B.W. Robinson.
- 14062 (Tui20), near T13/521 053 (5 level portal), Tui Mine, Ruakaka Vein, 2 level: Stage 2 medium to coarse grained sp, gn, py, cp, comb qtz (crystals up to 7mm) and vug qtz. Sample courtesy of Dr. B.W. Robinson.
- 14063 (Tui21), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, approximately 475m NE from access cross-cut: Stage 2 coarse grained, vug qtz, sp and gn. Sample courtesy of Dr A. Wodzicki.
- 14064 (Tui22), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, approximately 475m NE from access cross-cut: early Stage 2 qtz. Sample courtesy of Dr A. Wodzicki.
- 14065 (Tui23), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, approximately 475m NE from access cross-cut: Stage 2 coarse grained qtz, sp, gn, py and cp. Sample courtesy of Dr A. Wodzicki.
- 14066 (Tui 25), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level: Stage 1 medium to fine grained qtz, py, cp and hematite. Supergene goethite. Sample courtesy of Mr E. Coppard.
- 14067 (Tui26), near T13/521 053 (5 level portal), Tui Mine, Ruakaka Vein: Stage 2 medium grained sp and gn covered with Stage 3 qtz and ba. Plates of ba up to 8mm across. Sample courtesy of Mr E. Coppard.
- 14068 (Tui28), near T13/521 053 (5 level portal), Tui Mine, Champion Vein, 5 level, M stope: Stage 1 medium grained qtz cp and py, and Stage 2 qtz with vug crystals up to 6mm long. Sample courtesy of Dr H.W. Kobe.
- 14069 (Tui29), T13/521 053, Tui Mine, mullock heap: qtz.
- 14070 (W13), T13/028 538, Waiorongomai, Moa Vein (Fig. VIII-1): Stage 2 qtz (vug crystals up to 10mm long) coated with plates (up to 5mm across) of Stage 3 ba. Sample courtesy of Mr R. Ansin.
- 14071 (W116), T13/535 039, Waiorongomai, Canadian Creek (Fig. VIII-1) float: Stage 2 vug qtz, crystals up to 10mm long.
- 14072 (W121), T13/536 033, Waiorongomai, Diamond Gully, No.1 Reef, near a hopper on the tramway (Fig. VIII-1): Stage 1 medium grained qtz, sp, gn, cp and py, and Stage 2 qtz.
- 14073 (W122), T13/535 033, Waiorongomai, No.1 Vein exposed at the head of a waterfall in Diamond Creek (Fig. VIII-1): Stage 1 medium to coarse grained qtz, sp, gn, py, cp and el, and Stage 2 qtz with comb crystal up to 15mm long.
- 14074 (W125), T13/535 033, Waiorongomai, No.1 Vein exposed at the head of a waterfall in Diamond Creek (Fig. VIII-1): Stage 1 medium grained qtz, sp, gn, py and cp, and Stage 2 qtz with vug crystals up to 10mm long.
- 14075 (W127), T13/535 033, Waiorongomai, No.1 Vein exposed at the head of a waterfall in Diamond Creek (Fig. VIII-1): Stage 1 medium to coarse grained qtz, sp, gn, py and cp, and Stage 2 qtz.
- 14076 (W133), T13/535 038, Waiorongomai, Colonist Smithy level (Fig. VIII-2), loose material on floor of stope: Stage 1 medium to coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz.
- 14077 (W135), T13/535 038, Waiorongomai, Colonist Smithy level (Fig. VIII-2), loose material on floor of stope: Stage 1 medium grained qtz, sp, gn, cp, py, hs and el, and Stage 2 qtz with vug crystals up to 4mm long.

- 14078 (W139), T13/537 034, Waiorongomai, May Queen 2 level (Fig. VIII-1), mullock heap: Stage 1 medium to coarse ground qtz, sp, gn, cp and py, and Stage 2 qtz with vug crystals up to 9mm long. Supergene cv and goethite.
- 14079 (W141), T13/537 034, Waiorongomai, May Queen 3 level (Fig. VIII-1) mullock heap: Stage 1 medium to coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz with comb/vug crystals up to 12mm long.
- 14080 (W142), T13/537 034, Waiorongomai, May Queen 3 level (Fig. VIII-1), mullock heap: Stage 1 medium to coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz.
- 14081 (W145), T13/537 034, Waiorongomai, May Queen 3 level (Fig. VIII-1), mullock heap: Stage 2 qtz.
- 14082 (W153), T13/030 536, Waiorongomai, Bonanza (~3 Fools?) Vein (Fig. VIII-1), mullock heap outside collapsed adit: Stage 1 medium grained qtz, sp, gn, cp and py, and Stage 2 qtz and py.
- 14083 (W154), T13/030 536, Waiorongomai, Bonanza (~3 Fools?) Vein (Fig. VIII-1), mullock heap outside collapsed adit: Stage 1 medium to coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz and py.
- 14084 (W156), T13/029 537, Waiorongomai, Welcome Vein southern adit (Figs VIII-1, and VIII-9), 30cm qtz vein 8m in from portal: Stage 1 medium to coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz with vug crystals up to 4mm long.
- 14085 (W157), T13/029 537, Waiorongomai, Welcome Vein southern adit (Figs VIII-1, and VIII-9), loose material outside adit: Stage 1 medium to coarse grained qtz, sp, gn, cp and py, and Stage 2 qtz.
- 14086 (W158), T13/029 537, Waiorongomai, Welcome Vein southern adit (Figs VIII-1 and VIII-9), loose material outside adit: Stage 1 medium grained qtz, sp, gn, cp and py, and Stage 2 qtz.
- 14087 (W164), T13/534 033, Waiorongomai, Main Vein exposed at the head of a waterfall in Diamond Creek (Fig. VIII-1): Stage 1 medium grained qtz, gn, sp, py and cp, and Stage 2 qtz with vug crystals up to 7mm long.
- 14088 (W165), T13/534 033, Waiorongomai, Main Vein exposed at the head of a waterfall in Diamond Creek (Fig. VIII-1): Stage 1 medium grained qtz, gn, sp, py and cp, and Stage 2 qtz.
- 14089 (W166), T13/534 033, Waiorongomai, Main Vein exposed at the head of a waterfall in Diamond Creek (Fig. VIII-1): Stage 1 medium grained qtz, gn, sp, py and cp, and Stage 2 qtz.
- 14090 (W167), T13/534 033, Waiorongomai, 40cm thick qtz vein exposed 50m in from portal in an adit above the pack track (Fig. VIII-1) probably part of Main Vein: Stage 2 vug qtz with crystals up to 80mm long.
- 14091 (W180), T13/534 039, Waiorongomai, Main vein exposed at head of a large slip. (Fig. VIII-1): Stage 2 qtz, vug crystals up to 15mm long.
- 14092 (W183), T13/535 038, Waiorongomai, Colonist Smithy level (Fig. VIII-2), loose material on floor of stope: Stage 1 medium to coarse grained qtz, sp, gn, cp, py, hs and el, and Stage 2 qtz.
- 14093 (W187), T13/534 035, Waiorongomai, New Find, boulder of qtz, at northern end of opencut (Figs. VIII-1 and VIII-4): Stage 2 vug qtz, crystals up to 20mm long.
- 14094 (W189), T13/030 537, Waiorongomai, Welcome Vein, northern adit (Figs VIII-1 and VIII-8), vein exposed 1m in from portal: Stage 2 qtz, vug crystals up to 15mm long.
- 14095 (W190), T13/030 537, Waiorongomai, Welcome Vein, northern adit (Figs VIII-1 and VIII-8), Vein exposed 1m in from portal: Stage 2 qtz, vug crystals up to 20mm long.
- 14096 (W191), T13/030 537, Waiorongomai, Welcome Vein, northern adit (Figs VIII-1 and VIII-8), Vein exposed 1m in from portal: Stage 2 qtz, vug crystals up to 25mm long.
- 14097 (W192), T13/030 537, Waiorongomai, Welcome Vein, northern adit (Figs VIII-1 and VIII-8), Vein exposed 1m in from portal: Stage 2 qtz, vug crystals up to 20mm long.

14098 (W194), T13/030 537, Waiorongomai, Inverness Vein northern adit (Figs VIII-1 and VIII-8), loose block of qtz outside portal: Stage 2 vug qtz, crystals up to 25mm long.

14099 (W197), T13/030 536, Waiorongomai, Welcome Vein: single 40mm long crystal of qtz coated with plates (up to 5mm across) of Stage 3 ba (Fig. 4-34). Sample courtesy Mr E. Coppard.

14100 (W198), T13/538 036, Waiorongomai, McLean's 1100' level (Figs VIII-1 and VIII-2), mullock heap: Stage 1 medium grained qtz, sp, gn, py, cp, hs and altaite, Stage 2 qtz and supergene cv.