Stable isotope geochemistry of Paleocene to Early Eocene strata around southern New Zealand

By

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ABSTRACT

The Late Teurian (Paleocene) Tartan Formation is an organic-rich mudstone that has been identified in five of the eight exploration wells drilled in the Great South Basin, and three of four exploration wells drilled in the Canterbury Basin.

In this study, the geochemistry of two wells from the Great South Basin (Pukaki-1 and Rakiura-1) and four wells from the Canterbury Basin in southern New Zealand (Resolution-1, Clipper-1, Galleon-1, and Endeavour-1) have been investigated using elemental analyser isotope ratio mass spectrometric (EA-IRMS) analyses on selected sidewall core and cuttings samples. This study builds on previous geochemical work by the author from five other wells from the Great South Basin (Takapu-1A, Toroa-1, Pakaha-1, Kawau-1A, and Hoiho-1C).

All wells except Rakiura-1, Takapu-1A, and Resolution-1 showed geochemical characteristics that allowed recognition of the Tartan Formation. The formation is characterised by enrichments in TOC (typically above 3%) and ^{13}C (generally $\delta^{13}C$ ratios are between -21 and -17‰), indicating a significant marine contribution. C/N ratios recorded within the Tartan Formation are all above 20, which suggest that the organic matter contains a significant contribution from terrestrial and/or altered marine material. Geochemical evidence of samples within the Tartan Formation suggests that it contains a mixture of marine bacterial/plant/algal and C_3 terrestrial plant source components. This is consistent with the findings of Killops *et al.* (2000), who reported from biomarker studies that the organic matter of some Great South Basin samples contained organic matter derived from a marine source with varying degrees of terrestrial contribution.

The Tartan Formation is distinct from enclosing formations which are characterised by low organic contents (generally below 2%), isotopically light $\delta^{13}C$ values (typically around -26‰), which is indicative of terrestrial C_3 plant matter, and a wide range of C/N ratios (ranging from 4 to 64). The latter suggests that there were varying degrees of preservation of the deposited organic matter within these formations. Organic matter within enclosing formations appears to be derived from a combination of C_3 land plants and marine material.

The high TOC content of Tartan Formation sediments compared to the underlying formation suggests that it represents a profound change in depositional conditions. Conditions for the preservation and accumulation of organic matter were more favorable prior to deposition of the Tartan Formation than following it.

The enrichment of ^{13}C and the high TOC contents within the Tartan Formation are similar to those for the mid to Late Teurian Waipawa Formation that has been identified throughout many of New Zealand's major sedimentary basins; however, TOC and $\delta^{13}C$ values for the Tartan Formation exceed those previously reported for the Waipawa Formation.

Geochemical changes characteristic of the Tartan Formation are recognised below the lithological base of the formation in some wells, contemporaneous with the onset of the Paleocene Carbon Isotope Maximum (PCIM), and represent different lithostratigraphic expressions of that event. Termination of the environmental effects associated with the PCIM around New Zealand appears to have been diachronous and differences between the exact ages and stratigraphic positions of the Tartan and Waipawa formations are attributed to local environmental variations during deposition. TOC and $\delta^{13}C$ enrichments associated with the Tartan Formation are not ubiquitous, and the formation has variable thickness throughout the Great South and Canterbury basins. It is concluded that the Tartan and Waipawa formations are correlatives.

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CHAPTER 1

Introduction

1.1 Aim and significance of study

This study is an investigation of the stable isotope geochemistry of the Tartan Formation and adjacent formations in the Great South and Canterbury basins of southern New Zealand.

The Tartan Formation is mid to Late Teurian (Paleocene) in age and is of interest to the petroleum exploration industry because it is considered to be a lateral equivalent of the mid to Late Teurian Waipawa Formation that is widely distributed throughout most of New Zealand's major sedimentary basins (see Chapter 3). The Waipawa Formation is considered to be an important hydrocarbon source rock, especially in the East Coast Basin; however, discussion of the Tartan Formation as a hydrocarbon source rock is beyond the scope of the present study..

This study focuses on characterisation and correlation of geochemical signatures of the Tartan Formation and parts of the adjacent formations in the Great South and Canterbury basins. The geochemical relationship between the Tartan and Waipawa formations are investigated as well as the global environmental effects during Tartan Formation deposition. Deposition of the Tartan Formation appears to be coincident with at least part of the global Paleocene Carbon Isotope Maximum (PCIM) and may represent a facies that was deposited as a result of environmental changes associated with the PCIM (Hollis *et al.* 2005).

The present study builds on past research by the author on the Tartan Formation from five exploration wells in the Great South Basin (Meadows, 2008) and is expanded to include two further exploration wells from the Great South Basin and four exploration wells from the Canterbury Basin.

This study, and the study by Meadows (2008), on which the present study is based on, has examined the total organic carbon (TOC) content, C/N ratio and $\delta^{13}C$ values of cuttings and sidewall core samples. The Tartan Formation is defined by its lithology and is recognised by its gamma ray response (Cook *et al.* 1999). Here, TOC concentrations of the samples are of prime importance, as the organic richness of the samples acts as a proxy to allow formation boundaries to be identified and constrained. The nitrogen content for each sample was also recorded to be used in conjunction with the TOC results to give C/N ratios. The latter are important for determining the type and source of the organic matter present.

Stable isotope fractionation in chemical reactions is dependant on the bond strength between atoms. Bond strength is dependant on the mass of the atoms on each end of the bond; hence slight mass differences between isotopes will result in bond strength variations in a molecule. This effect causes equilibrium and kinetic differences in a given reaction, with the lighter or heavier isotopic system being preferentially favoured over the other, resulting in fractionation (Anbar and Rouxel, 2007). The type of carbon isotopic fractionation of relevance to this study is biological kinetic fractionation by photosynthesising plants and algae. Implications of this to determinations of the source of the organic content of the samples are discussed in Chapter 7.

Carbon stable isotope geochemistry is used here to identify and define geochemical boundaries within the wells investigated, to allow isotopic characterisation of the Tartan Formation, and to correlate global $\delta^{13}C$ changes during the Paleocene to Tartan Formation deposition. $\delta^{13}C$ studies can provide insight into the timing and extent of past environmental perturbations and indicate how conditions have varied throughout geological time. Sources of organic matter within the Tartan Formation are also interpreted, as these data can provide insight into the type of the organic matter present, as different plants, algae and marine bacteria have distinctive isotopic characteristics.

1.2 Area of study

The Great South Basin lies off the southeast coast of the South Island of New Zealand (Fig. 1.1). The basin covers an area of approximately 100,000 km^2, with water depths ranging from 100 m to 1250 m and with a mean depth of 700 m. The northern limit of the basin is taken as 46°S, and the southern limit is 50°S. The westernmost part of the basin lies at 168°E, and it extends east to 172°E (Cook *et al.* 1999).

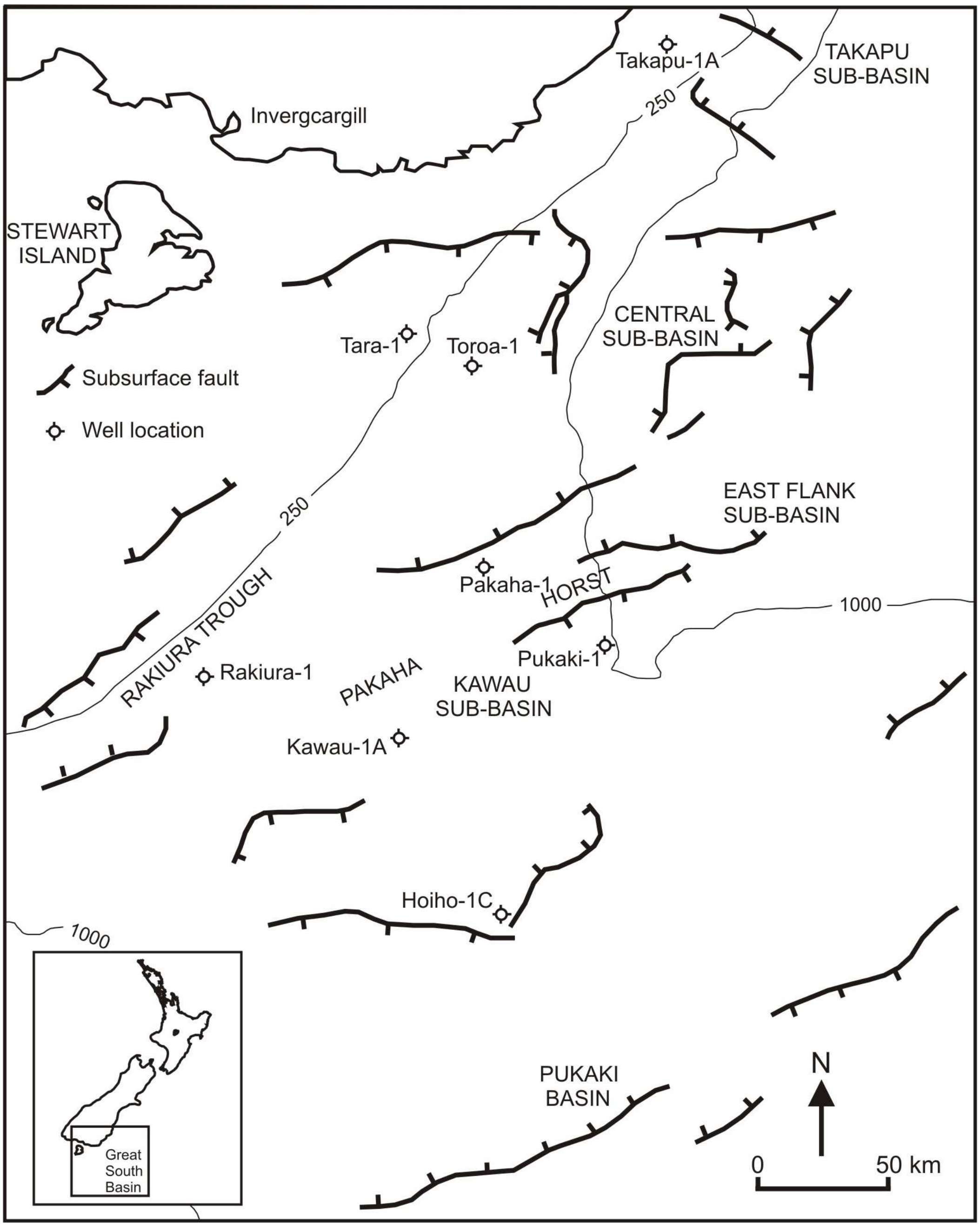

Figure 1.1 Location map and distribution of petroleum exploration wells of the Great South Basin (Redrawn from Crown Minerals, 2008a).

The Canterbury Basin extends from the onshore Canterbury Plains over an extensive offshore region east of the South Island of New Zealand (Fig. 1.2). The basin covers an area of approximately 55,000 km^2, of which around 30,000 km^2 is offshore (Killops *et al.* 1997). The northern limit of the basin is taken as 44°S and the southern limit approximately 46°S.

The westernmost area of the basin lies around 171°E, and it extends east to 174°E (deduced from Fig. 1, Killops *et al.* 1997).

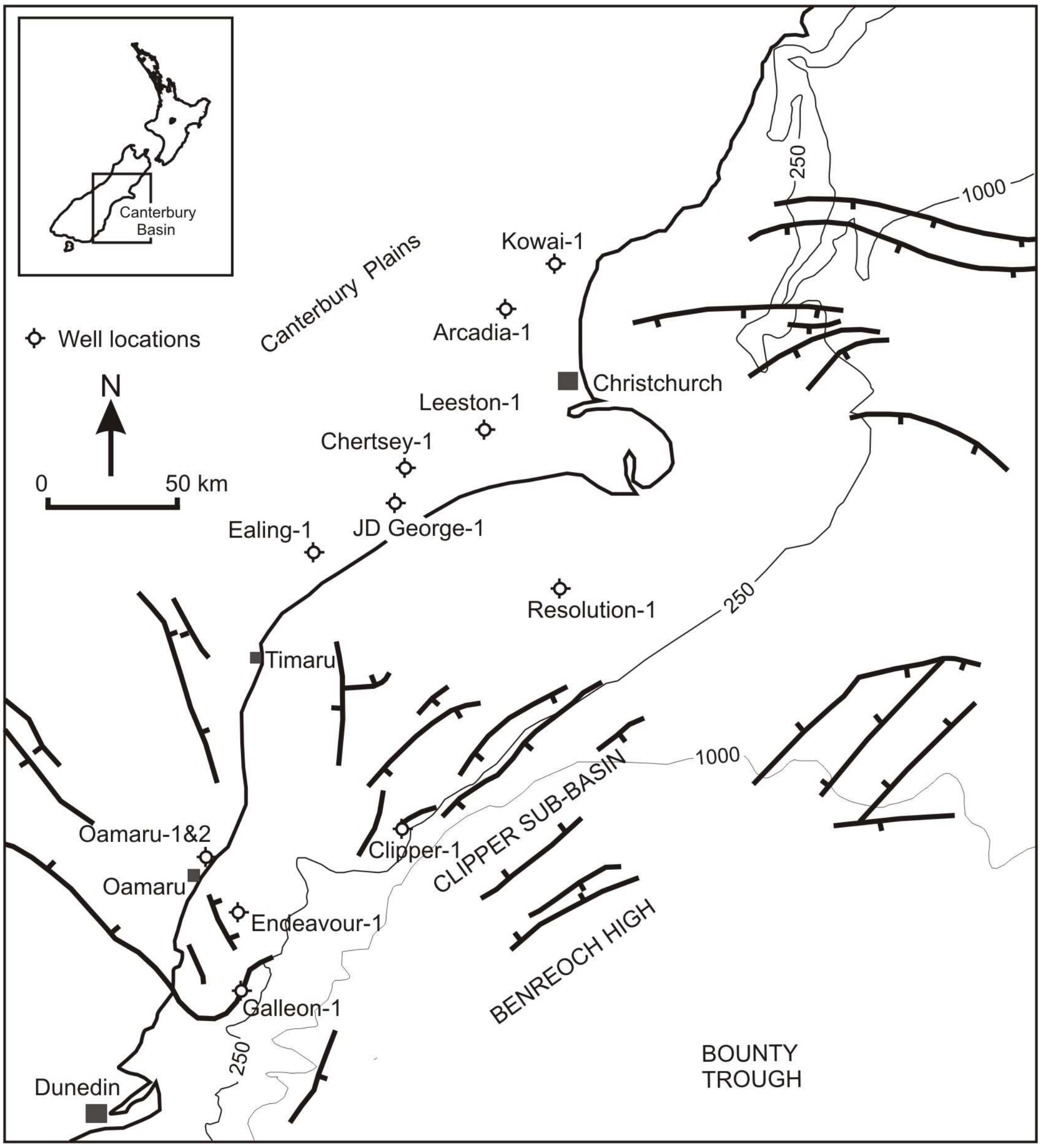

Figure 1.2 Location map and distribution of petroleum exploration wells of the Canterbury Basin (Redrawn from Crown Minerals, 2008b).

1.3 Exploration history

The Great South Basin was initially defined by geophysical surveys carried out by the Sea Hunt exploration group. Between 1968 and 1983 more than 30,000 line km of seismic reflection data were collected (Cook *et al.* 1999), with eight petroleum exploration wells drilled between 1976 and 1984. During 1976 and 1977, the Sea Hunt consortium drilled four wells in License 863 (Toroa-1, Pakaha-1, Kawau-1A, and Hoiho-1C; Fig. 1.1). In 1978 Petrocorp drilled two further wells, Tara-1 and Takapu-1A. The Placid Oil Company drilled Rakiura-1 and Pukaki-1 in 1983 and 1984 respectively. The four offshore petroleum exploration wells (Endeavour-1, Resolution-1, Galleon-1, and Clipper-1; Fig. 1.2) of the Canterbury Basin were drilled between 1970 and 1985 by BP Shell Todd (Canterbury) Services Limited.

1.4 Previous studies of the Great South and Canterbury basins

Great South Basin

The first comprehensive published accounts of the Great South Basin were compiled by Carter (1988a, b). Carter (1988a) defined a formal stratigraphic framework for the eastern South Island and placed the Great South Basin stratigraphy within this framework (Cook *et al.* 1999). Beggs (1993) proposed a revised stratigraphy for the Great South Basin, and Raine *et al.* (1993, 1994) provided a comprehensive review of the foraminiferal and palynological biostratigraphy for seven of the petroleum exploration wells in the basin. Killops *et al.* (1997) used geochemistry to report the petroleum potential and oil-source correlation in the Great South and Canterbury basins. Cook *et al.* (1999) have published a compilation of the Great South Basin petroleum industry exploration data and information from petroleum reports, including well logs, as one of the IGNS Cretaceous-Cenozoic geology monograph series. Well completion reports for each of the wells investigated from the Great South Basin (Placid Oil Co. 1984 a, b; Hunt International Petroleum 1977 a, b, c; 1978, a b) were useful for identifying structural and stratigraphical features of the basin and of each of the wells examined. The age and depositional environments of the Tartan Formation and enclosing formations were examined by Schioler and Roncaglia (2008) using detailed palynological analyses of the sidewall core samples from Great South Basin exploration wells.

As previously mentioned, the present study builds on previous research undertaken by the author (Meadows, 2008). That work involved $\delta^{13}C$, TOC and C/N examination of the Tartan Formation from five exploration wells in the Great South Basin. The research focused on the geochemical characteristics of the Tartan Formation and enclosing formations, the sources of organic matter within these formations and correlation to the

Waipawa Formation, a lithostratigraphic equivalent found in several other major sedimentary basins around New Zealand. A digital copy of Meadows (2008) is included with this dissertation.

Canterbury Basin

A detailed list of past studies of the Canterbury region and Canterbury Basin is given in Field and Brown (1989). Previous studies of the Canterbury Basin that are of greatest importance to the present research include the individual well completion reports for each well examined: Milne (1975); Wilding and Sweetman (1971); Hawkes and Mound (1984); and Wilson (1985), and the publication by Field and Brown (1989). Petroleum Reports by Anderton *et al* (1982); Mound and Pratt (1984); Simpson (1993); Shell BP Todd (1984); Olson (1996) were all useful in presenting detailed information on the tectonic history, stratigraphy, geochemistry, and petroleum geology of the Canterbury Basin.

1.5 Outline of this study

Chapter 1 provides a brief introduction into the aims and significance of this study together with a basic history of exploration and research of the Great South Basin. Ages are discussed in terms of both international and local subdivisions (Appendix 1; derived from Geological and Nuclear Sciences, 2003). Chapter 2 is a compilation of data that detail the stratigraphy and a brief structural history of areas of the basin relevant to this study. The general stratigraphy of the East Coast Basin is included here, and used as a comparison to the stratigraphy of the Great South and Canterbury basins and as a basis for discussion in later chapters. Chapter 3 details the nomenclature, distribution, depositional environments, characteristic lithological features and age of the Tartan Formation. Environmental conditions that are likely to have contributed to the deposition of the Tartan and Waipawa formations and equivalents found elsewhere in New Zealand are described in Chapter 4. Methods and analytical procedures employed in this study are described in Chapter 5. The results from mass spectrometry analyses are described and compared in Chapter 6. The main discussion and implications for the geochemical data are compared to other literature and are interpreted in Chapter 7, and important findings are summarised in Chapter 8.

CHAPTER 2

Geological Setting of the Canterbury and Great South Basins

2.1 Plate Tectonics

2.1.1 Tectonic evolution

Pre-Gondwanaland separation

Gondwanaland began to break up during the mid-Jurassic. Initial detachments from the supercontinent involved India, South America and Africa, while the section that contained Antarctica, Australia and New Zealand remained intact at this time (Anderton *et al.* 1982). Prior to the Late-Cretaceous the New Zealand continent, while still part of the Gondwana landmass, was adjacent to the Eastern Ross Sea Basin and Marie Byrd Land regions of Antarctica. During this time, the Bounty Trough was closed which caused the Chatham Rise to lie alongside the northern Campbell Plateau (Mound and Pratt, 1984).

The Rangitata II Orogeny was the final orogenic event prior to the break-up of eastern Gondwana. This event was the result of subducted oceanic crust beneath the New Zealand section of Gondwana and an associated accretion of a wedge of marine sediments on the seaward facing side of the continent (Mound and Pratt, 1984). The Rangitata II Orogeny was terminated by the initial breakup of Gondwanaland around the mid-Cretaceous (Shell BP Todd, 1984). This orogenic event ended with a period of stability for the Gondwana coastal areas, with gentle uplift and peneplanation of folded and metamorphosed rocks that were deformed during the Jurassic and Early-Cretaceous. The erosion of the peneplain continued until the Late-Cretaceous (Mound and Pratt, 1984).

Separation of New Zealand from Gondwana

Separation of the Antarctic-Australia-New Zealand landmass from Gondwanaland represents the final phase of fragmentation of the Gondwana Supercontinent (Mutter *et al.* 1985).

The New Zealand continent broke away from the Antarctic-Australian landmass during the mid-Cretaceous (~100 Ma). Early phases of this rifting set the basement terrain of New Zealand into an extensional regime. This phase resulted in crustal attenuation and reduced the continental crust thickness (from around 30 km to 20 km) (Anderton *et al.* 1982). Early Cretaceous plutons associated with the last phase of breakup resulted in the formation of large horst blocks and deep grabens (Anderton *et al.* 1982).

Widespread rifting around New Zealand during the period 105 to 80 Ma was associated with the final stage of Gondwana breakup. This involved the separation of: the Lord Howe Rise from Australia, which formed the Tasman Sea; East Antarctica from Australia, forming the Southeast Indian Ocean; and the Campbell Plateau from Marie Byrd Land, forming the South Pacific Ocean approximately 90 Ma (Cook *et al.* 1999).

Separation of Australia from East Antarctica was earlier than Australia-Lord Howe Rise and Campbell Plateau-Marie Byrd Land separation, with evidence for early rift phases during the Late Jurassic to Early Cretaceous. This was followed by the onset of slow spreading on the Southeast Indian Ocean Ridge around 96 Ma (Cook *et al.* 1999).

Based on magnetic anomaly data Mutter *et al.* (1985) have suggested that 86 Ma was the time of the initiation of spreading in the Tasman Sea, the initiation of spreading between New Zealand and Antarctica, and the time of major plate boundary reorganisations in the Indian Ocean. Veevers (1986) stated that sea-floor spreading between Australia and Antarctica began at or prior to 86 Ma.

The Tasman Sea began to open at its southwest end adjacent to Tasmania and the Challenger Plateau. Seafloor spreading propagated in a northwest direction (Cook *et al.* 1999).

Initial movements along normal faults began in the mid-Cretaceous with rift valleys and grabens developing on the New Zealand continent, parallel to the axis of rifting. This represents the change from compressional to extensional tectonics in the area to facilitate the extension (Anderton *et al.* 1982; Mound and Pratt, 1984). This extension divided the Campbell Plateau into several large depocenters, such as the Bounty Trough, which was initiated as a rift valley during this time, spreading the Campbell Plateau from the Chatham Rise (Anderton *et al.* 1982). The onset of tension across the Campbell Plateau and the Canterbury Basin reactivated some old Rangitata fault trends and created new fault lines. The main axis of tension across Campbell Plateau was controlled by the spreading between New Zealand and Antarctica, and also spreading in the Bounty Trough (Mound and Pratt, 1984). The Bounty Trough represents a failed rift arm that may have formed just before or during the earliest stages of seafloor spreading south of the Campbell Plateau. The trough may have initially formed prior to the Cretaceous, but was a region of intense Cretaceous crustal thinning, merging its eastern end with Cretaceous Oceanic crust (Cook *et al.* 1999).

New Zealand was a single continental block that had not began to break into its current microplates between 85 and 83 Ma. This block separated from the Antarctic-Australia landmass as a whole, moving away with the Pacific Plate. As spreading commenced, the New Zealand continental terrain of the Campbell Plateau faced the opening sea to the south (east in its present rotated location). Some further extensional faulting took place, brought on by rifting; however, basement topography was not significantly altered after this time (Anderton *et al.* 1982).

Towards the end of the Cretaceous period, spreading was progressing at different rates along the line of separation from the Antarctic-Australia block. The northern section of the Tasman Sea opened slowly while the southeastern section of the Ross Sea opened relatively rapidly. This created an anticlockwise rotation of New Zealand from Gondwana. The differential movement may have led to internal rotation within the Campbell Plateau itself, possibly initiating the dextral movement on the fault system which underlies the present shelf edge. Towards the end of the mid-Cretaceous many of the smaller fault movements ceased due to the transition from rifting to drifting. The larger faults continued to show movement; however, their throws were much less than during the rifting phase. By the end of the Cretaceous normal fault movement had almost entirely ceased, but did continue locally in the Great South and Canterbury basins (Anderton *et al.* 1982).

Post Gondwana separation

Plate motions in the Tasman and South Pacific region during the 80-53 Ma period were dominated by sea floor spreading (Cook *et al.* 1999). During the Late Cretaceous to Early Tertiary, as the New Zealand continental block drifted away from the site of lithospheric upwelling and heating, it cooled and underwent thermal contraction which resulted in subsidence of the continental margin and subsequent transgression of local seas (Gibbons and Fry, 1986.).

In central parts of the Campbell Plateau gentle uplift occurred during the mid to Late Paleocene. This uplift stage could have been connected with continued rotation of the entire Campbell Basin block (Anderton *et al.* 1982).

The New Zealand block continued to move as a single unit, but the termination of spreading in the Tasman Sea 60-55 Ma, as identified from magnetic anomaly data, locked the Lord Howe Rise onto the Indo-Australian Plate. At the same time, rifting between Australia and Antarctica commenced. Spreading between the Australian and Antarctic blocks occurred 56-33 Ma on the Southeast Indian Ocean Ridge. In this area the Pacific and Indo-Australian plates began moving away from Antarctica simultaneously. Spreading rates and direction of movement were slightly different on the Southeast Indian Ocean Ridge and the Pacific-Antarctic (Ross Sea) Ridge, causing strain on the New Zealand block (which became caught in between) and on the ocean-ocean boundaries north of New Zealand (Anderton *et al.* 1982).

Curved fractures zones at the Pacific Ridge indicate a significant change in the direction of spreading during the period 53-43 Ma (Cande *et al.* 1995). This change in spreading direction was accompanied by a significant reduction in the rate of spreading (Cande *et al.* 1995).

India collided with Asia during Late Eocene to Early Oligocene time (38 Ma). The resultant reorganisation of plate motions to accommodate the abrupt termination of relative northwest movements of the Indo-Australian Plate changed the direction of intersection with the Pacific Plate (Anderton *et al.* 1982; Shell BP Todd, 1984). A consequence of this was the immediate onset of subduction zone and arc formation north of New Zealand, and the rupture of the New Zealand continental block. This led to the initiation of the Alpine Fault around/or shortly after this time (36 Ma), and began dextral strike-slip separation of the newly formed Lord Howe and Campbell microplates (Anderton *et al.* 1982; Hawkes and Mound, 1984).

The stable drift conditions that prevailed during the Oligocene ended in the Miocene with the onset of subduction to the north of New Zealand and oblique compression to the south (Mound and Pratt, 1984). The mid-Miocene event is represented by the onset of the Kaikoura orogeny, recent uplift, and continued metamorphism of the Southern Alps flysch sequence. Spreading rates on the Pacific-Antarctic (Ross Sea) Ridge became slower in the southwest, towards the Macquarie Ridge, and faster in the northeast where it is offset from the East Pacific Rise spreading centre. This differential spreading created an anticlockwise rotation of the Campbell microplate. The subsequent microplate interaction caused a strong compressive component of movement on the Alpine Fault, which consequently led to uplift of the Southern Alps (Anderton *et al.* 1982).

The paleogeography of the New Zealand region is described and illustrated in detail by Cook *et al.* (1999; pages 99-103, figure 5.1).

2.1.2 Structure of the Great South Basin

The Great South Basin is a mid to Late Cretaceous intra-continental rift basin that formed as a result of regional extension in association with the opening of the Tasman Sea and separation of Australia from Antarctica (Olson, 1996). The structural history of much of the basin consists of initial syn-rift subsidence followed by Tertiary thermal subsidence (Olson, 1996).

The structure is principally governed by a system of sub-parallel normal faults that trend in a northeast-southwest direction, and the basin is comprised of a series of grabens, half grabens and tilted horsts (Anderton *et al.* 1982) that formed between the South Island of New Zealand and the Campbell Plateau. The deeper segments of the basin are comprised of five major structural provinces: the Central Graben, the Pakaha and associated horsts, the East Flank Sub-basin, the Rakiura Trough, and the Kawau Depression. These features are almost entirely aligned with and controlled by the above-mentioned fault patterns (Anderton *et al.* 1982).

Figure 2.1 displays a generalised cross section of the Great South Basin, which includes some of the more prominent features and the relative proximity of some of the exploration wells that have been drilled in the basin.

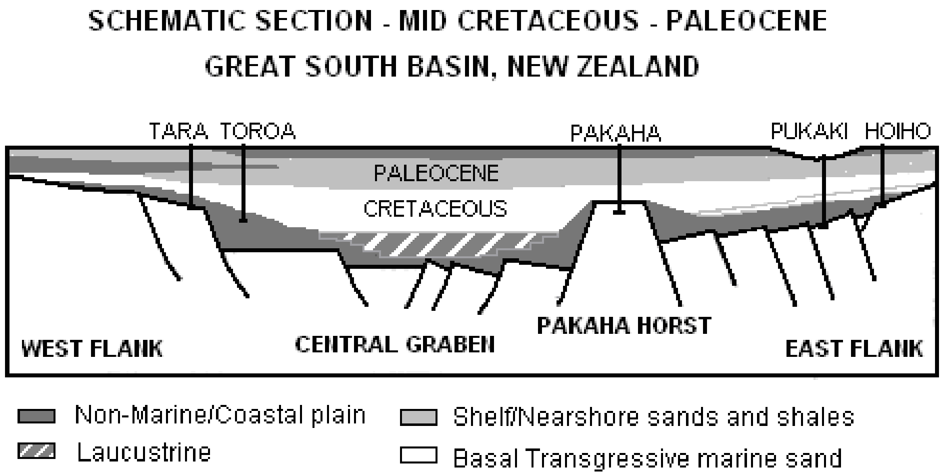

Figure 2.1 Cross section of the Great South Basin. Modified from Olson (1996).

The Central Graben floor is controlled by a series of relatively passive northeast-trending grabens and horsts which become increasingly complex towards the strike-slip fault zone on the northwest flank of the basin. The northwest flank has continued to be affected by dextral strike-slip faulting and this was responsible for post-Oligocene inversion of relief anticlinal features in this area (Anderton *et al*. 1982).

The East Flank Sub-basin is much smaller in area than the Central Graben and is dominated in its northwestern part by a series of east-northeast aligned half grabens that are tilted to the north-northwest and bounded by normal faults that are downthrown to the south-southeast. In southern parts of the province the normal faulting slopes to the opposite direction (Anderton *et al*. 1982).

2.1.3 Structure of the Canterbury Basin

The Canterbury Basin is bounded at its northern flank by the Chatham Rise, and to the northwest by the Bounty Trough (Killops *et al*. 1997). To the west, the basin extends onshore to the South Island of New Zealand, and is contiguous with the Great South Basin to the south (Baillie and Uruski, 2004).

The basin began to form during the early to mid-Cretaceous as a result of New Zealand splitting from Gondwana. This separation caused extensional tectonism that led to graben and half graben development as well as the formation of many structural highs in the form of horsts. Mid-Cretaceous extensional tectonism (a graben forming process) produced fault angle depressions that have been filled with over 4 km of sediment in some areas of the basin. Basement rocks were deformed during the Rangitata I and II orogenies between the Late Triassic and Early Cretaceous (Field and Browne, 1989).

Normal faults that formed during the Cretaceous are the dominant fault pattern in the Canterbury Basin. These faults typically trend in a northeast-southwest direction and are generally downthrown to the southeast (Field and Browne, 1989).

The Canterbury Basin consists of two main depocentres which developed in response to early to mid Cretaceous rifting. The northern depocentre is the offshore Clipper Sub-basin bound by the Endeavour High to the northwest and the Canterbury Rise to the southeast. The southern depocentre is the Central Trough of the Great South Basin as the southern sector of the Canterbury Basin is contiguous with the Great South Basin (Baillie and Uruski, 2004).

2.2 Stratigraphy of the Great South and Canterbury basins

2.2.1 The Great south Basin

A detailed account of the stratigraphy of the Great South Basin can be found in Cook *et al.* (1999); the following is a summary of the more important points from Cook *et al.* (1999) that are relevant to this study.

Figure 2.2 is a generalised representation of the stratigraphy of the Great South Basin.

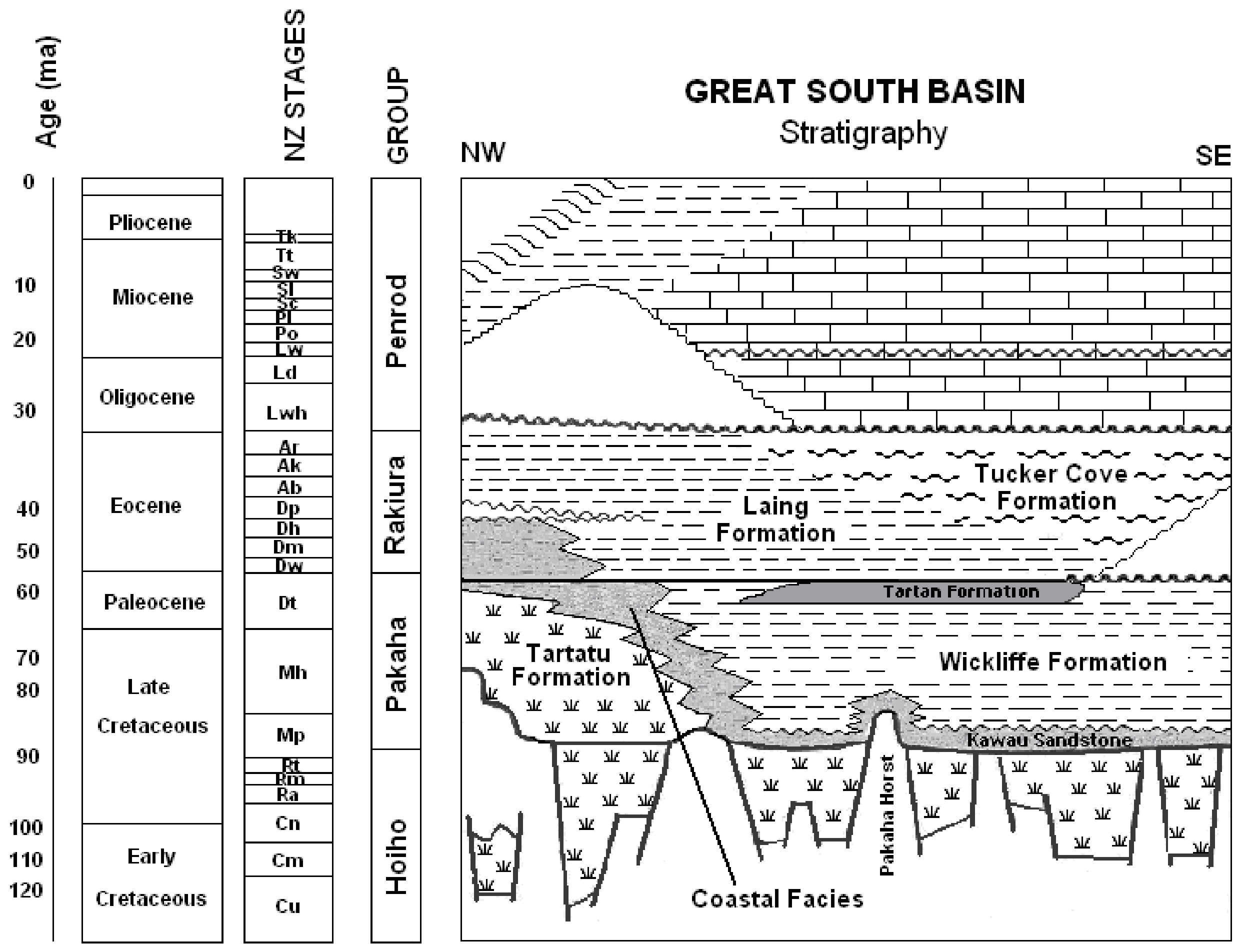

Figure 2.2 Generalised stratigraphy of the GSB (Modified from Cook *et al.* 1999).

Cook *et al.* (1999) have divided the stratigraphy of the Great South Basin into four lithostratigraphic groups: the Hoiho, Pakaha, Rakiura and Penrod groups.

Hoiho Group

The Hoiho Group is the oldest group recognised in the Great South Basin and is interpreted to be of mid to Late Cretaceous [Ngaterian (Cn) to Piripauan (Mp)] age. The lithology of the group consists of sandstones, shales, conglomerates and coals.

The Hoiho Group consists of a succession of non-marine clastic facies that can be subdivided into three separate time components: the Clarence Series (Cu-Cn), Raukumara Series (Ra-Rt), and the early Piripauan Stage (Mp). The Clarence Series represents the basal unit and is characterised by variable-amplitude reflectors with a discontinuous and wedge shaped geometry suggesting fluvial valley fill, and adjacent high-amplitude, steeply dipping reflectors that are interpreted to be fault scarp fans along the graben margins.

The middle unit is the Raukumara Series and seismic facies within the unit are highly variable which is interpreted to indicate a dominance of terrestrial paleoenvironments. The low-amplitude, discontinuous reflectors are believed to be lacustrine facies, while medium to high-amplitude and variably continuous reflectors are interpreted as coal measures.

The upper unit of the Hoiho Group, which contains sediments from the Piripauan Stage, has a chaotic, variable-amplitude seismic facies in the Eastern-Flank Sub-basin which has been interpreted to be deposits formed of reworked and winnowed earlier Cretaceous sediments that resulted from a deficiency of sediment supply coupled with wave and tidal action during periods of transgression.

The deposition of the Hoiho Group took place in a series of normal faulted depressions and sub-basins. Steeply dipping reflectors close to faults are indicative of widespread alluvial fan sedimentation. Distal fault scarps, fluvial and coal measure facies are interpreted to be the result of deposition in braided floodplain and lacustrine environments.

Pakaha Group

Overlying the Hoiho Group is the Pakaha Group, which ranges from Late Cretaceous to Paleocene [Late Piripauan (Mp) to Late Teurian (Dt)] in age and includes several formations. The base of the Pakaha Group is the Kawau Sandstone, which is overlain by the Wickliffe Formation, and is overlain by the Taratu Formation, which is in turn overlain by the Tartan Formation at the top of the group where Tartan Formation is present.

Sediments in the Pakaha Group were deposited after most normal faulting had rapidly begun to subside, and as a result, marine transgression continued. To the west of the basin was an eastward progression of depositional environments ranging from fluvial and coastal plain with extensive coal swamps, paralic, to shallow marine conditions. The major drainage systems formed alluvial fan complexes. The eastern margin gradually subsided to shelf depths (Cook *et al.* 1999; see Enclosure 1, maps 5 and 6 from that publication), and in the East Flank Sub-basin, carbonates began to accumulate as a result of reduced sediment supply.

The Kawau Sandstone is a white to grey, medium coarse, friable sandstone. It ranges in age from Piripauan (Mp) to Haumurian (Mh) (Raine *et al.* 1993). The formation is interpreted to have been deposited in a shallow marine, nearshore setting.

The Wickliffe Formation is bound by unconformities at both the base and the top, and ranges in age from Piripauan to Late Teurian (Raine *et al.* 1993). The formation generally consists of soft to firm, fissile, light grey shales and clays with subordinate darker brown shale and is glauconitic in places. Based on fossil faunas identified in the south and west of the basin within the Wickliffe Formation, a nearshore to inner-shelf marine environment, generally with restricted circulation depositional environment is inferred (Raine *et al.* 1993). The most widespread marine conditions seem to have been in about the Late Cretaceous, followed by shallowing to coastal environments during the Paleocene. The Wickliffe Formation has similar characteristics to the Whangai Formation found around the East Coast region of the North Island.

The top of the Taratu Formation is defined by the transition to marine facies of the Wickliffe Formation which interfingers laterally with the Taratu Formation. The Taratu Formation consists of interbeds of quartzose grit, pebble conglomerates, sandstone and shales with common coal measures. The sandstones are light brown, and fine to coarse grained, while the shale is chocolate brown, firm to blocky, micaceous and very carbonaceous. The coals range in rank from lignite to sub-bituminous. The base of the formation is at least Piripauan in age and possibly Late Haumurian at the top of the formation. Its deposition in the Great South Basin is believed to have taken place on a lower coastal plain, and it is possible that some of the coal measures were influenced by brackish conditions (Raine *et al.* 1994; Wilson and McMillan, 1996).

The uppermost member in this group is the formation of most importance to the present study. The Late Paleocene (Late Teurian) Tartan Formation is a dark brown, firm, carbonaceous, slightly calcareous, highly micaceous, and slightly glauconitic shale. The Tartan Formation very closely resembles the Waipawa Formation (also referred to as Waipawa Black Shale) widely found in many basins around New Zealand, including the Canterbury Basin (see Chapter 3) and is interpreted to be its equivalent. Deposition of the Tartan Formation is likely to have been similar to that of the Waipawa Formation but it was possibly deposited in a shallower environment in the Great South Basin than in other basins around New Zealand where it has been identified.

Rakiura Group

The Rakiura Group was deposited during the Eocene [with the lowermost formation deposited during the Waipawan (Dw) and the uppermost formation during the Runangan (Ar)]. The group is made up of the Laing and Tucker Cove formations.

In southern parts of the basin, the group is defined by an unconformity or by the base of a condensed section. In central parts of the basin the correlative surface lies immediately above the Tartan Formation, and is typically characterised by a sharp upward increase in carbonate content. The top of the group is defined by a regional unconformity towards central and northwestern parts of the basin, with overlying Penrod Group sediments progressively onlapping it from the west. In the Central Sub-basin, the boundary is characterised by a change in lithology from siltstones and clays of the Laing Formation to chalks or foraminiferal oozes of the Penrod Group. In the southeastern part of the basin, the Tucker Cove Formation overlies the Laing Formation and there is a change from the limestone of Tucker Cove Formation to foraminiferal oozes and chalks of the overlying Penrod Group.

Seismic facies appearing in the Rakiura Group are interpreted to represent slope-basin floor fans and turbidite fans, bathyal carbonates and clastics, and submarine canyon deposits.

The base of the Rakiura Group corresponds to the transition from restricted marine circulation with organic-rich shale deposition in the Late Paleocene to open ocean conditions. Pelagic carbonate sediments of the Tucker Cove Formation were deposited in the southeast of the basin during the earliest Eocene, and extended progressively to the west. From the Early Eocene, a broad prograding wedge formed at the eastward-curving shelf margin, from which a slope-basin floor fan complex developed, probably in outer shelf to upper bathyal depths (Raine *et al.* 1993). Submarine canyon and valley systems appeared at bathyal depths from at least the Early Eocene.

The base of the Laing Formation is defined by the regional unconformity to the southeast at the base of the Rakiura Group and is interpreted to be of Late Teurian age. Siltstones within the formation are laterally continuous with marls of the Tucker Cove Formation. In central and southeastern parts of the basin, there is an upward transition from the Laing Formation to the Tucker Cove Formation which is defined by a change from clastic to carbonate-dominated sedimentation.

The Laing Formation extended over most of the Great South Basin in the Early Eocene but by the end of the Eocene, clastic sedimentation was restricted to areas in the west of the basin. The Laing Formation in western parts of the basin consists of interbedded sandstones and siltstones, which are moderately calcareous, and contain glauconite and traces of pyrite. To the east, the formation consists of shales and calcareous clays. The Laing Formation is interpreted to have been deposited in a shelf to upper bathyal setting. Raine *et al.* (1994) provide evidence for gradual deepening from inner to mid-shelf depositional settings to the west of the basin during the Early Eocene, whereas an outer shelf to upper bathyal setting was present in the east of the basin. The Laing Formation is lithologically similar to the Wanstead Formation of the East Coast Basin, and is of similar age (Meadows, 2008).

The base of the Tucker Cove Formation is defined as the base of carbonate-rich marls and foraminiferal limestones which overlie the unconformity recognised near Late Paleocene strata. The top of the formation is the regional unconformity that separates the Rakiura Group from Penrod Group sediments. The Tucker Cove Formation consists of soft to firm, white to light grey, fine-grained, foraminiferal limestone with chert nodules and traces of pyrite and glauconite. The unit ranges in age from Waipawan (Dw) to Runangan (Ar). Deposition of the formation ranged from outer-shelf to mid-bathyal depths with open oceanic conditions in surface waters.

Penrod Group

The Penrod Group is the uppermost stratigraphic unit in the Great South Basin, with the upper limit of the unit representing the present sea floor. The lower boundary is a regional unconformity that is of Late Eocene or earliest Oligocene age. Oligocene strata lap onto the western margin where moderate to high-amplitude, continuous, slightly wedge-shaped seismic facies suggest deposition in deep water with restricted clastic sediment supply.

The depositional environment in the southern and eastern parts of the basin is inferred to have been under bathyal depths. Along the northwestern margin of the basin, increased sediment supply during Miocene-Recent time formed a shelf wedge that is over 800 m thick.

2.2.2 Stratigraphy and Structure of GSB Petroleum Exploration Wells Sampled

The basin floor that upper Cretaceous and Tertiary sediments were deposited upon was a peneplained series of anticlinal mountains of Triassic and Jurassic age. Periodic structural uplift throughout the Tertiary resulted in uplift and drape of the Tertiary sediments over the buried lower and mid-Mesozoic mountains that had a northwest-southeast trend. Seismic mapping shows that the greatest uplift, and hence structural drape, took place in the lower Tertiary (Cook *et al.* 1999).

The generalised stratigraphy of the two wells from the Great South Basin investigated in the present study are presented in Figure 2.3.

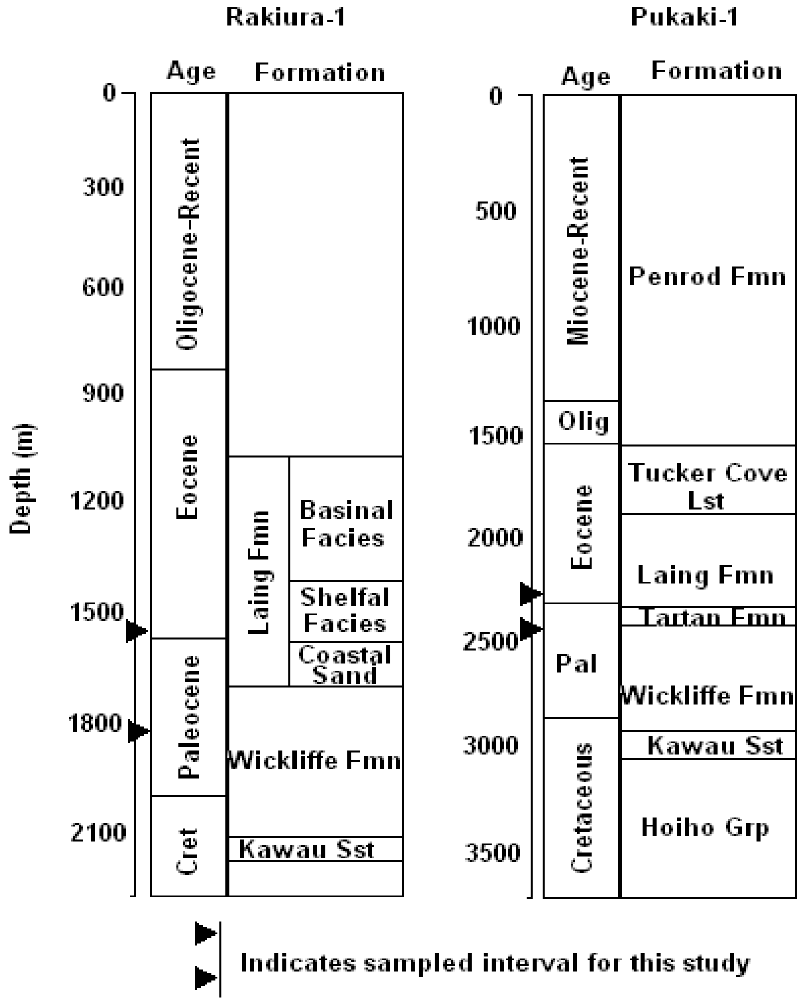

Figure 2.3 Generalised stratigraphy of Rakiura-1 and Pukaki-1.

Rakiura–1

The Rakiura-1 petroleum exploration well is located adjacent to the Rakiura Trough in the southwest quadrant of the Great South Basin (Fig. 1.1) under approximately 650 m of water. The Rakiura structure is essentially a normal faulted, basement-induced drape structure. The Rakiura Trough is effectively a southwestward extension of the Central Graben, but is separated by a basement high trending in a northwest-southeast direction. The structure has a closure area of up to 140 km^2 and a vertical closure of approximately 300 m (Placid Oil Co. 1984b).

Pukaki–1

The Pukaki-1 petroleum exploration well is located in the East Flank Sub-basin in the southeast section of the Great South Basin (Fig. 1.1) under approximately 880 m of water. The structure is the result of compaction of sediments draped over a complexly faulted basement. There is approximately 140 km^2 of closure area, and vertical closure of approximately 285 m (Placid Oil Co. 1984a). Vertical uplift is evident from seismic cross-sections of the Pukaki structure from at least the top of the Cretaceous to the acoustic basement.

Other wells in the Great South Basin

A full account of the stratigraphy and structural features of the six other exploration wells of the Great South Basin can be found in Meadows (2008; Chapter 2).

2.2.3 The Canterbury Basin

A detailed account of the stratigraphy of the Canterbury Basin can be found in Field and Browne (1989), and petroleum reports from data acquired and wells drilled in the basin. The following is a summary of the more important points from their work that are relevant to this present study.

Figure 2.4 is a generalised representation of the stratigraphy of the Canterbury Basin.

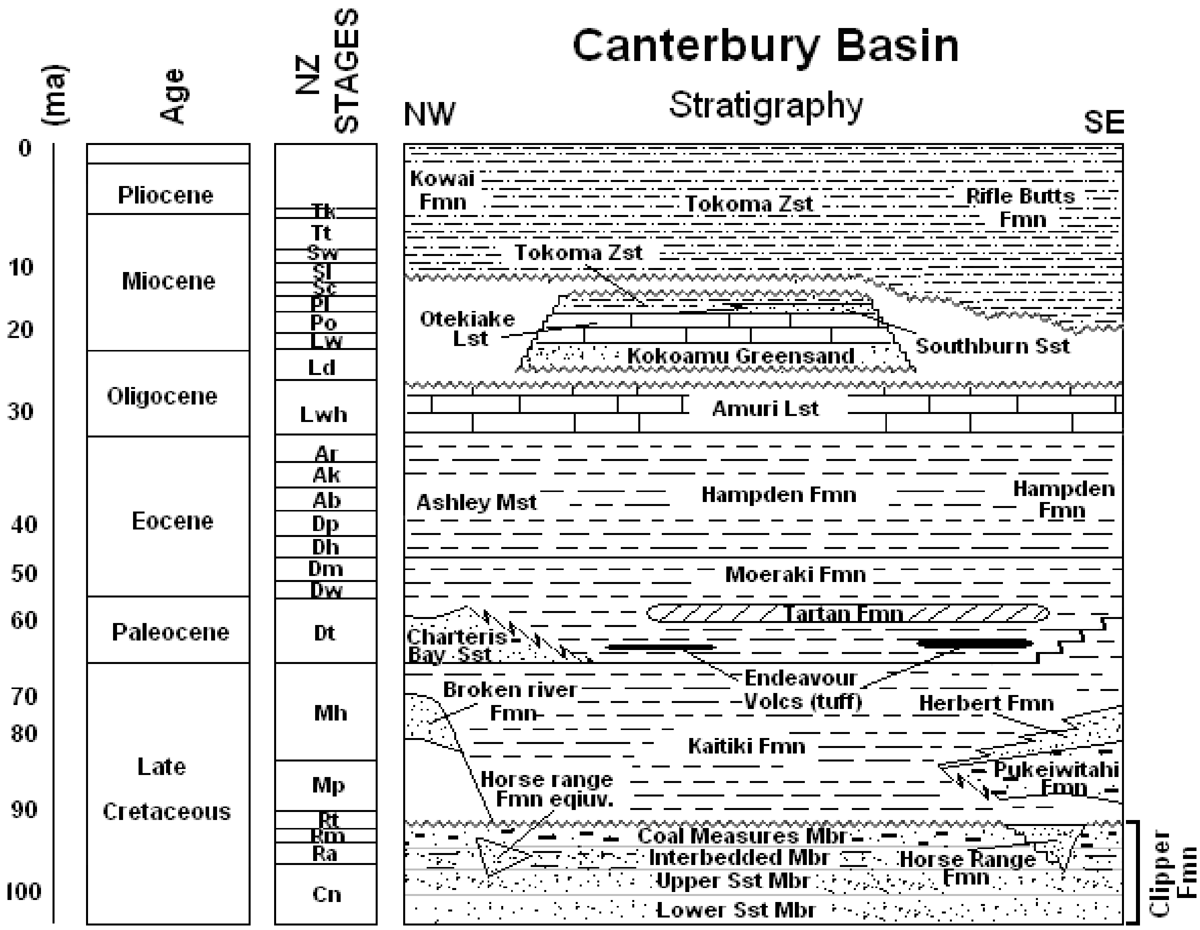

Figure 2.4 Generalised stratigraphy of the Canterbury Basin (Modified from Crown Minerals, 2008c; Field and Brown, 1989).

The oldest recognised sediments in the Canterbury Basin are those of the Clipper Formation, which has been tentatively assigned to the mid-late Cretaceous Clarence and Raukumara Series [approximately Ngaterian (Cn) to Teratan (Rt)] (Hawkes and Mound, 1984).

The following description of the Clipper Formation has been summarised from Hawkes and Mound (1984) unless otherwise stated.

The Clipper Formation has been sub-divided into four distinct members on the basis of lithological and electronic log responses. The four members recognised (from oldest to youngest) are: the Lower Sandstone member, Upper Sandstone member, Interbedded member, and the Coal Measures member.

The top of the Lower Sandstone member is defined by a reduction in gamma ray log response, which has been interpreted to correspond to the development of sandstone interbeds (5-20 cm thick) with a less well developed argillaceous matrix. Sandstones in this member are quartzose, sublithic, poorly sorted, and coarse to very coarse grained (Hawkes and Mound, 1984; Simpson, 1993). There are also interbedded mudstones present within this member; these mudstones are micaceous and carbonaceous.

The overlying Upper Sandstone member is defined by increases in the number of sandstone interbeds and greater variability in thickness of individual sandstone units (ranging from 1-10 m thick). Sandstones from this member are quartzose, fine to coarse grained, rounded to sub-angular, non-calcareous, and occasionally carbonaceous. A silica matrix is more commonly developed than the argillaceous matrix of the underlying Lower Sandstone member.

The Interbedded member is characterised by the presence of discrete sandstone interbeds (ranging in thickness from 1-5 m), within a mudstone dominated succession. The top of this member is marked by the last occurrence (first occurrence downhole) of sandstone within the Clipper Formation. Sandstones within this member are quartzose, very fine grained, micaceous and carbonaceous with an argillaceous matrix. Interbedded mudstones and siltstones are light to dark grey and highly carbonaceous.

The uppermost member of the Clipper Formation is the Coal Measures member. This member is dominated by light grey to medium brown, carbonaceous and non-calcareous mudstones and siltstones. Coals present are black and vitreous.

Simpson (1993) has stated that paleoenvironments of deposition of the Clipper Formation range from alluvial fan at the base of the formation to fluvio-deltaic near the top, with a paralic influence suggested by marine dinoflagellates within the Interbedded unit.

Unconfomibly overlying the Clipper Formation is the Katiki Formation, which has been assigned to the Mata Series of the Upper Cretaceous [Piripauan (Mp) to Haumurian (Mh)] (Hawkes and Mound, 1984).

The top of the Haumurian Stage is not characterised by a distinctive change in lithology, rather it is defined by a slight increase in carbonate content. Below this, sediments developed occasional white argillaceous limestone interbeds and are age equivalent to the Herbert Formation, which was deposited in the southwest of the Canterbury Basin (Hawkes and Mound, 1984).

Basal sediments of the Katiki Formation were deposited in a generally shallow marine environment (shelf to upper bathyal), deepening to bathyal in the central basin (around Clipper-1) (Simpson, 1993; Field and Browne, 1989). Towards the northeast (around Resolution-1) the Katiki Formation is represented by the Conway Formation (Field and Browne, 1989). To the southwest (around Endeavour-1), the Pukeiwitahi Formation (which was deposited within the Katiki Formation) was deposited in an extensive flood plain and coal swamp environment. The Pukeiwitahi Formation overlies the Zapata Limestone (a thin unit of argillaceous limestone that also lies within the Katiki Formation) (Wilding and Sweetman, 1971). The Pukeiwitahi Formation consists of quartz-rich, gritty coal measures (Simpson, 1993), carbonaceous siltstones and mudstones which are continuous with overlying Cretaceous sediments. White argillaceous limestone interbeds very occasionally occur throughout the succession (Hawkes and Mound, 1984).

The Herbert Formation overlies the Pukeiwitahi Formation, possibly disconformably (Wilding and Sweetman, 1971). The Herbert Formation is comprised of marine sandstones, and like the Pukeiwitahi Formation, is restricted to the southwest of the Canterbury Basin. The formation is conformably overlain by Katiki Formation (Simpson, 1993).

Overlying the Katiki Formation are sediments from the Dannevirke Series. Hawkes and Mound (1984) have stated that the series consists of a largely homogeneous succession of mudstones and siltstones with occasional sandstones. Wilding and Sweetman (1971) and Hawkes and Mound (1984) define the lowermost formation of this series to be the Otepopo Greensand Formation (Otepopo Formation), which has been inferred to have been deposited during the lower Teurian (Dt). Wilding and Sweetman (1971) describe the formation as being comprised of highly argillaceous, soft, glauconitic greensand and the basal contact as being sharp, possibly due to a disconformity.

The Moeraki Formation [Teurian (Dt) to Mangaorapan (Dm)] overlies the Otepopo Greensand Formation. Hawkes and Mound (1984) stipulate that the base of the Moeraki Formation is marked by a decrease in the glauconite content from the high proportion of greensand of the Otepopo Greensand Formation. The contact between the Moeraki and Otepopo formations is gradational and is taken where mudstone predominates over greensand (Wilding and Sweetman, 1971).

It is possible that the relationship between the Otepopo Greensand and Moeraki formations is connected to/or are correlatives of the Te Uri member (a highly glauconitic greensand unit) and the Waipawa Formation (mudstone) in the East Coast Basin of New Zealand as reported by Rogers *et al.* (2001).

The Moeraki Formation is a glauconitic and slightly carbonaceous, medium to dark brown mudstone which contains thin lenses of limestone and sandstone (Simpson, 1993; Hawkes and Mound, 1984). Within the formation lies a thin layer of dark brown to black, highly carbonaceous mudstone which resembles the Waipawa Formation of the East Coast Basin, and the Tartan Formation of the Great South Basin. It is this section that is of greatest importance to this present study.

The Moeraki Formation appears top be thickest in the central basin (around Clipper-1) and progressively thins towards the south (around Endeavour-1, and Galleon-1). To the northeast of the basin (around Resolution-1) the Moeraki Formation grades into Charteris Bay Sandstone (Simpson, 1993).

Field and Browne (1989) state that microfaunas indicate the Moeraki Formation was deposited in an outer neritic to upper bathyal paleoenvironments around Clipper-1 and Galleon-1, a nearshore setting at Endeavour-1, and shallower marine further southwards, towards Takapu-1A.

The top of Paleocene sediments are marked by distinctive changes from mudstone to siltstone lithologies, and an increased argillaceous content (Hawkes and Mound, 1984).

The top of the Dannevirke Series [Waipawan (Dw) to Porangan (Dp)] is tentatively correlated to the Abbotsford Mudstone Formation by Hawkes and Mound (1984); however, Field and Brown (1989) consider the Moeraki and Abbotsford formations to be correlatives. Their description of this section states that it predominantly consists of light to medium grey carbonaceous and glauconitic mudstones and siltstones.

Overlying the Dannevirke Series are strata from the mid to Late Eocene Arnold Series. The Arnold Series has been divided into two units. The lower unit, of Bortonian age (Ab), is the Hampden Formation, and is locally referred to as the Ashley Mudstone in the north of the Canterbury Basin (around Resolution-1). It consists of medium grey to brown micaceous, predominantly calcareous mudstone (Wilding and Sweetman, 1971; Hawkes and Mound, 1984) which was deposited in an outer shelf to bathyal paleoenvironment (Simpson, 1993). The upper unit is Runangan (Ar) to Kaiatan (Ak) in age, and is age equivalent to the Mokihi Formation (Hawkes and Mound, 1984). The unit consists of light grey argillaceous limestones and calcareous mudstones which are glauconitic and carbonaceous (Hawkes and

Mound, 1984). Field and Brown (1989) suggest that the Mokihi Formation should be included within the Hampden Formation.

Strata from the earliest Oligocene to Early Miocene [Whaingaroan (Lwh) to Waitakian (Lw)] of the Landon Series are dominated by the Amuri Limestone. Deposition of this formation began in the latest Eocene to earliest Oligocene (?Ar-Lwd) (Simpson, 1993) . The Amuri Limestone is locally referred to as the Amberly Limestone in the north of the Canterbury Basin. The Amuri Limestone is typically a marl or wackestone and occurs below a widespread upper Whaingaroan unconformity (Field and Brown, 1989). The formation has a fine to very fine grained texture, suggesting an outer shelf or slope paleoenvironments of deposition (Field and Brown, 1989; Simpson, 1993).

The Otekaike Limestone [Duntroonian (Ld) to Waitakian (Lw)] ranges from wackestone to grainstone in texture and has been interpreted by Field and Brown (1989) to have been deposited in an intra-shelf basin setting. Deposition of this formation continued in to the Early Miocene [Otaian (Po); the beginning of the Pareora Series] over most of the south of the Canterbury shelf basin. The Otekaike Limestone is overlain by the sandy basal sediments of the Tokama Siltstone, which consists of calcareous fine-sandy siltstones. Field and Brown (1989) state that this formation was deposited in a mid-neritic paleoenvironment and is a correlative of the Rifle Butts Formation identified towards the southwest section of the Canterbury Basin.

From Simpson (1993; Figure 2), Field and Browne (1989; Appendix 1-profile G), and Crown Minerals (2008c; Figure 1), it appears that the Tokama Siltstone (and its correlatives) is the dominant formation from the mid Miocene to Recent.

2.2.4 Stratigraphy and Structure of Canterbury Basin Petroleum Exploration Wells Sampled

The generalised stratigraphy of the four wells from the Canterbury Basin investigated in the present study are presented in Figure 2.5.

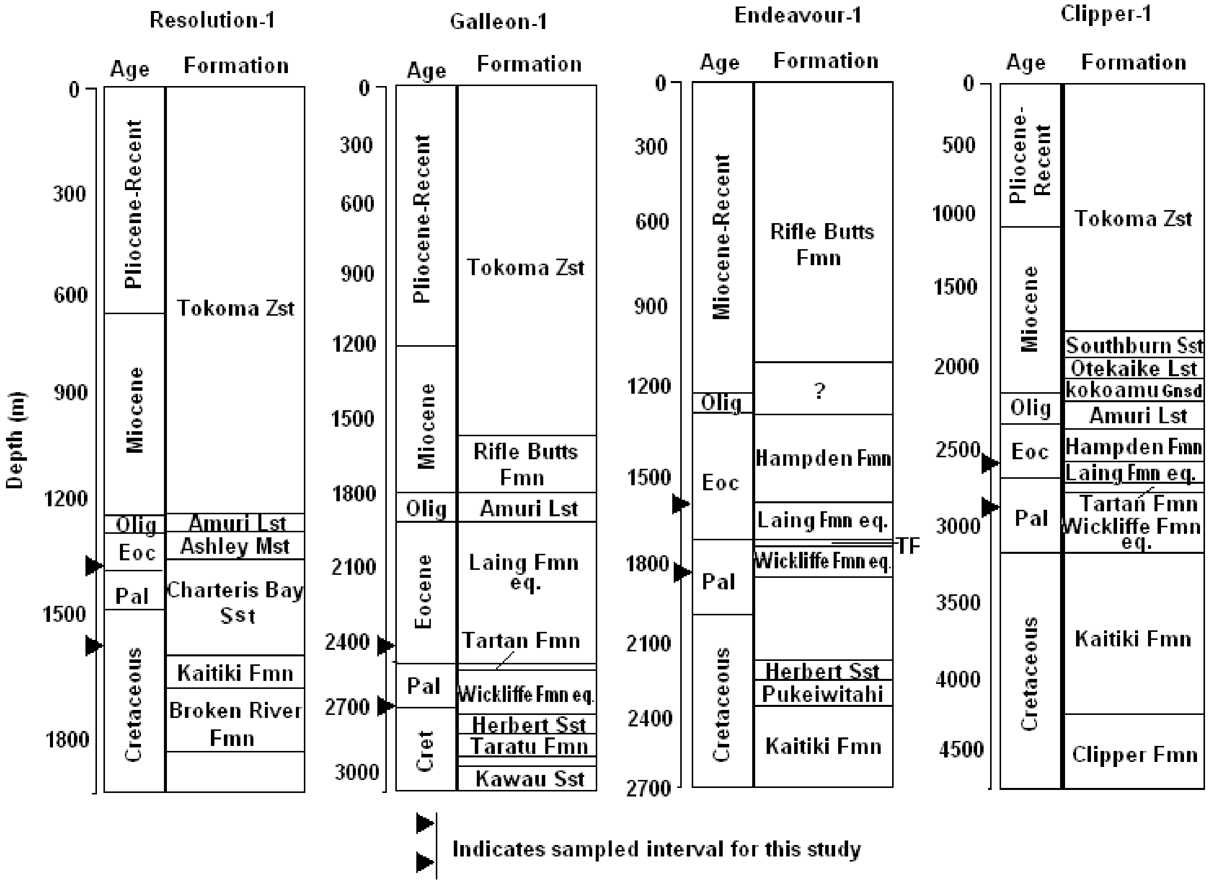

Figure 2.5 Generalised stratigraphy of Resolution-1, Galleon-1, Endeavour-1 and Clipper-1.

Resolution-1

The Resolution-1 petroleum exploration well is situated in the northeastern sector of the Canterbury Basin (Fig. 1.2) beneath 64 m of water. The Resolution structure comprises a NE-SW trending anticline that is thought to have developed as a result of igneous intrusions up-doming mid to Late Tertiary strata (Milne, 1975).

Endeavour-1

The Endeavour-1 petroleum exploration well is located in the southwestern sector of the Canterbury Basin (Fig. 1.2) below approximately 40 m of water. The well was drilled on a NE-SW trending anticlinal structure that was possibly raised as a result of early to mid Tertiary igneous intrusions (Wilding and Sweetman, 1971).

Galleon-1

The Galleon-1 petroleum exploration well situated in the southwestern sector of the Canterbury Basin (Fig. 1.2) under approximately 90 m of water. The Galleon structure is a four-way dip-closed, weakly faulted anticlinal drape feature that developed above a NE-SW trending basement high (Gibbons and Fry, 1986).

Clipper-1

The Clipper-1 petroleum exploration well is located in the centre of the Clipper Sub-basin, in the central-south area of the Canterbury Basin (Fig. 1.2) beneath approximately 150 m of water. The Clipper structure is an anticlinal drape feature over a basement rise. The structure has a closure area of approximately 50 km^2 and 275 m of vertical closure (Hawkes and Mound, 1984).

2.3 The East Coast Basin

The stratigraphy of the East Coast Basin is included here because of the importance of correlation between the Tartan Formation of the Great South and Canterbury basins and the Waipawa Formation of the East Coast Basin. This correlation will be discussed in more detail later.

2.3.1 Stratigraphy of the East Coast Basin

The Whangai Formation is a siliceous mudstone ranging from Late Piripauan/Haumurian (Late Cretaceous) to Early Teurian (Paleocene) in age. The formation is widely distributed through the eastern North Island, and is also present in other parts of New Zealand.

The formation is made up of five members: Rakauroa, Upper Calcareous, and Porangahau members, and two members with more local distribution, the Kirks Breccia and the Te Uri Member (Moore, 1988b) (Fig. 2.6). Whangai Formation in almost all exposures is conformably overlain by Waipawa Formation (Moore, 1989).

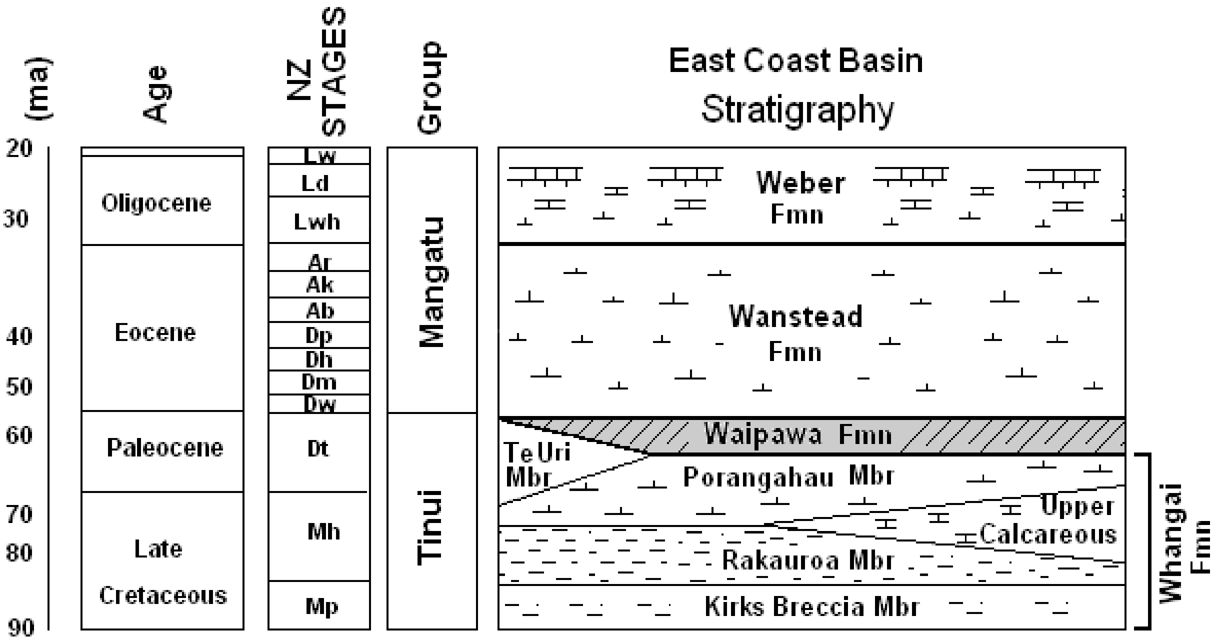

Figure 2.6 General stratigraphy of the East Coast Basin (Modified from Rogers *et al.* 2001).

The Late Piripauan (Mp)-Early Haumurian (Mh) Kirks Breccia is the lowermost member of the Whangai Formation. It contains poorly sorted, matrix to clast-supported breccia beds 30 m to 200 m thick. Clasts consist of fine sandstone, light and dark grey mudstone and concretions in a micaceous and gritty mudstone matrix (Moore, 1988b).

The next unit of the Whangai Formation is the Rakauroa Member. The member is primarily of Haumurian age, though some basal sediments may be Late Piripauan. The unit ranges from 40 m to 400 m in thickness but tends to average 200 m to 300 m. The Rakauroa Member comprises hard, typically very poorly bedded, rusty weathering, bioturbated, medium grey, non-calcareous, micaceous mudstone that has also has thin glauconitic sandstone beds, and scattered pyrite nodules and calcareous concretions. Fine laminations are present near the base the member, consisting of alternating light grey and dark grey siltstone and mudstone. Some areas are more strongly laminated than others (Moore, 1988b).

The Upper Calcareous Member is of Haumurian to Early Teurian age. The unit ranges in thickness from 50 m to 200 m and is a hard, generally very poorly bedded, light bluish-grey weathering, medium grey, slightly to moderately calcareous, bioturbated, laminated micaceous mudstone. The unit contains sporadic concretions, pyrite nodules, glauconitic sandstone beds and rare breccias, and the carbonate content generally increases upward (Moore, 1988b).

Overlying the Upper Calcareous Member is the Early Teurian Porangahau Member, with a thickness of 20 m to 300 m. The unit consists of mainly hard, well bedded, light grey, slightly to highly calcareous mudstone, which is usually moderately to highly bioturbated. Glauconitic sandstone beds are common (Moore, 1988b). The unit is commonly termed the "zebra facies", based on thin alternating light and darker grey mudstone layers through the Porangahau Member.

The Te Uri Member consists of approximately 35 m of interbedded glauconitic sandstone and hard, light grey, glauconitic, slightly calcareous, laminated siltstone, which disconformably overlies the Upper Calcareous Member. The Te Uri Member has a similar composition to the underlying Whangai mudstone, with the only major lithologic difference being the higher glauconite proportion of the Te Uri Member. The member is most likely Early Teurian in age. Moore (1988b) stated that the Te Uri Member appears to be a lateral equivalent, in part, of the Waipawa Formation.

Waipawa Formation conformably overlies the Whangai Formation and is widely distributed throughout the East Coast Basin. The formation is of mid-Late Teurian age and rarely exceeds a thickness of 50 m. The Waipawa Formation consists primarily of very poorly bedded, hard to moderately soft, dark brown-grey to brownish black, non-calcareous micaceous siltstone. Locally, there is a high proportion of glauconitic sandstone, and also some intervals of Whangai-like calcareous mudstone. In some places the shale is highly bioturbated, but contains very few macrofossils other than small bivalves and rare gastropods (Moore, 1988b, 1989). Upper and lower contacts are relatively sharp, although the basal contact with the Whangai Formation is commonly gradational over a few centimeters to several meters.

Waipawa Formation overlies different facies of the Whangai Formation across the East Coast region. Moore (1988b, 1989) stated that this was due to the base of the Waipawa Formation probably being diachronous based on his observation that the Waipawa

Formation overlies different members of the upper Whangai formation in different locations; however, Rogers *et al.* (2001) observed this as evidence for the upper members of the Whangai Formation to be diachronous, and facies dependent, rather than the Waipawa Formation.

Waipawa Formation is conformably overlain by Wanstead Formation, which is of Teurian (Dt) to Runangan age (Ar) (Late Paleocene-Eocene). The formation consists of poorly bedded, moderately hard, light grey to greenish-grey weathering, micaceous, slightly calcareous mudstone. The mudstone is intensively bioturbated and contains isolated glauconitic sandstone beds. The Wanstead Formation has a maximum thickness of 490 m (Leckie *et al.* 1992) but is poorly exposed, and thus accurate thickness determinations are difficult.

Wanstead Formation is conformably overlain by Weber Formation. This consists of up to 370 m of primarily fine-grained, hard, light-grey, bioturbated, calcareous mudstone with minor interbeds of glauconitic sandstone. Ages range from Whaingaroan (Lwh) (Early Oligocene) to likely Duntroonian (Ld)/Waitakian (Lw) (Late Oligocene-Early Miocene) (Leckie *et al.* 1992).

CHAPTER 3

The Tartan Formation

3.1 Nomenclature and distribution of the Tartan Formation (and equivalents)

Nomenclature

The name Waipawa Black Shale was first introduced by Finlay (1940) in a discussion of the distribution of *Conotrochammina whangaia* (Moore, 1989); however, it was Hornibrook and Harrington (1957) who made the first adequate description of the shale. It was formally defined in by Hornibrook (1959) who also termed the unit the 'Waipawa Black Siltstone'. Moore (1987, 1988b, 1989) referred to the unit as both the Waipawa Black Shale and the Waipawa Formation; the latter being more commonly used since by authors referring to the formation in the East Coast Basin and elsewhere around New Zealand (see Field and Uruski, 1997; Killops *et al.* 1996; Killops *et al.* 2000; Rogers *et al.* 2001; Hollis *et al.* 2005; Hollis *et al.* 2006). Killops *et al.* (1997) use the term 'Tartan Member' to refer to the Late Paleocene Waipawa Black Shale equivalent in the Great South Basin. Cook *et al.* (1999) raised this unit to formation status and 'Tartan Formation' is now generally accepted as the formal name for the formation in the Great South Basin. Cook *et al.* (1999) stated that the Tartan Formation closely resembles the Waipawa Formation of eastern North Island, but used the name Tartan Formation because of the wide geographical separation between the Great South and East Coast basins.

In keeping with Cook *et al.* (1999), the present author also refers to the Late Paleocene black shale of southern New Zealand as the Tartan Formation. Reports by Killops *et al.* (1997, 2000) referred to this section as the Waipawa Formation in the Canterbury and Great South basins. Baillie and Uruski (2004) considers the southern limit of the Canterbury Basin to be contiguous with the northern area of the Great South Basin (Section 2.1.3). I regard the proximity of the Great South and Canterbury basins, the stratigraphic position of the shale over these basins (see Chapter 2), and the data obtained from the study by Meadows (2008) (see Appendix 3 for table of results) and the present study (see Chapter 6; Results, and Appendix 4) as valid reasons to extend the term 'Tartan Formation' to the Canterbury Basin.

Distribution

The Tartan Formation and its stratigraphic equivalent, the Waipawa Formation, have been identified in several sedimentary basins around New Zealand. These are the Great South Basin, (Raine *et al.* 1993; Killops *et al.* 1997), the Canterbury Basin (Gibbons and Fry, 1986; Field and Browne, 1989; Killops *et al.* 1997), the East Coast Basin, from the Te Hoe River and East Cape in the northern region of the East Coast Basin to the Hawkes Bay-Wairarapa in the southern region of the East Coast Basin (Moore, 1988b, 1989; Field *et al.* 1997), Northland (Isaac *et al.* 1994; Hollis *et al.* 2005), northern Taranaki (Killops *et al.* 1994; King and Thrasher, 1996) and Marlborough (Strong *et al.* 1995). The formation is possibly also present in southern Westland (Nathan, 1976) (Fig. 3.1).

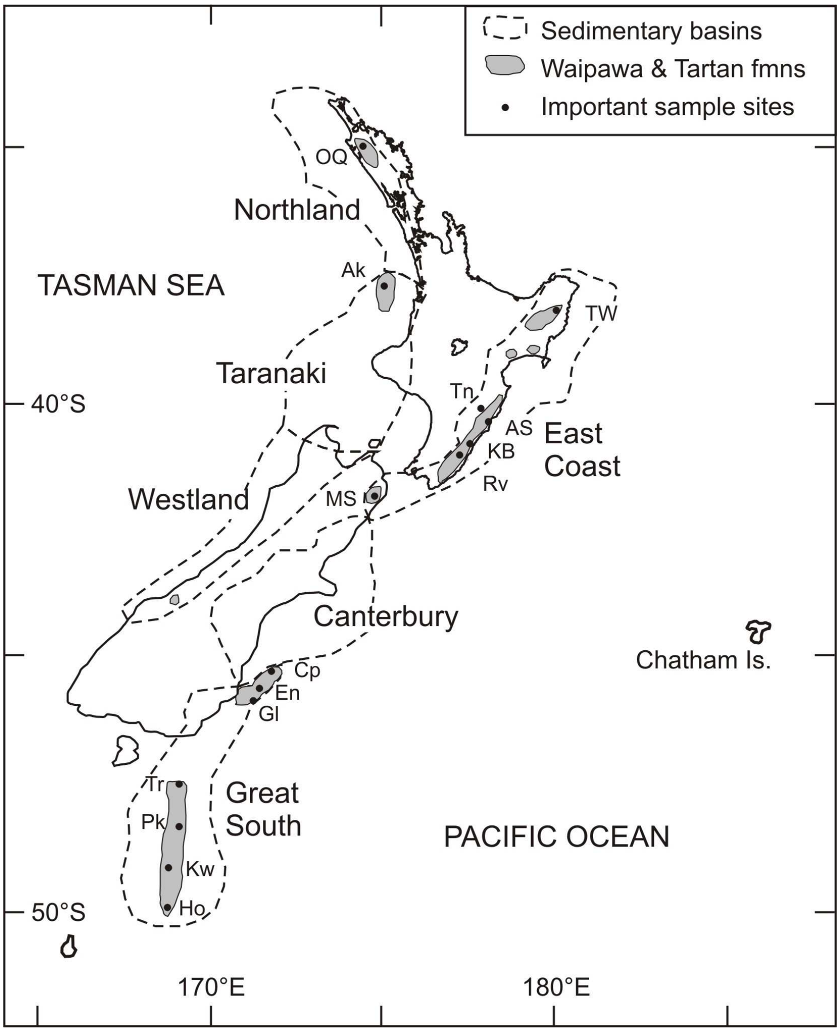

Figure 3.1 Regional distribution of the Tartan and Waipawa formations around New Zealand's sedimentary basins (Redrawn from From Killops *et al.* 1996, 2000).

Outcrops of Waipawa Formation in the East Coast Basin show the contact with the underlying Whangai Formation to be conformable and typically gradational over centimeters to meters, and that with the overlying Wanstead Formation to be sharp but conformable, as reported by Moore (1986a, 1988b, and 1989) and Killops *et al.* (2000). Correlatives of the Wanstead and Whangai formations are recognised in exploration wells in the Great South Basin in which Tartan Formation is present; and in the Canterbury Basin, where a Tartan Formation equivalent has also been identified. As in the East Coast Basin, there are gradual changes in sedimentological characteristics at the Whangai/Waipawa boundary (Killops *et al.* 2000), which is equivalent to the Wickliffe/Tartan boundary in the Great South Basin. Whangai Formation equivalents occur in the Northland Basin, with a conformable, gradational boundary with the overlying Waipawa Formation (Isaac *et al.* 1994), and a Waipawa Formation equivalent formation appears to be present in the Ariki-1 exploration well in the Taranaki Basin. In both Northland and Taranaki basins, the Waipawa Formation is overlain by deep-water facies that resemble the Wanstead Formation (Killops *et al.* 2000).

3.2 Thickness and depositional environment of the Waipawa and Tartan formations

The Tartan Formation has been identified in five exploration wells in the Great South Basin: Toroa-1 (57 m thick), Pakaha-1 (41 m thick), Hoiho-1C (39 m thick), Kawau-1A (44 m thick), and is also represented in Pukaki-1 (30 m thick) (Schioler and Roncaglia, 2008). In comparison, Tartan Formation and equivalents encountered in exploration wells in other basins are generally thinner, such as in the Canterbury Basin (Clipper-1, 35 m thick; Endeavour-1, 40 m thick; and Galleon-1, 10 m thick) and in the Taranaki Basin, where only one exploration well has a Tartan Formation equivalent (Ariki-1, 10 m thick) (Fig. 3.1) (Killops *et al.* 2000). Moore (1988b, 1989) stated that the Waipawa Formation in East Coast Basin outcrops rarely exceeds a thickness of 50 m.

During deposition of the Waipawa Formation, ocean surface waters were warmer than immediately prior to deposition of the formation (see Chapter 4). The global dysaerobic event that occurred during the latest Paleocene at the Teurian-Waipawan boundary, 55.5 Ma is defined by extinctions and by carbon and oxygen isotopic excursions in benthic foraminiferan tests at high latitudes in the Southern Hemisphere oceans (Kennett and Stott, 1991; Zachos *et al.* 1993; Thomas, 1990).

It is possible that the characteristic high organic content of the Waipawa Formation is the result of changes in oceanic circulation patterns prior to the benthic extinctions of the Late Paleocene warming (Field *et al.* 1997) (see Chapter 4).

The Waipawa Formation is interpreted to represent a condensed section that was likely to have been deposited at the peak of marine transgression or highstand of sea-level following a major lowering of the Late Paleocene sea-level (Haq *et al.* 1987; Strong *et al.* 1995; Rogers *et al.* 2001) during a period of global warming that began in the mid-Paleocene and climaxed during Late Paleocene to Early Eocene time (Zachos *et al.* 1993). Schioler and Roncaglia (2008) have reported that the Tartan Formation was deposited during a maximum regression in the Thanetian (Late Paleocene) (see Section 3.5).

Paleogeographic reconstructions (Fig. 3.2) show areas where the Waipawa Formation (and Tartan Formation) was deposited widely over the New Zealand landmass (Field *et al.* 1997).

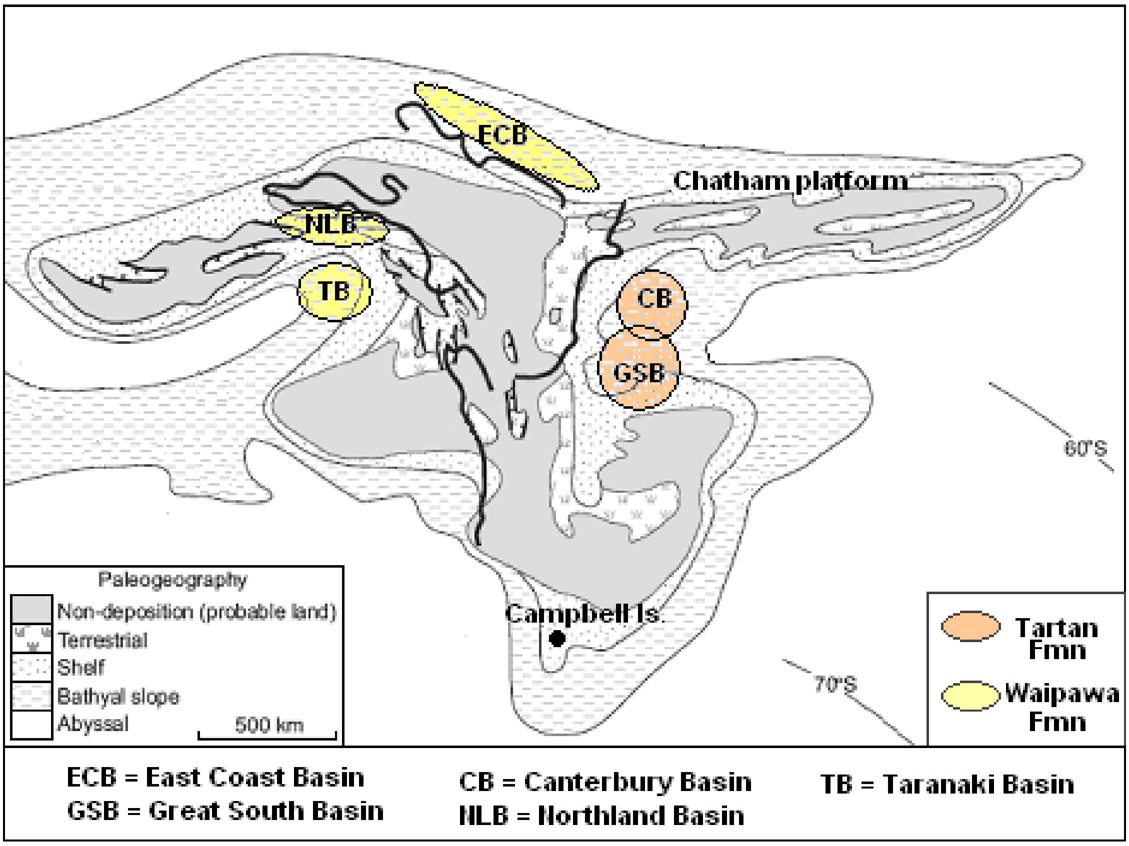

Figure 3.2 Paleogeographic reconstruction of the New Zealand microcontinent during the Late Cretaceous displaying basins where the Waipawa and Tartan formations have been identified. Modified from Hollis (2003).

Dysaerobia has been associated with the deposition of the Waipawa Formation by Killops *et al.* (2000). This dysaerobia may have been instigated by high biological oxygen demand in the water column due to biological scavenging and reworking of descending organic matter. The biochemical degradation of this organic matter would have resulted in reduced oxygen saturation levels within the water. Killops *et al.* (2000) stated an important point, in that the change in circulation pattern from a thermohaline to halothermal system would create an oxygen-depleted water body below a depth of 200 m, which may have also contributed to or had a profound influence on dysaerobic conditions during the deposition of the Waipawa Formation.

From the wide distribution of the Waipawa Formation and its equivalents throughout New Zealand it is unlikely that it was deposited contemporaneously in a number of basins with restricted bottom water circulation (Field *et al.* 1997). Wind-driven upwelling may have had a partial influence on high organic content of the Waipawa Formation in some places, but was unlikely to have been the cause of distinctive features of the formation such as the high sterane content and its paleodistribution around much of the New Zealand landmass (Killops *et al.* 1996; Killops *et al.* 2000; Field *et al.* 1997). It is probable that the degradation of a significant amount of organic matter below an area of high phytoplankton productivity, resulting from upwelling, led to sediments rich in organic content being deposited over a large part of the New Zealand region (Field *et al.* 1997).

To produce almost entirely anoxic bottom waters in an open, well-oxygenated marine setting from the aerobic decomposition of organic matter would require exceptionally high productivity in the surface waters, and this unusually high productivity would have had to have taken place over a large area to account for the distribution of the Waipawa Formation. Field *et al.* (1997) pointed out that there is no clear evidence that the Waipawa Formation is associated with such extreme high productivity, although the authors concluded that the high organic content of the formation did suggest that high productivity was involved. In some places, biogenic reworking and degradation prevented the preservation of organic carbon in equivalent condensed stratigraphic intervals, such as in the East Coat Basin. A likely example of this is documented by Rogers *et al.* (2001) for Tawanui. Here, the presence of greensands of the Te Uri Member rather than the coeval black shale of the Waipawa Formation observed in the nearby Angora Stream, approximately 10 km away, suggest that conditions were oxygenated enough for biologic degradation of organic matter deposited in the Tawanui area but not oxygenated enough for degradation of organic matter at Angora Stream.

Abundant sulfur and its large range of isotopic fractionation, shown by negative $\delta^{34}S$ values for kerogen and bitumen samples, suggest sulfate reduction with an unrestricted supply of fresh sulfate, which is typical of anoxia in an open marine system was likely to have taken place during the deposition of the Waipawa Formation (Killops *et al.* 2000).

Killops *et al.* (2000) have stated that 28, 30-Dinorhopane has a very high abundance in some Waipawa Formation samples from wells in the Great South Basin, such as Pakaha-1 and Kawau-1A. Waples and Machihara (1991) mention that sediments containing large amounts of 28, 30-Dinorhopane are often indicative of deposition under anoxic conditions. The high abundance of 28, 30-Dinorhopane is suggested to be evidence of anoxic conditions developing rapidly within the sediments (Cook *et al.* 1999; Grantham *et al.* 1980). Killops *et al.* (2000) concurred, stating that anaerobia must have developed rapidly within the sediments based on the sulfur isotopic composition and content, benthic faunal abundances, and gamma ray logs of samples analysed from the Waipawa Formation.

The Waipawa Formation has an unusually high abundance of 24-n-propylcholestanes, which is diagnostic of a marine algal or phytoplankton contribution (Killops *et al.* 2000). Killops *et al.* (2000) stated that surface water conditions must have favoured phytoplankton that preferentially synthesised the C_{30} sterol precursors. Deposition of the Waipawa Formation coincides with a sharp increase in the abundance of 24-n-propylcholestanes; however, the relative abundance of 24-n-propylcholestanes began increasing gradually prior to the deposition of the Waipawa Formation earlier in the Teurian, during the deposition of the Upper Calcareous Member (UCM) of the Whangai Formation (Killops *et al.* 2000).

Deposition of the Waipawa Formation under dysaerobia is marked by very limited bioturbation in most exposures and low abundances of benthic microfossils (Killops *et al.* 2000). It is likely that the water immediately above the sediment/water interface was not completely anoxic, as shown by the presence of bioturbation within the Waipawa Formation.

The Waipawa Formation has very poor preservation of foraminifera; however, there is some evidence for changes in the foraminiferal assemblages through time. Below the Waipawa Formation sediments are dominated by benthic species, while the formation above the Waipawa Formation primarily contains planktonic species. Within the Waipawa

Formation faunas are poor but most are planktonic species together with some calcareous and agglutinated benthics (Strong *et al.* 1995).

Strong *et al.* (1995) proposed that the *Haplophragmoides*-dominated assemblages that are commonly recovered may indicate environmental stress that could have resulted from low oxygen/high organic matter deposition. The "elongate nodosariids" are indicative of dysaerobia (Kaiho, 1991) and the presence of *Alabamina* is considered to be an indicator of deposition under a sub-oxic environment (Kaiho, 1994).

Strong *et al.* (1995) stated that there is no evidence for a major depth change at the time of deposition, suggesting that the Waipawa Formation was deposited under bathyal conditions. Killops *et al.* (2000) reached a similar conclusion and suggested that an open marine depositional environment, beyond the neritic zone, was associated with the deposition of the underlying Whangai and the overlying Wanstead formations. Waipawa Formation deposition corresponds to inner shelf or basal slope/abyssal environments (Killops *et al.* 1996; Killops *et al.* 2000). Field *et al.* (1997) and Cook *et al.* (1999) also concluded that in places that the Waipawa Formation was deposited, the formation was deposited in fairly deep water, below the limit of wave action (>200 m) and possibly on the upper continental slope, whereas deposition in the Great South Basin appears to have taken place in a relatively shallow, restricted marine environment (Raine *et al.* 1993).

The upwelling event that is associated with the deposition of the Waipawa Formation would have provided nutrients to the surface waters around the shelf break and could have caused shoaling of the oxygen minimum layer so that it impinged on the upper continental slope (Killops *et al.* 1996; Killops *et al.* 2000). The high primary productivity that accompanied the deposition of the Waipawa Formation could have occurred during a period of high sea-level that followed a glacio-eustatic fall. This period of glacio-eustatic fall during the mid Paleocene is marked by dropstones in the Upper Calcareous Member of the upper Whangai Formation that underlies the Waipawa Formation (Leckie *et al.* 1995).

At some locations where the Waipawa Formation is present, it is represented by two organic-rich black mudstone units separated by a less organic-rich and more calcareous unit (Killops *et al.* 1996, Hollis *et al.* 2005). The organic-rich layers may correspond to more intense episodes of upwelling (Field *et al.* 1997). Degradation of large amounts of organic detritus sinking through the water column would have intensified dysaerobia, enhancing preservation of the organic matter in the formation.

The differences between the Tartan Formation of the Great South and Canterbury basins and the Waipawa Formation present elsewhere in New Zealand are likely related to the deposition of the Tartan Formation in relatively shallow water behind a near-surface ridge that was present from the Late Cretaceous to the Paleocene. This ridge was present immediately to the west of and extended parallel to the line of wells in the Great South Basin from which the Tartan Formation has been identified (Killops *et al.* 1996; Killops *et al.* 2000; Cook *et al.* 1999). The conditions associated with the deposition of the Waipawa Formation were present in the Great South and Canterbury basins; however, differences between the Tartan and Waipawa formations are likely due to local variations during deposition (Hollis *et al.* 2005).

3.3 Lithology and recognition of the Tartan Formation

Cook *et al.* (1999) described the Tartan Formation as a dark brown, firm, carbonaceous, slightly calcareous, very micaceous, and slightly glauconitic shale. Sidewall core and cuttings samples also exhibit clear visual changes in lithology, from the light grey shales and clays of the underlying Wickliffe Formation to the dark brown shales of the Tartan Formation, which is in turn overlain by siltstones and calcareous clays of the Laing Formation.

The Tartan Formation characteristically produces a higher than normal gamma ray response (Cook *et al.* 1999), which is very distinctive when compared to the responses produced by surrounding formations (see Figure 7.1).

3.4 Tartan geochemical facies

Reports by Cook *et al.* (1999) and Schioler, (pers. comm. 2008) define the Tartan Formation by its lithology and is recognised by its gamma ray log response. The suite of geochemical analyses performed in Meadows (2008) agree with the gamma ray data in defining the top of the Tartan Formation; however, the geochemical data (both TOC and $\delta^{13}C$) from some wells demonstrate changes that appear below the recognised base of that formation (particularly in Kawau-1A and Pakaha-1), in the top of underlying Wickliffe Formation. For this reason, a geochemical facies termed the Tartan geochemical facies (TGF) was used to describe this interval by Meadows (2008).

In light of new data and further correlation the author has decided to discontinue using this name for the interval. The apparent differences between the gamma ray logs and geochemical data have now been inferred as having been the result of local conditions' response to the Paleocene Carbon Isotope Maximum (PCIM). The relationship between the Tartan Formation is further discussed in Section 3.5 and in Chapter 7.

3.5 Age of the Tartan Formation (and equivalents)

The age of the Tartan Formation has been reported in several publications, most citing deposition during the Late Paleocene; however, few have provided a specific age for the formation.

Cook *et al.* (1999) stated that the Tartan Formation was deposited during the Late Teurian (Late Paleocene), and from the gamma ray depths provided in that publication, and that by Schioler and Roncaglia (2008), correlation to the biostratigraphic review of the Great South Basin has been made by Raine *et al.* (1993) (see above biostratigraphic summaries of Great South and Canterbury basin wells). From their work, it is accepted here that the Tartan Formation was deposited between the mid Teurian (Dt) to earliest Waipawan (Dw) Stages.

Schioler and Roncaglia (2008) reported that the Tartan Formation was deposited during a peak regression during the Thanetian (58.7 to 55.8 Ma) Stage of the Late Paleocene, which approximately correlates to the duration of the Paleocene Carbon Isotopic Maximum (PCIM) 59.5 to 55.5 Ma presented in Zachos *et al.* (2001; Figure 2) (Chapter 4). Tartan Formation deposition took place between a regressive trend in the Paleocene Wickliffe Formation and a Late Paleocene to Early Eocene transgression in the Laing Formation.

Killops *et al.* (2000) stated that the Waipawa Formation (in the Great South Basin and elsewhere around New Zealand) was deposited within a third-order eustatic rise in sea level (Haq *et al.* 1987), preceded by a climatic cooling at 59.1 Ma (as described by Leckie *et al.* 1995), and a thermal maximum at 55.5 Ma, which Killops *et al.* (2000) mentioned is co-incident with the Teurian-Waipawan (Paleocene-Eocene) boundary above the top of the formation. Killops *et al.* (2000) state that the top of the Waipawa Formation may be older than 55.5 Ma. They reported that there is commonly an undated stratigraphic gap between the top of the Waipawa Formation and the Teurian-Waipawan boundary due both to a scarcity of dateable microfossils and to sampling gaps within this section (which had previously been noted by Moore (1989) in East Coast Basin outcrops. At the Angora Stream outcrop (East Coast Basin), approximately 15 m of strata from the Teurian Wanstead Formation (see section 2.3) overlie Waipawa Formation. Similarly, in Kawau-1A (Great

South Basin) the top of the Teurian lies approximately 80 m above the top of the Waipawa (Tartan) Formation, and in Galleon-1 (Canterbury Basin) there appear to be between 60 m and 100 m of Teurian deposits overlying Waipawa (Tartan) Formation (Killops *et al.* 2000). Killops *et al.* (2000) attempted to further constrain the age of the Tartan Formation by inferring constant depositional rates throughout the Teurian (based on rates estimated for Kawau-1A, Pakaha-1, and Toroa-1), and concluded that the formation was deposited over roughly 1.5 Myr between approximately 57.5 and 56 Ma.

Hollis *et al.* (2005) correlated Late Paleocene organic rich mudstones outcropping at Mead Stream outcrop (inland Marlborough) to the Waipawa Formation. The Waipawa Formation equivalent mudstone is suggested to represent the lower interval of the PCIM at Mead Stream (Hollis *et al.* 2005). Biostratigraphic constraints placed on the Waipawa Formation equivalent at Mead Stream and Tawanui (East Coast Basin) by Hollis *et al.* (2000) and Rogers *et al.* (2001) restricted the depositional age to between 58-57 Ma (Hollis *et al.* 2005).

The correlation between Tartan Formation deposition and the global Paleocene Carbon Isotope Maximum is further discussed in Chapter 7.

The biostratigraphy of the individual wells examined in this study and that by Meadows (2008) are discussed in Appendix 2.

CHAPTER 4

Environmental conditions during the Late Paleocene and Early Eocene

4.1 Early Paleogene temperature fluctuations

Records from the Ocean Drilling Project (ODP) around the Southern Ocean indicate that a period of rapid climate change culminated in a brief transient climate of exceptional warmth during the Late Paleocene. This transient climate, referred to as the Late Paleocene Thermal Maximum (LPTM) (based on $\delta^{18}O$ and temperature records), was a time of global warming that began to develop during the mid-Paleocene. The LPTM climate extreme was not stable and lasted only a few 100 kyr.

The time of the Paleocene-Eocene boundary was one of global transgression and was also the warmest period of the Cenozoic, with temperatures climaxing at the boundary (Field *et al.* 1997). Paleontologic proxies indicate that high latitude marine and terrestrial environments experienced near sub-tropical conditions (Zachos *et al.* 1993).

During the Early Paleogene, significant Antarctic warmth and higher precipitation may have caused a large reduction in deep waters derived from the high latitudes and polar sources. The highest temperature of the deep oceanic water was around 11-15 °C during the Early Eocene (Kennett and Stott, 1991).

Preceding the Late Paleocene to Early Eocene warming was a period of cooling, which is marked by a decline in deep sea water temperatures derived from $\delta^{18}O$ benthic records from 65 to 62 Ma (Corfield and Cartlidge, 1992). This period also recorded a significant carbon isotope excursion (CIE) (Figure 4.1), which Corfield and Cartlidge (1992) referred to as the Paleocene Carbon Isotope Maximum (PCIM) (based on $\delta^{13}C$ records). They stated that the event was brought on by both internal carbon isotope fractionation effects (such as fractionation within the oceanic reservoir of total dissolved carbon) and external carbon isotope fractionation effects (such as exchange between carbon reservoirs). Haq *et al.* (1987) presented a figure that depicts the eustatic curve through the Cenozoic, where the interval coinciding with the PCIM recording a drastic lowering of sea level, indicating a period of regression.

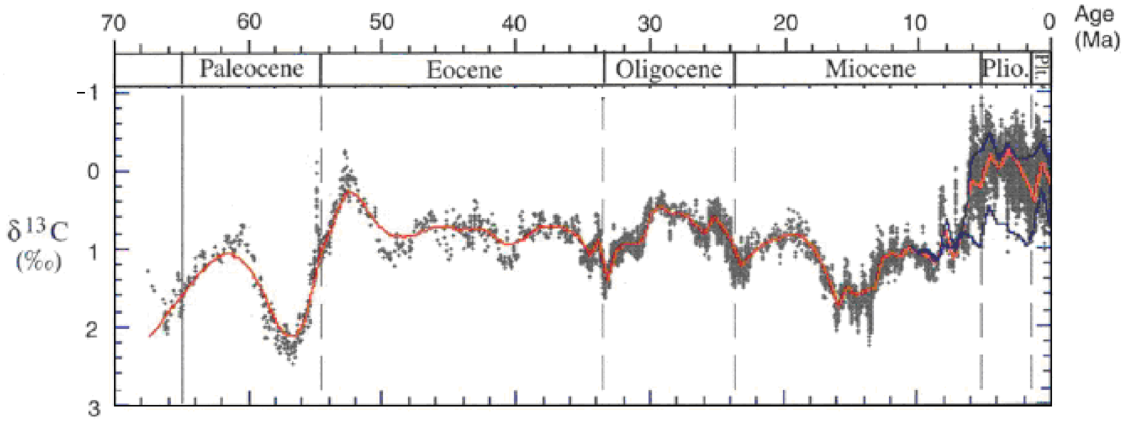

Figure 4.1 $\delta^{13}C$ record through the Cenozoic (from Zachos *et al.* 2001; Fig. 2). Typically, negative $\delta^{13}C$ values correspond to cooler periods, whereas positive $\delta^{13}C$ excursions correspond to warmer periods.

Kurtz *et al.* (2003) stated that the PCIM began 2 Myr after the Cretaceous-Tertiary boundary and peaked during the mid-Paleocene, then declined through the Late Paleocene into the Early Eocene.

Zachos *et al.* (1993) stated that, during the latest Paleocene, deep waters warmed to temperatures close to those at the ocean surface. This deep ocean warming temporarily eliminated the vertical temperature gradient between deep and surface waters, and carbonate records show decreases in both $\delta^{18}O$ and $\delta^{13}C$. The oceanic temperature gradient was re-established 30 kyr after the initial isotopic excursion.

The LPTM transient climate was accompanied by a re-organisation in ocean circulation and was marked by reduced oceanic turnover, and decreases in both marine productivity and global $\delta^{13}C$. Benthic foraminiferal oxygen isotopic records show that, from the Late Paleocene to Early Eocene, deep sea temperatures warmed from 8 °C to 12 °C. During this time, surface water temperatures increased by 5-6 °C, with maximum temperatures exceeding 20 °C (Zachos *et al.* 1993). This warming transition appears to have taken place in less than 10 kyr and did not persist. Following this period of extraordinary warmth, temperatures almost immediately began to decrease, gradually cooling over the next 100 kyr but remaining 1-2 °C higher then before the beginning of the excursion (Zachos *et al.* 1993; Kennett and Stott, 1991).

4.2 Paleoceanographic conditions from the Paleocene to Eocene

Based on $\delta^{13}C$ studies by Corfield and Cartlidge (1992) concluded that during the Early Paleocene and part of the Late Paleocene (66 and 60 Ma), deep water production was more likely to have occurred at higher latitudes than low to mid latitudes. The decline in basinal $\delta^{13}C$ gradients between the Atlantic and Pacific oceans from 60 to 56.2 Ma possibly indicates a change in the deeper regime. Corfield and Cartlidge (1992) have mentioned that more than one deep water source was active or that a low latitude source become more predominant or a high latitude source became less dominant during the interval 60 to 56.2 Ma. They also stated that the changes over this interval may have been the result of warm, saline, deep water (WSDW) production. This WSDW may have played an important role in deep water circulation between 60 and 56.2 Ma, and peaked during the LPTM and, following this period, deep waters are likely to have been produced at higher latitudes (Corfield and Cartlidge, 1992). The Southern Ocean could have been a source area for bottom waters as early as the Paleocene, with the exception of the interval between 60 and 56.2 Ma, climaxing near the Paleocene-Eocene boundary (Corfield and Cartlidge, 1992).

Deep ocean oxygen concentrations are primarily controlled by deep water formation processes. In the modern ocean, almost all dense, oxygen-rich waters are produced at high latitudes as a result of cold temperatures in combination with moderately high salinity (Kennett and Stott, 1991). Thomas (1990) suggested that during the LPTM there was a change from the formation of sinking, high latitude deep waters to the formation of deep to intermediate waters in the oceans by evaporation at lower latitudes. It is possible that these deep waters may have formed at sub-tropical latitudes, where evaporation strongly exceeds precipitation. As a result, heavy, dense, WSDW could have formed. This water would have likely been depleted in oxygen due to the lower solubility of oxygen at higher temperatures.

Today's oceanic circulation is thermohaline, which is essentially driven by the temperature differences between cold, well oxygenated, high latitudinal water. Zachos *et al.* (1993) stated that because the LPTM was a time of high temperatures and significant warmth, there would have been smaller planetary temperature gradients between high and low latitudes. During this time, deep sea water temperatures were similar to high latitudinal surface waters. The contribution of warm, saline waters to the overall deep circulation was likely to have been small, but as the higher latitudes began to warm during the mid-Paleocene, climaxing in the

Early Eocene, the density distribution of the ocean should have changed, shifting the ratio of deep water formation between high and low latitudes. At some threshold, deep ocean circulation may have changed into a form closer to a halothermal mechanism, driven by heavier, more dense, warm, saline surface waters originating from low to mid latitudes around 20-30° (Zachos *et al.* 1993; Kaiho *et al.* 1993). These surface waters would have been heavier and more dense than contemporaneous high latitudinal surface waters (Kaiho *et al.* 1993). There was a global dysaerobic event in the oceans associated with this change that is thought to have resulted from the switch from thermohaline to halothermal circulation (Killops *et al.* 2000). ODP data from the Southern Ocean suggest there was a short period of non-production of deep waters at high Southern latitudes at the Paleocene-Eocene boundary (Thomas, 1990).

During the LPTM, surface water temperatures had maximum temperatures surpassing 20 °C. At the same time, bottom waters increased to 15 °C (Zachos *et al.* 1993; Kaiho *et al.* 1993). Warm, saline, shallow surface waters from mid to low latitudes may have sunk to the bottom of the ocean to drive slow circulation (Kaiho *et al.* 1993). When deep water temperatures reach or exceed 10 °C, deep water circulation originating at high latitudes must disappear because heavy, cold water will not be produced at this temperature (De boar, 1986). Thus deep water oxygen levels would have declined if production was constant due to increasing oxygen consumption by biological activity. If circulation was slower this oxygen consumption would have been augmented (Kaiho *et al.* 1993).

It is possible that if oxygen consumption was sufficiently intense, bottom waters may have become anoxic. However, there is no record of the existence of total anoxia (Zachos *et al.* 1993).

Associated with the Late Paleocene-Early Eocene warming were major benthic foraminiferal extinctions. The process that caused the widespread extinctions was rapid (≤ 3 kyr) and had the capacity to affect great volumes of deep ocean very quickly. The extinctions were thought to have occurred at about the rate of replacement time of the Early Paleogene oceans (Kennett and Stott, 1991).

The absence of significant planktonic extinctions with respect to vast benthic extinctions and the nature of carbon and oxygen isotopic records have been suggested to reflect a decoupling of shallow and deep water ecosystems (Zachos *et al.* 1993). Elimination of ocean temperature gradients indicates vertical ocean mixing and homogenisation of nutrient distributions. Whole ocean $\delta^{13}C$ decreased by 2.5-3‰ in less than 10 kyr during the Paleocene-Eocene warming episode. Such a rapid reduction in oceanic carbon composition requires an abrupt change in the flux of depleted carbon either to or from the ocean. A possible explanation was provided by Zachos *et al.* (1993), who suggested that lower global temperature gradients led to a decline in the vigor of atmospheric circulation, thus dampening wind driven upwelling and amplifying the reduction in nutrient flux to the oceans photic zone. As the result of vertical mixing and deep water turnover, nutrient fluxes would have declined, lowering the production and export of particulate carbon to and from the mixing layer.

4.3 Isotopic and biological variations during the Paleocene to Eocene

The deep sea $\delta^{13}C$ record provides insights into the nature of global carbon cycle perturbations and on first order changes in deep sea circulation patterns (Zachos *et al.* 2001). Corfield and Cartlidge (1992) attributed some of the cause of the PCIM to increased ocean productivity, which in effect, implied greater photosynthesising biomass (and increased carbon burial). This may have had the effect of decreasing pCO_2 of surface waters, resulting in the drawdown of atmospheric CO_2 and a subsequent decline in pCO_2. This decline may have led to global cooling (Corfield and Cartlidge, 1992), coinciding with the contemporaneous lowstand of sea level during this time (see Section 4.1) that gave way to a warming period during the early stages of the Late Paleocene.

The LPTM was marked by reduced oceanic turnover and decreases in global $\delta^{13}C$ and marine productivity (Zachos *et al.* 1993). The event is characterised by a ~3.0‰ $\delta^{13}C$ excursion of the marine, atmospheric, and terrestrial carbon reservoirs (Zachos *et al.* 2001). During the LPTM $\delta^{18}O$ and $\delta^{13}C$ records show a global dysaerobic event that is associated with the Paleocene warming. This dysaerobia affected benthic taxa but not surface planktonic species (Field *et al.* 1997; Zachos *et al.* 1993; Kennett and Stott, 1991). The climatic warming event was recognised in a pelagic sequence from the Maud Rise in the Atlantic sector of the Southern Ocean (Kennett and Stott, 1991).

$\delta^{18}O$ analyses of foraminifera revealed abrupt, brief warming of deep ocean, high latitude surface waters coincident with a major extinction of benthic epifaunal foraminifera (Fig. 4.2).

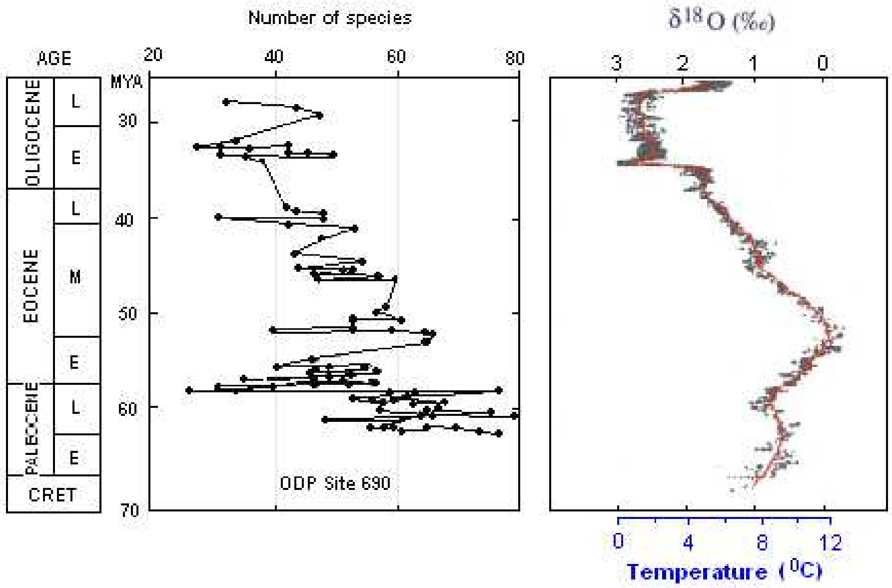

Figure 4.2 Lower Tertiary benthic epifaunal foraminifera variations at ODP 690 compared with global deep-sea oxygen isotope records. Modified from Zachos *et al.* (1993), and Zachos *et al.* (2001).

Thomas (1990) noted that benthic foraminiferal diversity dropped by 50% over a period of less than 25 kyr during the latest Paleocene, and this is corroborated by other authors such as Kennett and Stott (1991) who reported that benthic communities deeper than the continental shelf (>100 m depth) declined. During the widespread benthic epifaunal decline at the peak of the LPTM there were no extinctions of surface dwelling or terrestrial organisms on a comparable magnitude. This warming period was actually a time of low overall extinction rates (Thomas, 1990).

From the Late Paleocene to the Eocene, high latitudinal planktonic foraminiferal faunas and nannofossils became increasingly more diverse. Characteristic subtropical fauna and flora appeared in the Southern Oceans by Late Paleocene and reached peak abundance during the Early Eocene. These subtropical species slowly disappeared by the mid-Eocene as the temperature cooled to slightly higher than those temperatures before the Paleocene warming (Stott *et al.* 1990; Zachos *et al.* 1993).

Abundance records from the Late Paleocene to Early Eocene show deep sea benthic foraminiferal species underwent mass extinctions and epifaunal taxa disappeared. However, at the same time, planktonic biota diversity increased. This change is thought to have resulted from a reduction of oxygen in bottom waters. The turnover in benthic species composition was abrupt, with most disappearances occurring just below the Paleocene-Eocene boundary (Zachos *et al.* 1993).

Thomas (1990) has proposed that deep sea benthic foraminiferal faunas reflect the characteristics of deep waters. The benthic extinction event was likely due to changes in the oceanic conditions, with the replacement of a cold, well oxygenated water mass originating from high latitudes, with warm, heavy, saline, oxygen depleted water from mid to low latitudes, brought on by a change in water circulation patterns due to the LPTM warming (Field *et al.* 1997). Isotopic data from benthic foraminifera suggest that there was a short period of intense warm-saline water production during the Late Paleocene (Thomas, 1990).

Surface to deep water $\delta^{13}C$ gradients, as reconstructed from planktonic and benthic foraminifera, briefly declined to near zero in less than 10 kyr during the peak of the LPTM event (Zachos *et al.* 1993). Killops *et al.* (1996) stated that because benthic extinctions occurred at high latitudes and the main effect of the extinctions was encountered at intermediate depths, there was a loss in the oceanic temperature gradient between deep and surface waters. Kennett and Stott (1991) presented data that support this (Fig. 4.3).

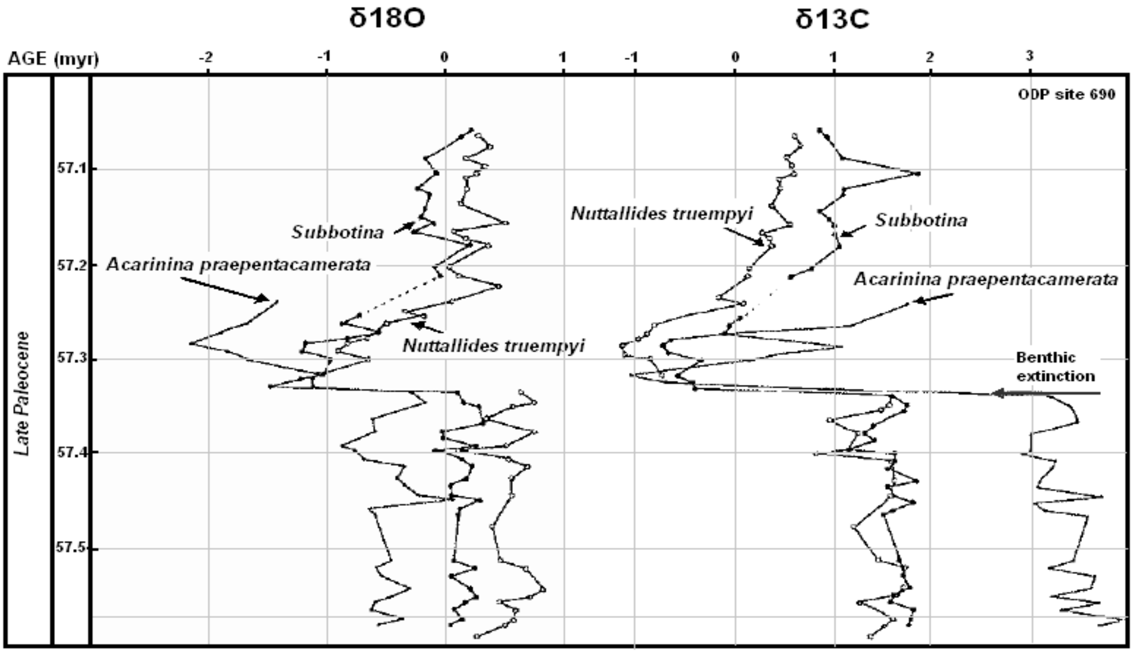

Figure 4.3 Late Paleocene $\delta^{18}O$ and $\delta^{13}C$ records from ODP site 690. Modified from Kennett and Stott (1991).

$\delta^{13}C$ levels immediately preceding the extinction event are the highest in the entire Cenozoic. $\delta^{13}C$ Benthic foraminiferal values at 57.32 Ma are almost identical to contemporaneous surface water planktonic records, and there is usually a 2‰ gradient between surface and deep waters. Zachos *et al.* (1993) suggested that a decrease of over 3‰ in the $\delta^{13}C$ records took place at this time.

From ODP research, Thomas (1990) concluded that the epifaunal benthic extinctions occurred over less than 25 kyr and were followed by approximately 350 kyr of low diversity and a strong dominance of planktonic species. This short interval is characterised by extremely low $\delta^{18}O$ and $\delta^{13}C$ values in benthic foraminiferal records. The dominance of infaunal species following the epifaunal reduction suggests the extinctions may have been caused by an increase in surface productivity, causing a strong increase in the abundance of infaunal biota. Such fauna appear to indicate high productivity of primary producers in the surface waters, good preservation of organic matter, and hence a lack of oxidation, or a combination of these. Dominance of infaunal taxa has been recorded from areas with a high flux of organic carbon to the ocean floor, or with low dissolved oxygen in the bottom waters.

As oceanic circulation during the LPTM was slow, more of the oxygen in deep waters must have been consumed by bacteria (Figures 4.3 and 4.4; Kaiho *et al.* 1993) and epifaunal species could not survive in such an oxygen-depleted environment.

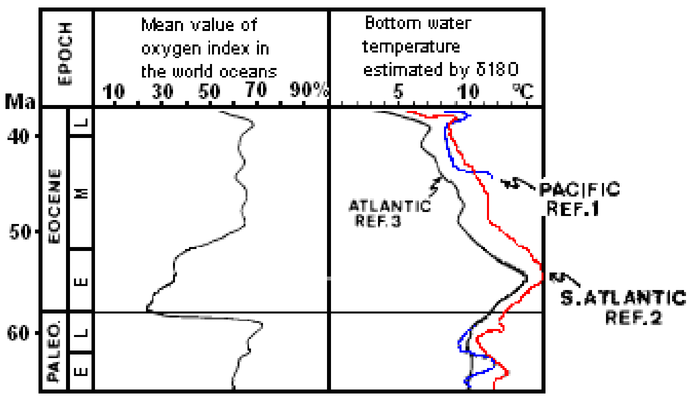

Figure 4.4 Low oxygen in the world's ocean compared with $\delta^{18}O$ records. Modified from Kaiho *et al.* (1993).

Thomas (1990) later proposed that the benthic extinctions were most likely neither the result of an increase or decrease in surface productivity, but that rather the main cause was due to the deep ocean changes at the Paleocene-Eocene boundary.

CHAPTER 5

Methods and analytical procedures

Geochemical analyses were performed on cuttings and sidewall core samples from two wells from the Great South Basin, and four wells from the Canterbury Basin. Mass spectroscopy was undertaken at the GNS National Isotope Centre (Gracefield, Lower Hutt) using an elemental analyser isotope ratio mass spectrometer (EA-IRMS) to determine the total organic carbon (TOC) content, nitrogen content, and the carbon stable isotope ratio ($\delta^{13}C$) of each sample.

5.1 Sampling

Washed cuttings and sidewall cores were collected from the National Petroleum Core Store at Gracefield, Lower Hutt (now located in Featherston). Ninety cuttings samples were taken from four wells (Rakiura-1, Pukakai-1, Resolution-1, Endeavour-1, Clipper-1, and Galleon-1); five sidewall cores were also taken from Resolution-1. Samples were taken to approximately 75-200 m above and below the Tartan Formation interval, with a nominal sampling interval of 10-50 m. Within the Tartan Formation, closer sampling intervals of 3-5 m were used where possible.

In the present study, cuttings sample depths are not represented as a depth range (for example, Galleon-1; 2400-2405 m); instead, the depth intervals are given as the middle value of the depth range in order to clarify graphical interpretations and referencing (for example, Galleon-1; 2400-2405 m is represented as 2403 m).

5.2 Sample preparation

Samples were prepared following the methods outlined by Rogers (pers. comm, 2008) and are as follows: Coarse cuttings fragments were hand picked using a microscope in order to select fragments that were most appropriate and closest resembled the average type of material from that particular cuttings sample. Selected cuttings and sidewall core samples were ground to fine powder using a mortar and pestle. This was then demineralised by placing the powdered sediment into 50 mL sample tubes, followed by the addition of approximately 10 mL of 1 mol HCl to remove the inorganic carbon (CO_3^{2-}). In some instances, 2 mol HCl, followed by heating at 50 °C in a water bath was used where it was thought that more intense treatment was required to remove more resilient calcareous material from the sample. The tubes were shaken vigorously and the acid left in the tube for at least 24 hours. Next, the acid was removed from the samples, and was neutralised by adding approximately 50 mL of distilled water and centrifuging at 3000 rpm for 10 minutes. This neutralisation process was repeated and the powdered sediment allowed to dry in an oven at around 35-40 °C.

5.3 Mass Spectrometry

In this study carbon isotopic ratios, nitrogen contents and organic contents were measured by Dr K. Rogers of GNS Science using a Europa Geo 20-20 isotope ratio mass spectrometer, interfaced to an ANCA-SL elemental analyser in continuous flow mode (EA-IRMS). Around 6-80 mg of demineralised, powdered sediment was weighed in duplicate into tin capsules. The tin capsules were tightly crimped to avoid any trapping of air that would disturb the combustion process. After O_2 injection, each capsule was dropped individually into a catalytic combustion furnace at a temperature around 1040 °C. When O_2 is introduced, tin oxidation creates an exothermic 'flash combustion' at 1800 °C, ensuring complete combustion and oxidation of the sample (Grassineau, 2006). The carbon dioxide and nitrogen gases were resolved using gas chromatographic separation on a column at 60 °C, and analysed simultaneously for isotopic abundance as well as total organic carbon (TOC) and nitrogen (%N) content. Fry *et al.* (1992), and Grassineau (2006) provide detailed overviews of the stages concerning the method in which the $\delta^{13}C$ data is derived.

Standards and blanks were included during the run for internal calibration. The analytical precision of the carbon isotopic measurements are ±0.1‰. The final carbon isotopic ratio measurements are expressed using the standard δ notation (see Equation 5.1; White, 2001), as *per mil* (‰) deviations relative to the Pee Dee Belemnite (V-PDB) standard for carbon.

Equation 5.1 $\delta^{13}C = 1000 \times [(^{13}C/^{12}C)\text{ sample} - (^{13}C/^{12}C)\text{ standard}]/(^{13}C/^{12}C)\text{ standard}$

C/N ratios were calculated by dividing the TOC content by the total nitrogen content (TN or %N) and multiplying by 14 (the atomic number of nitrogen) over 12 (the atomic number of carbon) (see Equation 5.2).

Equation 5.2 $C/N = (TOC/TN) \times (14/12)$

Total Organic Carbon values recorded in the present study are accurate to one decimal place, and nitrogen contents are less accurate. Thus, C/N calculations are rounded to the nearest whole number.

CHAPTER 6

Results

Geochemical analyses of six petroleum exploration wells from the Great South and Canterbury basins were undertaken using cuttings and sidewall core samples. Ninety cuttings and five sidewall core samples were selected, prepared (see Methods, Chapter 5) and analysed in duplicate for their TOC, $\delta^{13}C$ and nitrogen contents using an elemental analyser isotope ratio mass spectrometer (EA-IRMS) (see Section 5.3). Results for TOC, $\delta^{13}C$ and nitrogen contents for five other petroleum exploration wells from the Great South Basin (Takapu-1A, Hoiho-1C, Kawau-1A, Pakaha-1, and Toroa-1) are given in Meadows (2008) and in Appendix 3 here.

Graphical summaries of geochemical results are presented in Figures 6.1 to 6.6 for each well examined in this study, and Appendix 4 contains a complete list of all TOC, %N, C/N and $\delta^{13}C$ values for each sample analysed.

6.1 Rakiura-1

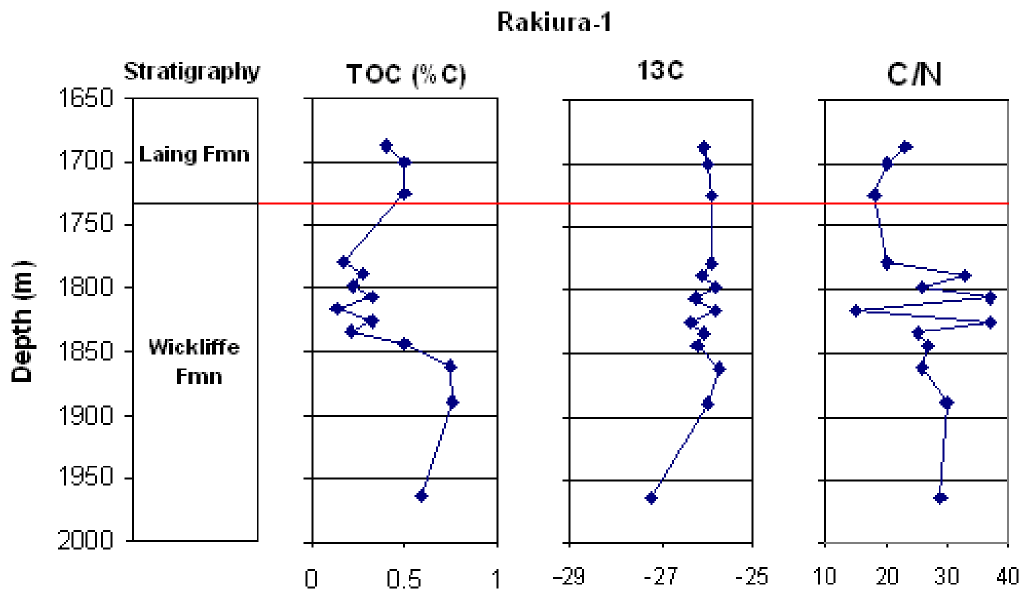

Figure 6.1 Geochemical results from Rakiura-1.

Total Organic Carbon (%C)

All cuttings samples analysed from this well have low TOC contents, consistent with the absence of the Tartan Formation. Samples selected range from Early Teurian to Late Waipawan {based on interval depths presented by Cook *et al.* (1999)}; none however recorded TOC values exceeding 1.0%. The three deepest samples from 1964 m, 1889 m, and 1861 m contain the highest TOC values of 0.6, 0.8, and 0.7% respectively. The remaining eleven samples have low TOC contents that range from 0.1 to 0.5%, with the minimum value of 0.1% having been recorded in the sample from 1816 m.

$\delta^{13}C$

For the purposes of this study, δ^{13}C values with an isotopic value around -25‰ and lighter are considered isotopically light, while values around -22‰ and heavier are considered heavy.

All samples examined in this well exhibit isotopically light δ^{13}C, with a narrow range, from -27.2 to -25.7‰ (1.5‰ variation over 14 samples spanning 276 m).

The deepest sample from 1964 m contains the lightest recorded δ^{13}C value (-27.2‰). Over the following 13 samples, from 1889 m to 1688 m, δ^{13}C values range from -26.3 to -25.7‰ (a 0.6‰ variation over these 13 samples).

Nitrogen content (%N)

Nitrogen contents from all samples in this well are very low, and all recorded values below 0.1%.

Carbon/Nitrogen Ratio

The deepest five samples analysed, from 1964 m to 1834 m, all have moderate C/N ratios that range from 25 to 30. A considerable increased was recorded in the sample from 1825 m, which has a high ratio of 37. This is followed by a relatively low C/N ratio in the sample from 1816 m with a value of 15, which is the lowest value recorded in this well. Above this, the following sample from 1807 m has a high C/N ratio of 37. Samples from 1798 m and 1789 m recorded ratios of 26 and 33 respectively. The following four samples, from 1779 m to 1688 m, have moderate to low ratios that range between 18 and 23. There is a general trend throughout the sample set which appears to display increasingly higher C/N ratios with increasing depth.

6.2 Pukaki-1

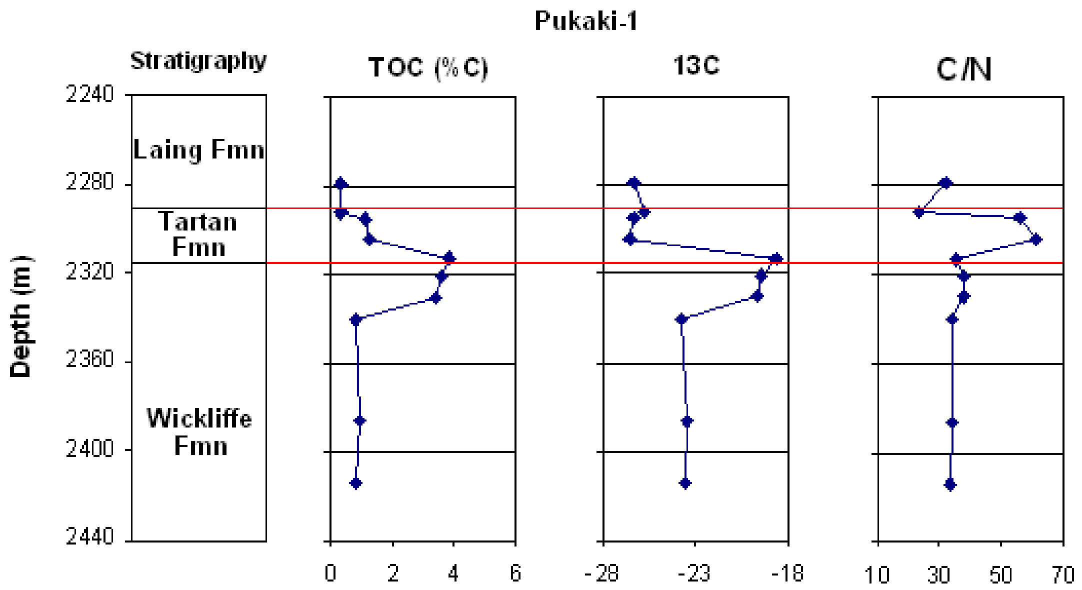

Figure 6.2 Geochemical results from Pukaki-1.

Total Organic Carbon (%C)

The three deepest samples examined, from 2414 m to 2340 m, have low to moderate TOC contents that range from 0.8 to 0.9%. The first noticeable increase in TOC content was recorded in the sample from 2330 m, with a value of 3.4%. The two samples immediately above this, from 2321 m and 2313 m also contain high TOC concentrations, with 3.6 and 3.9% respectively. The sample from 2313 m (3.9%) has the highest recorded concentration of TOC of all samples investigated in this well. These three high TOC samples lie close to and within the Tartan Formation interval as identified by Schioler and Roncaglia (2008), once sample cavings have been accounted for (sample contamination from cuttings, where samples from higher depths are incorporated into samples received from deeper in the borehole). The next two samples, from 2304 m and 2295 m, have moderate TOC values of 1.3 and 1.1% respectively. The shallowest samples from 2292 m and 2279 m have low TOC concentrations, each with a value of 0.3%.

$\delta^{13}C$

The deepest three samples examined in this well, from 2414 m, 2386 m, and 2340 m, have very similar δ^{13}C values of -23.6, -23.5, and -23.8‰ respectively, with a mean value of -23.6‰. The following three samples from 2330 m, 2321 m, and 2313 m recorded isotopically heavy δ^{13}C values of -19.7, -19.4, and -18.7‰ respectively. The mean δ^{13}C for these three samples is -19.3‰. The sample from 2313 m (-18.7‰) recorded the heaviest δ^{13}C value of all samples in Pukaki-1. The remaining four samples from 2304 m to 2279 m all contain light δ^{13}C values ranging from -26.6 to -25.8‰, with an average of -26.3‰.

It is evident from the data presented in Figure 6.2 that the samples below the heavy isotopic excursion (from 2330 m to 2313 m) are much heavier than those above the isotopic excursion.

Nitrogen content (%N)

Samples from 2414 m to 2340 m have low nitrogen contents, all below 0.1%. The three samples from 2330 m, 2321 m, and 2313 m display higher values, each containing 0.1% nitrogen. These three samples also have the highest TOC and heaviest δ^{13}C values of all samples examined in this well. The four uppermost samples, from 2304 m to 2279 m, each have nitrogen contents of less than 0.1%.

Carbon/Nitrogen Ratio

The six deepest samples from 2414 m to 2313 m all contain high C/N ratios ranging from 33 to 38. Samples from 2304 m and 2295 m both recorded exceptionally high C/N ratios of 61 and 56 respectively. The two shallowest samples from 2292 m and 2279 m have moderate ratios of 23 and 32 respectively. The mean C/N ratio for all samples in this well is 39.

6.3 Resolution-1

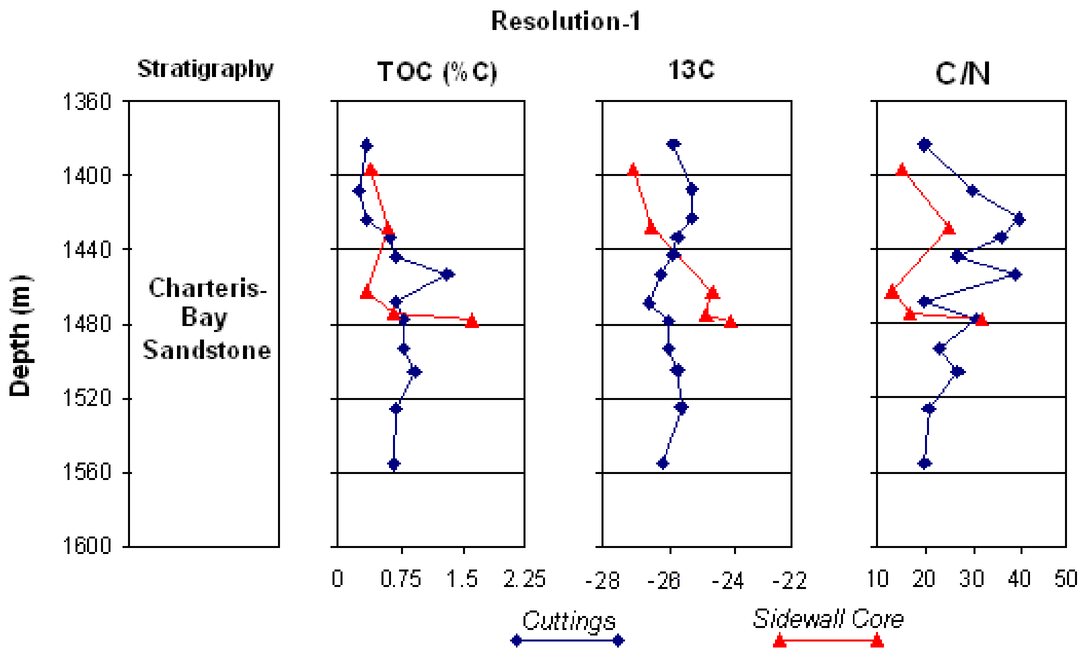

Figure 6.3 Geochemical results from Resolution-1.

Total Organic Carbon (%C)

Sidewall cores:

Of the five sidewall cores analysed from this well, only one recorded a TOC value greater than 1.0%. This came from the deepest sample from 1478 m, with a value of 1.6%. Above this, from 1474.5 m to 1396.5 m, TOC contents are low, ranging from 0.3 to 0.7%.

Cuttings:

Cuttings samples from 1555 m through 1468 m have low to moderate TOC values ranging from 0.7 to 0.9%. The sample from 1453 m has the highest TOC concentration of all Resolution-1 cuttings analysed with a value of 1.3%. This is considered to be a relatively low value compared with many samples around this interval from other wells investigated in this study. Samples from 1443 m through 1383 m gradually display lower concentrations of TOC, from 0.7% at 1443 m to 0.3% in the sample from 1383 m. The average TOC content for all cuttings samples is 0.7%, identical to the mean of the sidewall core samples.

$\delta^{13}C$

Sidewall cores:

Only five sidewall core samples were examined in this well from the 1478 m to 1396.5 m interval.

A trend observed from the data shows that the isotopic δ^{13}C becomes heavier with increasing depth (as shown in Figure 6.3). The deepest sample, from 1478 m, has the heaviest δ^{13}C value with -23.9‰. The overlying samples from 1474.5 m and 1462.5 m recorded δ^{13}C values of -24.7 and -24.5‰ respectively. The shallowest samples from 1428 m and 1396.5 m each displayed isotopically light δ^{13}C with values of -26.5 and -27.0‰ respectively. The mean value for this set of sidewall core samples was -25.3‰.

Cuttings:

Although many of the cuttings sampled in Resolution-1 are of similar depths to the above reported sidewall cores, the δ^{13}C data obtained varies considerably. Over the twelve cuttings samples investigated from this well, there is relatively little variation in δ^{13}C. All samples lie between -26.6 and -25.1‰ (a 1.5‰ difference over the 172 m sample set), with a mean value of -25.8‰. The mean δ^{13}C for cuttings samples is 0.5‰ lighter than the mean δ^{13}C from the sidewall core samples.

All δ^{13}C values from cuttings in this well are considered to be isotopically light.

Nitrogen content (%N)

All five sidewall core samples analysed show low nitrogen contents, with values less than 0.1%.

As in the sidewall core samples, low nitrogen contents of less than 0.1% are recorded for all twelve cuttings samples.

Carbon/Nitrogen Ratio

Sidewall cores:

Of the five sidewall core samples examined from this well only one recorded a moderate to high C/N ratio. This was from 1478 m with a value of 32. The remaining four samples from 1474.5 m to 1396.5 m recorded ratios that range from 13 to 25. The lowest value of 13 (from 1462.5 m) is the lowest C/N ratio of all samples examined in Resolution-1 (including cuttings samples). The mean C/N ratio for these sidewall core samples was 20.

Cuttings:

The two deepest samples examined, from 1555 m and 1525 m, have C/N ratios of 20 and 21 respectively. A ratio of 27 was recorded in the sample from 1505 m, followed by 23 from 1493 m. A moderate ratio of 31 was recorded in the sample from 1478 m. The following two samples from 1468 m and 1453 m have vastly different ratios from one another despite a relatively small sampling gap, with values of 20 and 39 respectively. Two samples from 1443 m and 1433 m have ratios of 27 and 36. The highest recorded C/N ratio in this well was identified in the sample from 1423 m, with a ratio of 40. The two shallowest samples from 1408 m and 1383 m have C/N ratios of 30 and 20 respectively.

Throughout the twelve cuttings samples analysed there is little consistency from one sample to the next (Figure 6.3). However, the overall trend throughout the well suggests that the C/N ratio lessens downwards in the well. The average C/N ratio over this set of Resolution-1 cuttings is 28, compared to the mean ratio of 20 recorded from the sidewall core samples.

6.4 Endeavour-1

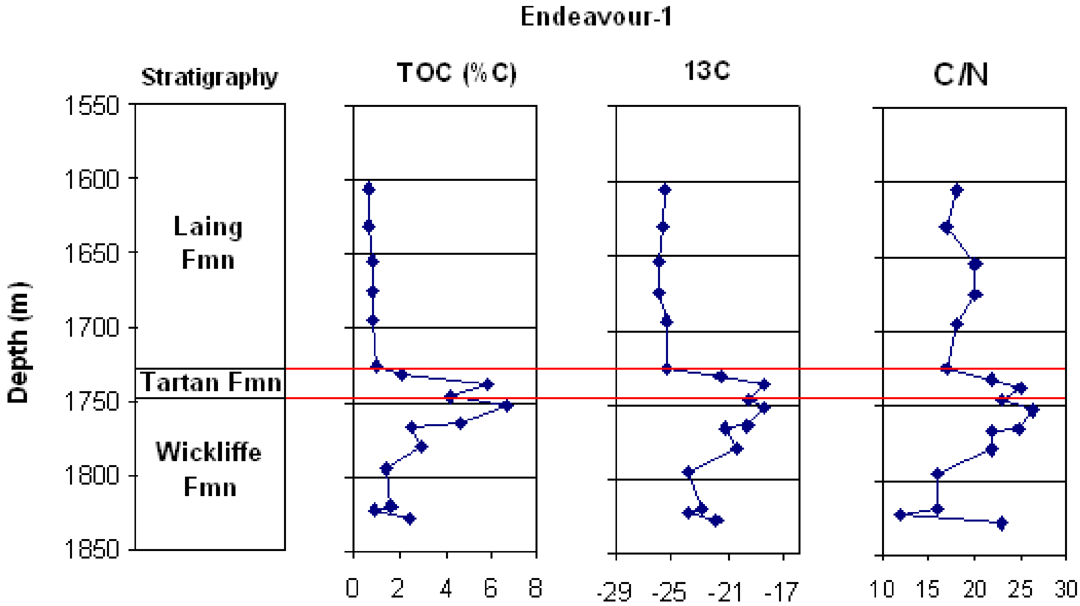

Figure 6.4 Geochemical results from Endeavour-1.

Total Organic Carbon (%C)

The deepest sample analysed for this well, from 1828 m, has a relatively high TOC content of 2.4%. This sample is approximately of mid-Paleocene age (inferred from Crown Minerals, 2008c). The next three samples, from 1822 m to 1795 m, have moderate TOC contents ranging from 0.9 to 1.6%. A significant increase in the TOC content is first observed in the sample from 1779 m (3.0%). At 1766 m a slightly lower value of 2.5% was recorded, increasing to 4.6% in the sample from 1764 m. The sample from 1752 m has the highest recorded TOC content of all Endeavour-1 samples investigated here, with a value of 6.6%. The overlying sample from 1746 m has a noticeably lower TOC content of 4.2%, followed by a significantly higher value of 5.9% in the sample from 1737 m. The sample from 1731 m is the shallowest to display a significantly elevated TOC content (2.1%). The remaining six samples above these elevated TOC samples have recorded low to moderate TOC values that generally show decreasing TOC values upwards in the well, from 1.0% in the sample from 1725 m to 0.7% in the shallowest sample analysed from 1605 m.

It is evident from the data that the TOC content of samples below the elevated TOC interval (from 1779 m to 1731 m) is higher than that of samples above the elevated TOC interval.

$\delta^{13}C$

The deepest sample analysed (1828 m) has a relatively heavy δ^{13}C value of -21.9‰. The following three samples from 1822 m, 1819 m, and 1795 m recorded moderately heavy δ^{13}C values of -23.9, -22.9, and -23.9‰ respectively. Over the 33 m depth that covers these deepest four samples there is 2.0‰ of variation in δ^{13}C. The next seven samples from 1779 m through 1731 m have all recorded heavy δ^{13}C values. The deepest of these heavy δ^{13}C samples (1779 m) recorded a δ^{13}C value of -20.4‰. The next sample from 1766 m has a slightly lighter value of -21.3‰, and the following four samples from 1764 m to 1737 m contain the heaviest δ^{13}C values in this well. The sample from 1764 m recorded a δ^{13}C value of -19.7‰, followed by -18.5‰ in the sample from 1752 m. A slightly lighter value of -19.5‰ was recorded from 1746 m, followed by a return to -18.5‰ in the sample from 1737 m. Both of the samples from 1752 m and 1737 m contain δ^{13}C values of -18.5‰, which is the heaviest value obtained from these set of analyses. The final sample to display a heavy isotopic character came from 1731 m (-21.5‰). Over the 48 m sample depth that covered these seven samples there is 3.0‰ variation in $\delta^{13}C$, with a mean value of -19.9‰. The six overlying samples from 1725 m to 1605 m all contain isotopically light $\delta^{13}C$, ranging from -26.0 to -25.3‰ (0.7‰ variation over 120 m). The mean value for these six samples is -25.6‰, which is considerably lighter than the mean value of samples between 1779 m and 1731 m (-19.9‰), and of samples below the heavy isotopic excursion, from 1828 m to 1795 m which have a mean $\delta^{13}C$ of -23.2‰.

Nitrogen content (%N)

The four samples from 1828 m through 1795 m have nitrogen contents of 0.1% or less. A significant increase in the nitrogen content is observed in the overlying seven samples from 1779 m to 1731 m, where values range from 0.1 to 0.3%. These samples also contain much higher TOC contents, and have isotopically heavier $\delta^{13}C$ values than those samples with low nitrogen contents. The six samples above 1731 m all have very low nitrogen values of less than 0.1%.

Carbon/Nitrogen Ratio

The deepest sample analysed from this well, from 1828 m, recorded a C/N ratio of 23. The three following samples from 1822 m to 1795 m have low ratios ranging between 12 and 16. These lowermost four samples have a mean C/N ratio of 17. There is a distinctive increase over the next seven samples from 1779 m to 1731 m, where ratios range from 22 to 26, with a mean value of 24. The six shallowest samples from 1725 m to 1605 m have lower ratios of from 17 to 20, with a mean of 18. It is evident (Figure 6.4) that the sample set is separated into three sections. Between 1828 m and 1795 m there is a low mean C/N ratio (17), followed by a considerable increase in the average C/N ratio of samples between 1779 m and 1731 m (24). Above this, from 1725 m to 1605 m, is a return to a lower mean value of 18.

Low to moderate C/N ratios are dominant for the seventeen samples examined from Endeavour-1. The highest value of 26 was recorded in the sample from 1752 m, whereas the lowest ratio of 12 came from a deep sample from 1822 m. The latter recorded the lowest C/N ratio of all samples examined in this set of analyses. The average C/N ratio calculated for all samples in this well is 20, which is the lowest mean value for any of the six wells investigated in this study; however, two wells investigated by Meadows (2008), Pakaha-1 and Toroa-1 (sidewall cores), have recorded lower mean C/N ratios (Appendix 3).

6.5 Galleon-1

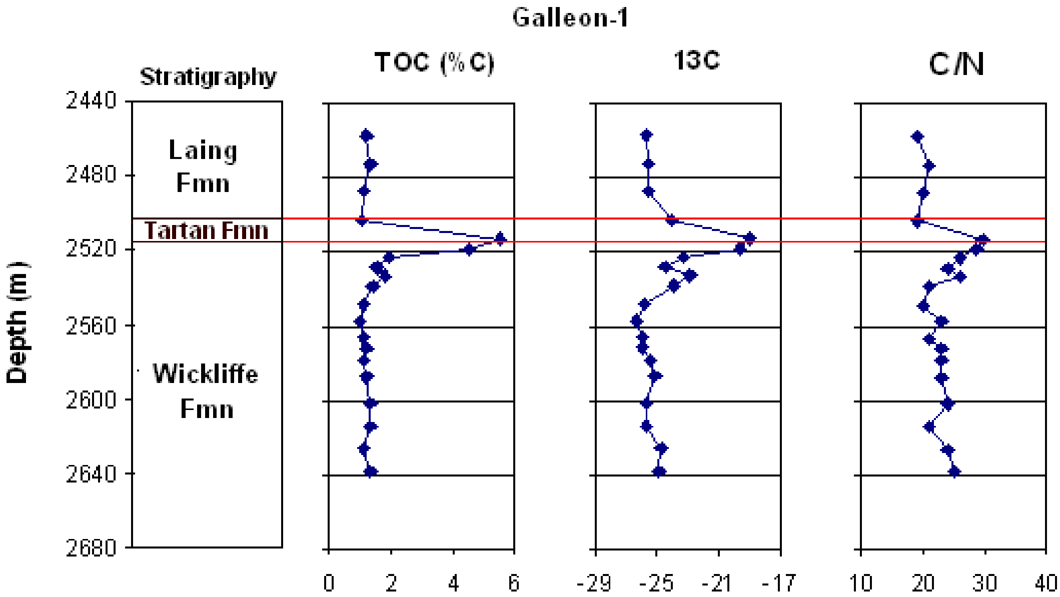

Figure 6.5 Geochemical results from Galleon-1.

Total Organic Carbon (%C)

Of the twenty cuttings samples examined only four recorded TOC values exceeding 1.5%. The eleven deepest samples from 2638 m through 2538 m all have very consistent TOC contents which range from 1.0 to 1.4%, with a mean value of 1.2%. These samples lie within the earliest to mid-Paleocene time interval (Crown Minerals, 2008c). The sample from 2533 m is the deepest to display an elevated TOC content (1.8%), followed by a slightly lower value of 1.5% in the sample from 2528 m. Over the next three samples from 2523 m, 2518 m, and 2513 m there are gradual increases in TOC content with recorded values of 2.0, 4.5 and 5.6% respectively. The sample from 2513 m (5.6%) contains the highest concentration of TOC in this well. These five consecutive moderate to high TOC concentration samples have a mean value of 3.1%. Above this, a return to low-moderate TOC contents is observed. The four samples from 2503 m to 2458 m, which represent the uppermost Paleocene to earliest Eocene, have values ranging from 1.1 to 1.4%, with a mean TOC content of 1.2%, similar to that of the deepest samples.

$\delta^{13}C$

The eleven lowermost samples from 2638 m through 2538 m all contain isotopically light $\delta^{13}C$ ranging from -26.4 to -24.0‰ (2.4‰ variation over 100 m), with a average value of -25.4‰. A trend observed throughout these eleven samples shows the $\delta^{13}C$ value becoming isotopically lighter the shallower the sample is located in the well. The sample from 2533 m contains a moderately heavy $\delta^{13}C$ value of -22.9‰, followed by an isotopically light sample from 2528 m (-24.5‰) and, above this, at 2523 m, a moderately heavy value of -23.3‰. The two samples from 2518 m and 2513 m both contain isotopically heavy $\delta^{13}C$, with -19.6 and -19.0‰ respectively. These two samples are the heaviest recorded from all samples examined from Galleon-1. The four shallowest samples from 2503 m to 2458 m all contain isotopically light $\delta^{13}C$, ranging from -25.7 to -24.1‰ (with a mean value of -25.2‰). Samples above the heavy isotopic excursion have a similar mean value to those samples below it.

Nitrogen content (%N)

Of the fourteen samples analysed from 2638 m through 2523 m, ten have nitrogen contents of 0.1%, and the remaining four have values below 0.1%. Only two samples from this well have nitrogen contents above 0.1%. These samples (2518 m and 2513 m) each recorded values of 0.2%, and also have the highest TOC contents and heaviest $\delta^{13}C$ values recorded in this well. The four samples above 2513 m all have significantly lower nitrogen contents, all less than 0.1%.

Carbon/Nitrogen Ratio

The eleven samples analysed, from 2638 m to 2538 m, have similar C/N values ranging from 20 to 25. Samples from 2533 m, 2528 m, and 2523 m recorded C/N ratios of 26, 24, and 26 respectively. The highest C/N ratios of 29 and 30 were recorded in the samples from 2518 m and 2513 m respectively. The four shallowest samples from 2503 m to 2458 m all have similar ratios that range between 19 and 21. The overall mean value for these twenty samples is 23, with a relatively narrow range between 19 and 30.

6.6 Clipper-1

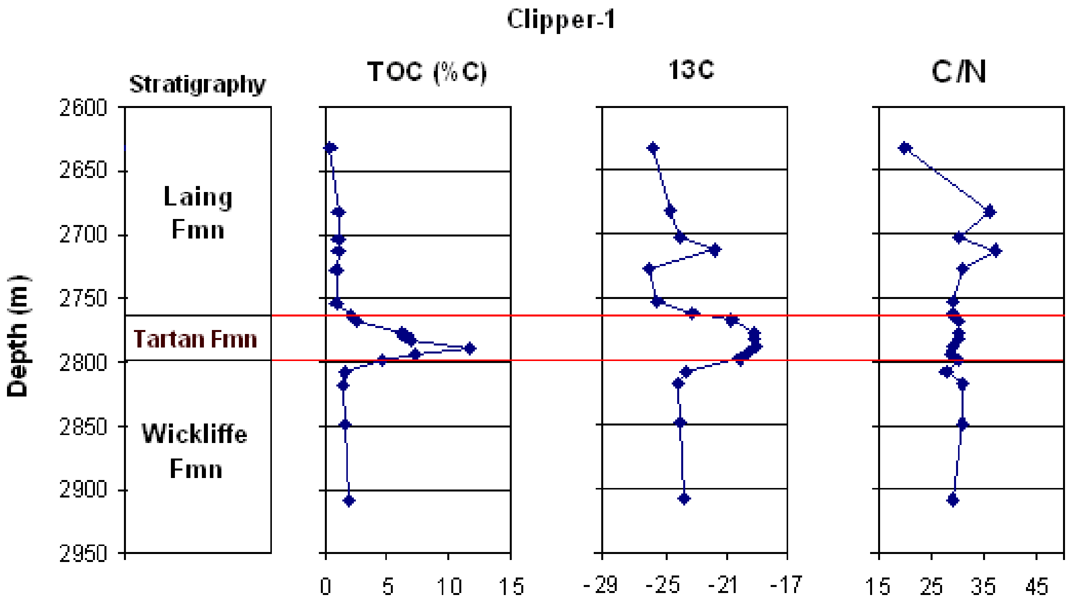

Figure 6.6 Geochemical results from Clipper-1.

Total Organic Carbon (%C)

The deepest four samples examined, from 2908 m through 2808 m, contain moderate TOC contents ranging from 1.3 to 1.8%, with a mean value of 1.5%. The sample ages are mid-Paleocene (Crown Minerals, 2008c). The overlying seven samples of mid to Late Paleocene age all have high TOC contents. The deepest of these, from 2798 m has a TOC content of 4.6% followed by a gradual rise in carbon content over the next two samples from 2793 m (7.1%) and 2788 m (11.7%). The sample from 2788 m has the highest TOC content of all samples examined in this set of analyses by a considerable margin (the highest TOC content outside of this well was a value of 6.6%, recorded from Endeavour-1). There is a gradual decrease in the TOC content over the following four samples, from 6.8% in the sample from 2783 m, to 2.0% in the sample from 2763 m. The shallowest six samples from 2753 m to 2633 m represent the uppermost Paleocene to earliest Eocene. They exhibit low to moderate TOC contents, ranging from 0.4 to 1.0%, with a mean value of 0.8%. This mean value is considerably lower than the TOC content of samples below the seven elevated samples from 2798 m to 2763 m.

$\delta^{13}C$

The four samples from 2908 m to 2808 m exhibit moderately light $\delta^{13}C$ values ranging from -24.1 to -23.5‰ (0.6‰ variation over 100 m), with a mean $\delta^{13}C$ of -23.8‰. There are six consecutive samples from 2798 m to 2768 m that have recorded isotopically heavy $\delta^{13}C$. The deepest of these samples, from 2798 m, recorded a $\delta^{13}C$ value of -20.1‰. The following two samples from 2793 m and 2788 m become increasingly heavier with values of -19.5 and -19.0‰ respectively. The sample from 2788 m (-19.0‰) has the heaviest $\delta^{13}C$ value in Clipper-1. The next two samples from 2783 m and 2778 m both contain heavy $\delta^{13}C$, with recorded values of -19.2 and -19.1‰. The shallowest of these six isotopically heavy samples from 2768 m has a $\delta^{13}C$ value of -20.6‰. The mean value for this heavy $\delta^{13}C$ excursion interval is -19.6‰, and there is 1.6‰ of variation over the 30 m sample interval. The shallowest seven samples contain light to moderately light $\delta^{13}C$ values with the exception of the sample from 2713 m, which has a relatively heavy $\delta^{13}C$ of -21.6‰. These seven samples range from -25.9 to -21.6‰, with a mean value of -24.3‰. This mean value is isotopically lighter than that of the average of the four samples that lie below the heavy $\delta^{13}C$ excursion.

Nitrogen content (%N)

The deepest samples analysed, from 2908 m to 2818 m, have nitrogen contents below 0.1%. From 2808 m through 2763 m, eight samples were analysed, all of which recorded high nitrogen values between 0.1 and 0.5%. The highest recorded value of 0.5% came from 2788 m, which also has the highest TOC content, and the heaviest $\delta^{13}C$ values of all samples investigated in this well. This sample has the highest nitrogen content of all samples analysed in this study. Once again, all samples from this well that have high nitrogen contents have significantly higher TOC contents and isotopically heavier $\delta^{13}C$ values than samples with low nitrogen contents. The six shallowest samples from 2753 m through 2633 m all recorded values below 0.1%.

Carbon/Nitrogen Ratio

The thirteen samples from the deepest sample examined at 2908 m to the sample from 2728 m contain very similar C/N ratios that range from 28 to 31. The sample from 2713 m recorded the highest ratio, with a value of 37. The sample from 2703 m has a ratio of 30, followed by another high C/N ratio in the sample from 2683 m (C/N = 36). The shallowest sample, from 2633 m, contains the lowest value of all samples examined in this well with a ratio of 20. The average C/N ratio of all seventeen samples analysed in Clipper-1 is 30.

6.7 Discussion of TOC contents between wells across the Great South and Canterbury basins

Total Organic Carbon (TOC) data provide a measure of how much organic matter is present in sediments. In this section, discussion will focus on the TOC changes throughout the sampled sections of each of the wells investigated and the most likely causes for such changes. Key concepts relating to the deposition and source of the Tartan Formation in the Great South and Canterbury basins combining all relevant geochemical data are discussed later in Chapter 7.

Rakiura-1

Samples investigated from Rakiura-1 generally display low organic richness ranging from 0.1 to 0.8% TOC. Unlike other wells studied here, and in most wells studied by Meadows (2008), there is no noticeable TOC increase in Late Paleocene to Early Eocene samples (approximately 1800-1750 m depth in this well as deduced from well logs in Placid Oil Co. 1984b), indicating that the Tartan Formation is absent from this well. Cook *et al.* (1999) describe this interval as having a sandier lithology and only locally carbonaceous. The gamma ray log response is not as marked as in other wells where the Tartan Formation is present and Schioler and Roncaglia (2008) do not recognise the Tartan Formation in this well. In fact, TOC contents are lower in the mid Paleocene than in the Early Paleocene, and this low organic content continues throughout the Late Paleocene until slightly higher organic contents are recorded from Early Eocene samples (Fig. 6.7; Rakiura-1).

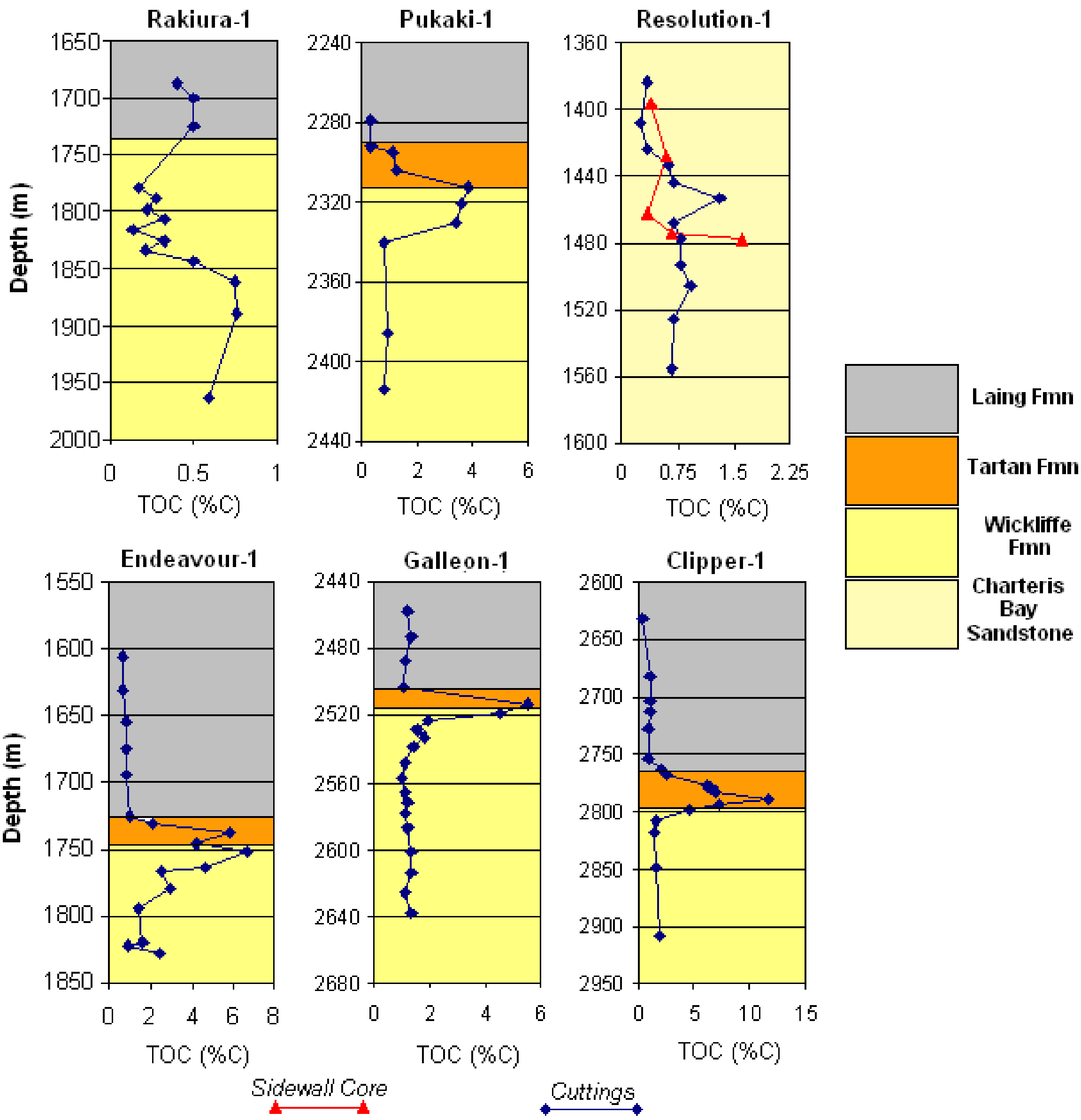

Figure 6.7 Well by well comparison of TOC content (note different depth and TOC scales).

Pukaki-1

Three cuttings samples from Pukaki-1 have high organic contents (2330 m, 2321 m, and 2313 m). These have TOC contents of 3.4, 3.6, and 3.9% respectively (Fig. 6.7; Pukaki-1). They are believed to belong to the Tartan Formation based on the gamma ray log response (see Section 7.1). Samples analysed from the overlying Laing and underlying Wickliffe formations have low to moderate TOC contents ranging from 0.3 to 1.3%. It is thus evident that there was a profound change in the conditions under which the Tartan Formation accumulated and was preserved during deposition in this area of the Great South Basin with respect to the adjacent formations.

The relatively low organic richness of the Wickliffe and Laing formations is likely the result of low organic input and/or poor organic preservation of deposited organic matter. This gave way to good preservation of deposited organic matter, likely combined with increased organic input, during deposition of the Tartan Formation.

Resolution-1

Analysis of five sidewall cores and twelve cuttings samples from Resolution-1 yielded only two samples with TOC contents exceeding 1%. The one sidewall core sample from 1478 m has the highest recorded TOC content of all samples in this well with an organic content of 1.6% TOC. This sample is believed to be from the earliest Paleocene, well below the Paleocene-Eocene boundary (approximately 1410-1435 m from GR logs). Samples examined around this Late Paleocene interval have low TOC contents ranging from 0.3 to 0.6%. The only other sample from this well to exceed 1% TOC came from a cuttings sample from 1453 m (1.3% TOC), and like the previously mentioned sidewall core sample, is from an early to mid Paleocene horizon. Late Cretaceous to Early Paleocene samples from Resolution-1 have slightly higher organic richness than those from the Late Paleocene to Early Eocene (Figure 6.7). This is the only well in this study where this trend is observed and it provides some evidence to suggest the absence of the Tartan Formation in Resolution-1. This trend also suggests that conditions for the preservation and accumulation of organic matter were slightly more favorable during the Early to mid Paleocene than they were during the Late Paleocene to Eocene in the Resolution-1 area of the Canterbury Basin.

Endeavour-1

Analysis of cuttings from Endeavour-1 between 1828 m and 1605 m yielded seven samples with high organic richness believed to represent the Tartan Formation. These seven samples, from 1779 m to 1731 m, range in TOC content from 2.1 to 6.6% (Figure 6.7; Endeavour-1). Endeavour-1 displays a gradual increase in the TOC content from 3.0% in the sample from 1779 m (the deepest sample to show an elevated organic content) through to the peak TOC content of 6.6% recorded in the sample from 1752 m. A gradual decline in organic content is observed in the following Tartan Formation samples up to the shallowest elevated TOC sample from 1731 m (2.1%). It should be noted that the sample from 1746 m has a TOC value of 4.2% and is directly between two higher TOC samples (6.6% below, and 5.9% above). This could be attributed to natural variation between samples (due to local depositional factors or even contamination of the cuttings in the well) or it could be evidence of a double pulse. Killops *et al.* (1996, 2000) have reported instances where a double pulse of organic richness in sedimentation is observed in outcrops of Waipawa Formation. In both Angora Stream (East Coast Basin) and Mead Stream (Inland Marlborough) the organic rich Waipawa Formation contains a unit of less organic rich, more calcareous sediment (Hollis *et al.* 2005). Killops *et al.* (1996, 2000) also report a similar double pulse in the Tartan Formation of Pakaha-1 and possibly Kawau-1A (Great South Basin), from results of TOC plotted against depth.

The TOC content of samples from below the Tartan Formation is, on average, higher than those from above it (1.6% mean below, 0.8% mean above). This suggests that there was greater organic input and conditions for the preservation and accumulation of organic matter were greater prior to the deposition of the Tartan Formation than following it.

Galleon-1

A total of twenty cuttings samples were examined from Galleon-1 from 2638 m to 2458 m (Fig. 6.7; Galleon-1). Four of these samples displayed the high organic richness associated with the Tartan Formation (from 2533 m to 2513 m), with the deepest, from 2533 m, recording a TOC content of 1.8%. This is considered to be a relatively low value for a sample from the Tartan Formation; however, on comparison with the heavy $\delta^{13}C$ value recorded from this sample, it would appear to be characteristic of the Tartan Formation. The overlying sample from 2528 m does not appear to possess the characteristically high TOC content and heavy $\delta^{13}C$ value associated with the Tartan Formation, as it has a relatively low TOC content of 1.5% (and an isotopically light $\delta^{13}C$ value of -25.5‰). It is possible that this low TOC sample represents the intervening organically poor layer between two organic rich layers of the unit as discussed above (Endeavour-1; TOC discussion). The next three samples from 2523, 2518, and 2513 m each contain high organic contents with TOC values of 2.0, 4.5, and 5.6% respectively.

Samples from underlying and overlying formations contain similar mean TOC values, suggesting that in this area of the Canterbury Basin conditions for the preservation and accumulation of organic matter were similar both prior and post Tartan Formation deposition. This situation is unique to this well, as other wells investigated in the present study and by Meadows (2008), where Tartan Formation is present, commonly show samples from underlying formations with greater organic richness than that of samples from above the Tartan Formation. This will be discussed further below.

Clipper-1

In Clipper-1, six of the seventeen samples analysed from 2908 m to 2633 m recorded high organic richness that is consistent with Tartan Formation (Fig. 6.7; Clipper-1). The deepest of these, from 2798 m, has a TOC content of 4.6%, and a gradual rise in organic content occurs over the following two samples from 2793 m and 2788 m with values of 7.1 and 11.7% respectively. The sample from 2788 m (11.7%) has the highest TOC content of all samples examined here. Over the following four samples, from 2783 m to 2763 m, there is a gradual decrease in the organic richness from 11.7% at 2788 m to 2.0% at 2763 m. The pattern for Clipper-1 Tartan Formation samples (Fig. 6.7; Clipper-1) suggests that environmental perturbations associated with deposition of the formation were less pronounced during the initial and final stages of deposition, but were at their peak during the mid stages of deposition, coinciding with the higher TOC values of 7.1, 11.7, and 6.8% at 2793, 2788, and 2783 m respectively. Figure 6.7 (Clipper-1) shows that samples below the Tartan Formation contain, on average, higher TOC contents than that of those samples above the Tartan Formation.

6.8 Nitrogen contents of samples from wells from the Great South and Canterbury basins

For the purposes of this study, the nitrogen contents were primarily recorded and used in conjunction with the TOC data to calculate the C/N ratio for each sample. The nitrogen content data are not discussed individually; instead, Section 6.9 details the importance of these data when combined with TOC data. The nitrogen contents of all samples examined in this study are presented in Appendix 4.

6.9 Discussion of C/N between wells across the Great South and Canterbury basins

C/N ratios can be used to distinguish between marine and terrestrial origins in sedimentary organic matter (Meyers, 1994). Fresh, unaltered algae typically have atomic C/N ratios between 5 and 8 (Emerson and Hedges, 1988; Meyers, 1994), whereas vascular land plants have C/N ratios of ≥ 20 (Meyers, 1994). This distinction is caused by the absence of cellulose in algae and its abundance vascular plants (Meyers, 1994), and also the protein richness of algal organic matter (Rau *et al.* 1987; Twichell *et al.* 2002). Meyers (1994) has stated that C/N ratio variability can also result from changes in the proportions of C_3 and C_4 plant material.

Meyers (1992) suggested that elevated C/N ratios may be associated with high rates of marine productivity, possibly under conditions of low nitrogen availability, and this has been observed in modern sediments (Meyers *et al.* 2006). The organic matter produced under these conditions would be lipid-rich and nitrogen-poor. Organic-rich strata may have elevated C/N ratios as a result of selective loss of nitrogenous organic compounds (Rau *et al.* 1987). Verardo and MacIntyre (1994) have proposed that high C/N ratios can indicate faster loss of nitrogen over carbon during the sinking of marine organic matter from the photic zone. They reasoned that nitrogen-containing proteinaceous matter is more readily utilised by microbes than carbohydrate compounds. Meyers (1997) made a similar point in that partial degradation of algal organic matter during sinking can selectively reduce proteinaceous compounds, thus raising the C/N ratio. Van Mooy *et al.* (2002) stated that degradation of organic matter is different under oxic and suboxic conditions. They concluded that suboxic microbial degradation by denitrification preferentially utilises nitrogen-rich amino acids, leaving a larger portion of the nitrogen-poor organic components intact than under an oxic environment, and thus the C/N ratios of the surviving organic matter are higher.

Selective degradation of organic matter components during early diagenesis can also modify C/N ratios of organic matter in sediments (Meyers, 1997). The C/N source signature of sub-aqueous sediments is generally well preserved despite the large reduction of the total amount of organic matter during sinking. Both C/N and $\delta^{13}C$ values appear to experience little diagenetic change through time once deposited on the seafloor (Meyers, 1994; Twichell *et al.* 2002), and thus the source information gathered from C/N ratios in sub-aqueous sediments is generally reliable (Meyers, 1997).

Meyers *et al.* (2006) stated that elevated C/N ratios are typical of black shales, and indicate depressed organic matter degradation associated with suboxic conditions in the water column, which preferentially favors preservation of carbon-rich forms of marine organic matter over nitrogen-rich components. Meyers *et al.* (2006) also mentioned that C/N values between 20 and 40 in black shales are unusual for marine organic matter but are common in mid-Cretaceous black shales (Rau *et al.* 1987; Meyers, 1989; Dumitrescu and Brassell, 2006).

There are circumstances where the C/N ratios impart misleading indications of bulk organic matter origins. The majority of sediments contain low inorganic nitrogen (IN) concentrations compared to the organic nitrogen content and thus C/N ratios usually represent organic matter concentration closely. However, in some sediments that contain low organic matter concentrations, where the TOC content is less than 0.3%, the proportion of inorganic nitrogen can occasionally constitute a large fraction of the residual nitrogen, and so C/N ratios based on residual nitrogen could be artificially low (Meyers, 1997). Rau *et al.* (1987) made a similar point, and further suggested that C/N ratios may also be depressed because of significant adsorbed inorganic nitrogen from bacterial degradation of organic material. Rogers (pers. comm, 2008) considered that C/N ratios in samples with low organic contents (below 0.3%) become more difficult to accurately detect using present analytical methods, and hence analytical errors become larger. These views are taken into consideration in the C/N discussion in Chapter 7.

The C/N ratios calculated from the TOC and nitrogen contents in this study are of particular importance. Previous studies of the Tartan/Waipawa Formation by Killops *et al.* (1996) and Killops *et al.* (2000) have stated that the formation had a predominantly marine origin with variable terrestrial components incorporated. Terrestrial components are present in many samples examined from the Waipawa Formation in the East Coast Basin, and traces of black, coaly material are also present in samples examined from the Great South Basin from Kawau-1A, Pakaha-1 and Toroa-1 (Killops *et al.* 2000).

Of the four wells studied here that appear to contain Tartan Formation, no sample from within the Tartan Formation interval has a C/N ratio below 20 (Fig. 6.8).

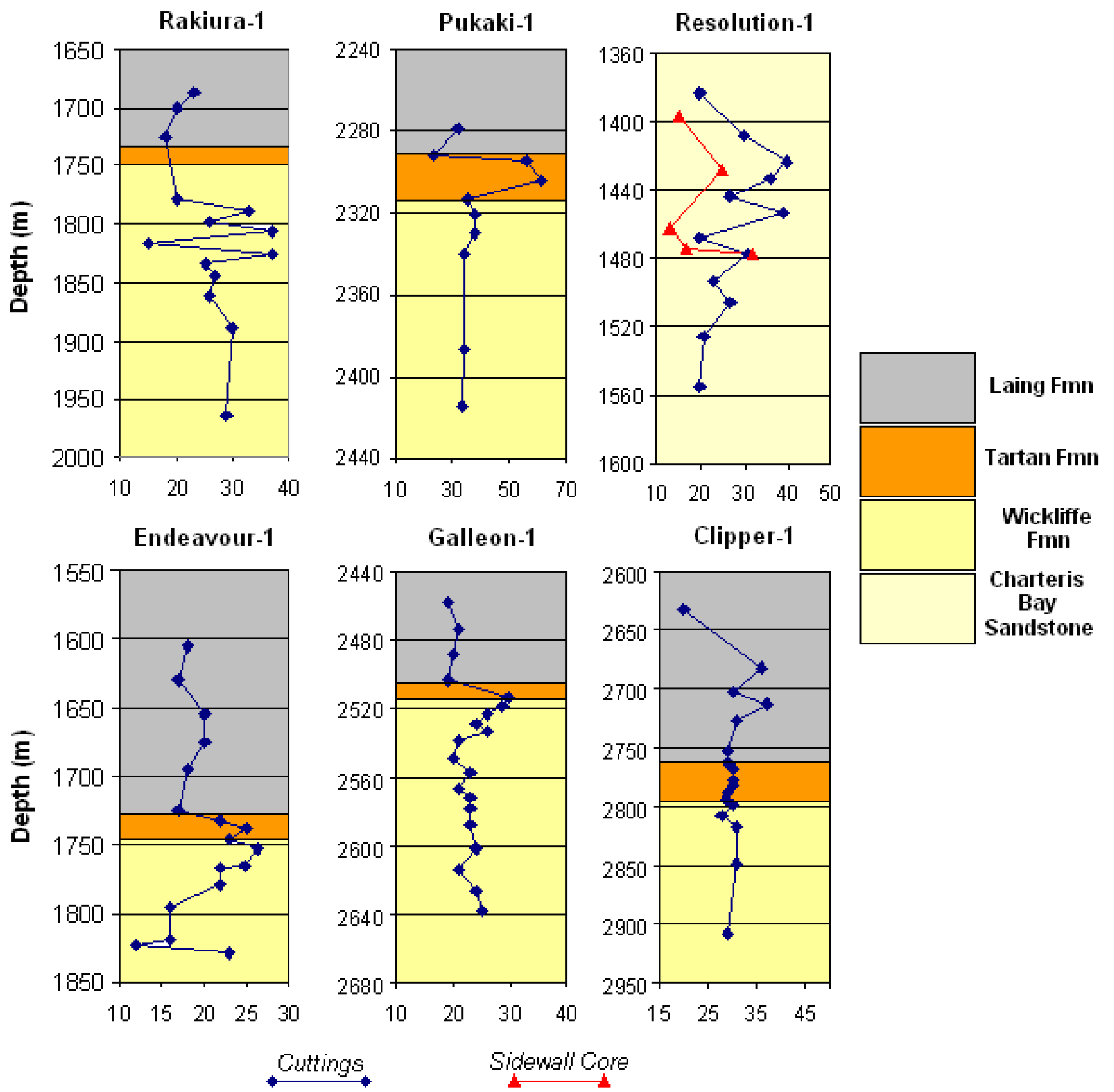

Figure 6.8 Well by well comparison of C/N ratio (note different depth and C/N scales).

As discussed above, typical unaltered algal organic matter has low C/N ratios between 5 and 8, and C/N ratios of 20 or greater are associated with vascular land plants, whereas ratios between 10 and 20 are considered to have been derived from a mixed marine and terrestrial source. The approximately twenty samples from four wells with Tartan Formation present have C/N ratios between 22 and 38.

C/N results presented in Figure 6.8 of samples within the Tartan Formation interval indicate that the organic matter is derived from a predominantly terrestrial source, with possibly some marine contribution that has elevated C/N ratios as a result of preferential nitrogen loss during biological degeneration. Overall, 79 of 90 cuttings and 2 of 5 sidewall core samples have C/N ratios of 20 or greater, and all 95 samples examined have ratios exceeding 10 (Appendix 4).

Rakiura-1

In Rakiura-1, where the Tartan Formation does not appear to be present, C/N ratios range from 15 to 37, with a mean value of 26, indicating that some samples contain a mixed marine and terrestrial origin and others contain organic matter derived from a predominantly terrestrial source but that overall the organic matter is primarily derived from a terrestrial vascular plant type.

Pukaki-1

The three Tartan Formation samples analysed from Pukaki-1, from 2330 m to 2313 m, each recorded similar C/N ratios ranging from 36 to 38, indicating a constant source of organic matter that was likely derived from predominantly terrestrial plants. The two samples from 2304 m and 2295 m have exceptionally high C/N ratios of 61 and 56 respectively. These values could be the result of a very high terrestrial composition, and selective nitrogen loss within the organic matter during sediment deposition by microbial reworking. Remaining samples from above and below the Tartan Formation interval have C/N ratios ranging from 23 to 34, which suggests that there is a high proportion of terrestrial organic matter contained within these samples; however, the terrestrial organic matter contained within these samples differs from the terrestrial organic matter contained within the Tartan Formation samples, as shown by the C/N ratio differences.

Resolution-1

Sidewall core analyses from Resolution-1, between 1478 m and 1396.5 m, indicate a mixed marine and terrestrial organic matter origin for three of the five samples (C/N ratios range from 13 to 17), and two samples which exhibit a primarily terrestrial character (ratios of 25 and 32). Cuttings sampling of Resolution-1 between 1555 m and 1383 m recorded C/N ratios between 20 and 40, with a mean ratio of 28. This indicates that the organic matter contained within samples over this sampling range was primarily derived from a terrestrial source. No Tartan Formation appears to be present in Resolution-1 from analyses of both sidewall core and cuttings samples. Upon examination of Figure 6.8 (Resolution-1) it is apparent that sidewall core and cuttings samples give relatively similar trends for C/N ratios; however, the sidewall core samples appear to contain, on average, slightly lower C/N ratios. The slight ratio differences between sidewall cores and cuttings may indicate that the marine component is better preserved in the sidewall core samples than it is in cuttings samples, which may be contaminated by cavings, where samples from higher depths are incorporated into samples received from deeper in the borehole.

Endeavour-1

Sampling of cuttings from Endeavour-1 recorded C/N ratios that range between 12 and 26, with a mean of 20 (Fig. 6.8; Endeavour-1). Seven of the seventeen samples examined from 1828 m to 1605 m lie within the Tartan Formation interval (samples 1779 m through 1731 m) and have C/N ratios between 22 and 26 (mean = 24). It appears that the formations that immediately enclose the Tartan Formation contain mixed marine and terrestrial organic matter, with relatively low C/N ratios, whereas those samples within the Tartan Formation with high C/N ratios have a greater terrestrial organic matter component.

Galleon-1

Of the twenty samples examined from Galleon-1 between 2638 m and 2458 m, four have the geochemical characteristics associated with the Tartan Formation (from 2533 m to 2513 m). C/N ratios are high in these four samples, ranging from 26 to 30 (mean = 28). This is considerably higher than for samples from above and below the Tartan Formation interval and for the overall C/N mean for all Galleon-1 samples (23). This suggests that the Tartan Formation was under a greater terrestrial influence than adjacent formations. The C/N ratio appears to decrease with decreasing depth (excluding the four Tartan Formation samples Figure 6.8 [Galleon-1]). This may indicate that a more marine influence developed during the course of deposition from 2638 m to 2458 m (Early Paleocene to mid-Late Paleocene).

Clipper-1

Analyses of seventeen cuttings samples from Clipper-1 showed six to lie within the Tartan Formation interval boundaries as recognised by gamma ray log response (see Section 7.1). These are from 2798 m to 2768 m and have C/N ratios ranging from 29 to 30, indicating a primarily terrestrial organic matter source. This consistent C/N range over the 30 m of

Tartan Formation samples suggests that the conditions under which the Tartan Formation was preserved was consistent throughout deposition. Samples lying outside the Tartan Formation interval have C/N ratios that range from 20 to 37, with a mean ratio of 30. The most likely origin of the organic matter in this sample set is again terrestrial.

6.10 Discussion of $\delta^{13}C$ between wells across the Great South and Canterbury basins

Carbon isotopic ratios are useful for distinguishing between marine and continental plant sources of organic matter and for identifying different types of land plant contributions in marine sediments (Meyers, 1994, 1997).

Biochemical fractionation of carbon isotopes is primarily a kinetic process (White, 2001) and occurs during photosynthesis (Meyers, 1994). In marine plants such as phytoplankton, carbon isotopic fractionation is controlled by many factors such as temperature, availability of CO_2 (aqueous), light intensity, nutrient availability and pH, as well as physiological factors such as cell size and growth rate (Hoefs, 2004). Most photosynthetic plants incorporate carbon into organic matter using the C_3 Calvin-Benson metabolic pathway, which biochemically discriminates against ^{13}C to produce a $\delta^{13}C$ shift of approximately -20‰ from the isotopic ratio of the inorganic carbon source (Meyers, 1994). Approximately 90% of modern plants utilise the Calvin-Benson metabolic pathway, producing C_3 plants. These include most trees and shrubs, algae and autotrophic bacteria and most cultivated vegetation. Isotopic ranges for organic matter of C_3 type marine plants are approximately -20‰ for bacterial carboxylation and -29‰ for higher plant species (White, 2001). Organic matter produced from atmospheric CO_2 ($\delta^{13}C \sim -7$‰) by land plants using the C_3 pathway consequently has average $\delta^{13}C$ values between -29 and -26‰ PDB (Meyers, 1994).

Some plant species incorporate carbon into organic matter using the C_4 Hatch-Slack pathway, which creates less carbon isotopic fractionation and gives heavier $\delta^{13}C$ values (White, 2001). Meyers (1994) stated that organic matter derived from C_4 type plants has $\delta^{13}C$ values around -14‰. Modern C_4 plant types include many grasses, corn and sugarcane (White, 2001).

Hayes (1993) concluded that the ^{13}C content of each biomolecule depends primarily on four factors: (1) the ^{13}C content of the carbon source, (2) isotopic effects associated with the assimilation of carbon, (3) isotopic effects associated with metabolism and biosynthesis (i.e. during respiration and uptake of CO_2), and (4) cellular carbon budgets at each branch point (at each point within the cellular reaction network, distribution of carbon among products will affect isotopic compositions). White (2001) suggested that $\delta^{13}C$ compositions become slightly heavier moving up the food chain. The carbon isotopic compositions of organic matter reflect principally the dynamics of carbon assimilation during photosynthesis and the isotopic composition of the source (Hayes, 1993).

Marine algae (all C_3 type plants; White, 2001) and bacteria are isotopically heavier than C_3 land plants (Meyers, 1994), as the main chemical compounds (lipids and carbohydrates) in terrestrial plants are usually isotopically lighter than those of marine plants (Tissot and Welte, 1978). Hayes (1993) stated that lipids contain less heavy ^{13}C than other products of biosynthesis and hence are isotopically lighter. The distinction between marine and terrestrial organic matter reflects the isotopic composition of the carbon source for photosynthesis; marine plants utilise dissolved carbonate components in seawater, whereas terrestrial plants use atmospheric CO_2, with an isotopically lighter $\delta^{13}C$ ratio (Tissot and Welte, 1978). Freshwater algae utilise dissolved CO_2, which is usually in isotopic equilibrium with atmospheric CO_2. The source of inorganic carbon for marine algae is dissolved bicarbonate, which, with a $\delta^{13}C$ value of approximately 0‰ (Meyers, 1994), is heavier than atmospheric CO_2 ($\delta^{13}C$ ~ -7‰). Thus marine organic matter is generally isotopically heavier than terrestrial organic matter.

Late Cretaceous black shales are commonly isotopically lighter than Cenozoic organic-rich marine sediments. Dean *et al.* (1986) concluded from carbon isotopic studies that the isotopic differences between Cretaceous black shales (-29 to -26‰) and Neogene organic-rich sediments (-23 to -16‰) were the result of dissolved CO_2 availability to marine algae. They reported that CO_2 availability during the Late Cretaceous was higher than in the Neogene, thus resulting in isotopically lighter $\delta^{13}C$ ratios in Cretaceous black shales.

Carbon isotope results from this study will be discussed initially as a well by well description of results and later, in Chapter 7, will integrate all relevant geochemical data to provide an overall interpretation of possible sources and conditions surrounding the deposition of the organic matter present in the Tartan Formation. Further correlation and comparison are also discussed in Chapter 7 where geochemical data from the present study are integrated with the findings from Meadows (2008).

Rakiura-1

$\delta^{13}C$ results from Rakiura-1 (Fig. 6.9; Rakiura-1) display a narrow range in light isotopic values (from -27.2 to -25.7‰). As there is such little variation in $\delta^{13}C$ over the 276 m sampling range, it is likely that there was a consistent source of deposited organic matter throughout the sampled section of this well. The isotopically light nature of samples from in this well suggests that the organic matter contains a significant proportion of terrestrial plant material, which was most likely derived from plants that utilised the C_3 Calvin-Benson metabolic pathway.

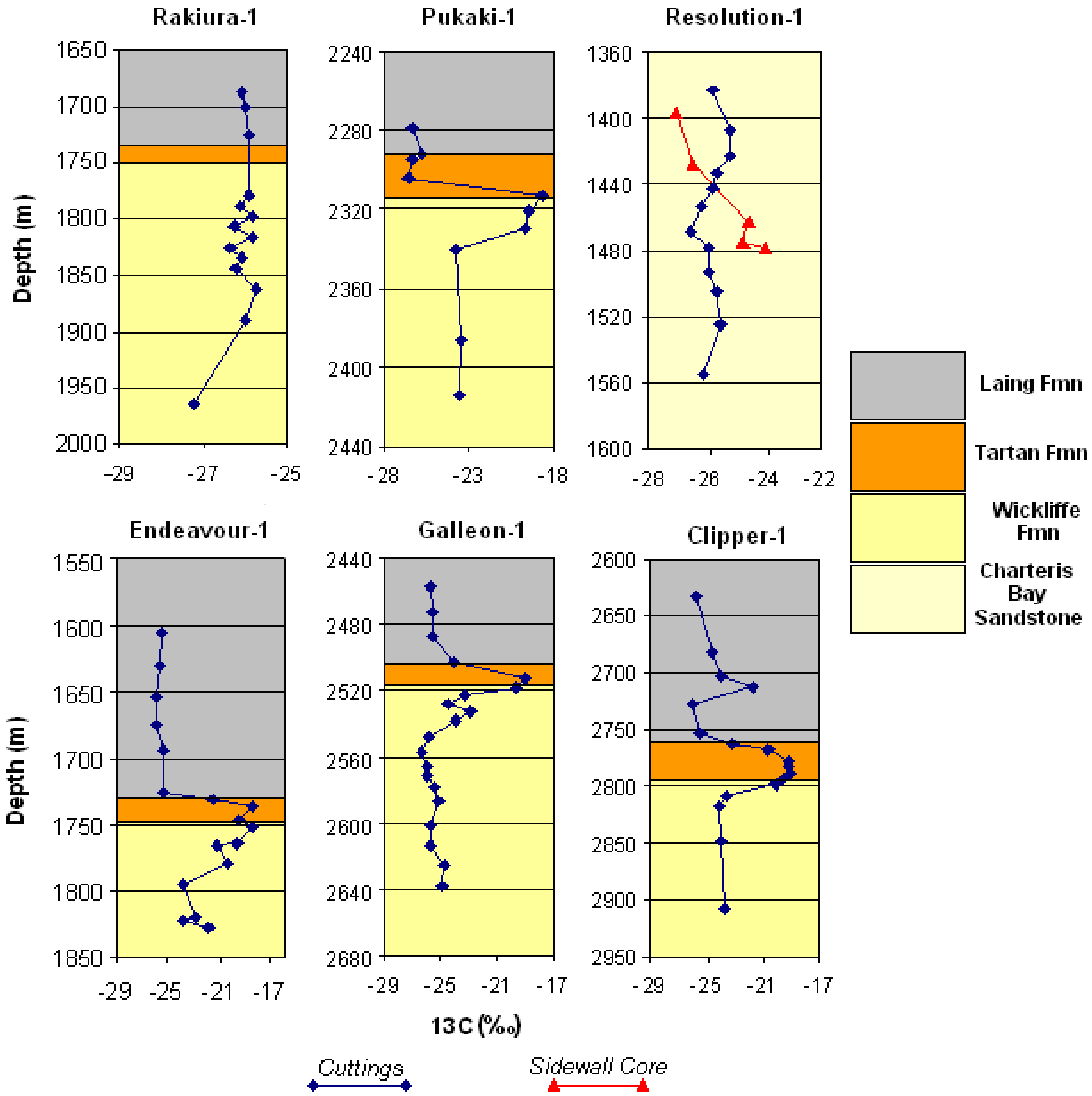

Figure 6.9 Well by well comparison of $\delta^{13}C$ (note different depth and $\delta^{13}C$ scales).

Pukaki-1

Ten samples from Pukaki-1, from 2414 m to 2279 m, were analysed and a positive isotopic excursion was recorded over the three samples from 2330 m, 2321 m, and 2313 m (Fig. 6.9; Pukaki-1). These three samples have $\delta^{13}C$ values ranging from -19.7 to -18.7‰. Figure 1 from Meyers (1994) shows that C_3 marine algae and C_3 land plants can record values around -20‰; however, C_3 terrestrial plants average approximately -27‰. To get the heaviest value of -18.7‰ recorded in the sample from 2313 m it is possible that there was a significant contribution from marine plant and bacterial material, possibly with C_3 land plants. Possible origins of the organic matter contained within these samples will be discussed in greater detail in Chapter 7.

The three samples analysed from below the Tartan Formation positive excursion in Pukaki-1 have an isotopic range from -23.8 to -23.5‰. This isotopic range is indicative of C_3 marine plants, marine bacteria and algae, and/or C_3 terrestrial plants. Above the Tartan Formation excursion, from 2304 m to 2279 m, the $\delta^{13}C$ range is lighter than that of samples below the Tartan Formation excursion, ranging from -26.6 to -25.8‰. It is likely that the organic matter contained within these samples is derived from a predominantly C_3 land plant source. The approximately 2.5‰ lighter $\delta^{13}C$ difference in samples from above the Tartan Formation interval indicates that there is a higher concentration of C_3 terrestrial plants in these samples compared to the isotopically heavier samples below the Tartan Formation excursion.

Resolution-1

$\delta^{13}C$ analyses of five sidewall core samples from Resolution-1 between 1478 m and 1396.5 m recorded isotopically light values that range from -27.0 to -23.9‰. It is likely that organic matter contained within these samples was derived from a predominantly C_3 terrestrial source. The deepest sample examined from 1478 m, which recorded a moderately heavy $\delta^{13}C$ value of -23.9‰ may have a mixed C_3 marine and C_3 land plant source.

Analyses of twelve cuttings samples from Resolution-1, from 1555 m to 1383 m, recorded a narrow $\delta^{13}C$ isotopic range from -26.6 to -25.1‰. These isotopically light $\delta^{13}C$ values are indicative of predominantly C_3 land plant-derived organic matter. The relatively small variations throughout the sample set suggest a constant source of organic matter throughout deposition. The cuttings samples overlap the $\delta^{13}C$ range of the Resolution-1 sidewall core samples from similar depths; however, the sidewall cores, on average, have slightly heavier $\delta^{13}C$ values than the cutting samples (Fig. 6.9; Resolution-1).

Endeavour-1

Seven of the seventeen cuttings samples analysed from Endeavour-1 between 1828 m and 1605 m were from the Tartan Formation interval (between 1779 m and 1731 m). Each of these seven gave isotopically heavy $\delta^{13}C$ values ranging from -21.5 to -18.5‰ (Fig. 6.9; Endeavour-1). The organic matter contained in samples from the Tartan Formation in this well was most likely derived from C_3 marine plants and bacteria with some C_3 land plant contribution. The four samples examined from below the Tartan Formation, from 1828 m to 1795 m, have relatively heavy $\delta^{13}C$ values ranging from -23.9 to -21.9‰. These are much heavier than the mean $\delta^{13}C$ values of the six samples from above the Tartan Formation interval (from 1725 to 1605 m), which have a light isotopic character ranging from -26.0 to -25.3‰ (mean = -25.6‰). It is evident that environmental conditions and/or source material deposition were different before and after Tartan Formation deposition (Figure 6.9; Endeavour-1). These differences could be caused by differences in the relative proportions of marine and terrestrial components incorporated into the deposited organic matter. The organic matter contained in these samples is likely to be a mixture of marine and terrestrial C_3 plant material. The lighter $\delta^{13}C$ samples from above the Tartan Formation interval most probably have a higher proportion of C_3 land plant material than that of the samples below the Tartan Formation, accounting for the lighter $\delta^{13}C$ character observed.

Galleon-1

Twenty cuttings samples were examined from Galleon-1, between 2638 m and 2458 m (Fig. 6.9; Galleon-1). Of these samples, four are thought to represent the Tartan Formation (from 2533, 2523, 2518, and 2513 m). The latter have a $\delta^{13}C$ range from -23.3 to -19.0‰, with a mean value of -21.2‰, and probably contain organic matter derived from a mixture of C_3 terrestrial plant and C_3 marine plant sources. The eleven samples from below the Tartan Formation interval have all recorded relatively light $\delta^{13}C$ values ranging from -26.4 to -24.0‰, with a mean of -25.2‰. Samples above the Tartan Formation interval have very similar $\delta^{13}C$ parameters, ranging from -25.7 to -24.1‰, with a mean of -25.2‰. It is possible that around this area of the Canterbury Basin the source of organic matter was similar both prior and post Tartan Formation deposition. The relatively light isotopic nature of these samples suggests that the organic matter source was predominantly C_3 terrestrial plants, with some small C_3 marine plant contributions in the heavier non-Tartan Formation samples.

Clipper-1

Six of the seventeen samples analysed between 2908 m and 2633 m from Clipper-1 lie within the Tartan Formation interval. These six samples, from 2798 m to 2768 m, have recorded heavy $\delta^{13}C$ values which range from -20.6 to -19.0‰, with a mean of -19.6‰. The organic matter here is most likely to have been derived from a mixture of sources. Organic matter with $\delta^{13}C$ values of around -20‰ could have been sourced from C_3 marine plants that were derived from bacterial carboxylation, and marine algae, and possibly some C_3 land plant contribution. There are two samples from 2808 m and 2763 m, from above and below the Tartan Formation interval respectively, which have intermediate $\delta^{13}C$ values of -23.5‰ and -23.2‰. Close inspection of Figure 6.9 (Clipper-1) suggests that these two samples possibly represent the initial and final stages of Tartan Formation deposition. If this is the case, then an explanation for the slightly lighter $\delta^{13}C$ character of these samples, compared to the heavy Tartan Formation samples, could be a gradual onset of and decline from the environmental changes that built up to the Tartan Formation deposition in this area of the basin. The three remaining samples below the Tartan Formation contain intermediate $\delta^{13}C$ values, with a mean of -23.9‰. These samples are on average heavier than those samples above the Tartan Formation interval, which recorded a mean $\delta^{13}C$ of -24.5‰. It is probable that the organic matter present in these samples was derived from a mixed marine and terrestrial source. The sample from 2713 m had an anomalously heavy $\delta^{13}C$ value of -21.6‰. This is well above the recognised Tartan Formation interval, and its heavy $\delta^{13}C$ character could be the result of a brief period of increased marine contribution to the organic matter; however, the high C/N ratio of 37 indicates a predominantly terrestrial origin, complicating the origin of its organic mater. The samples taken directly above and below this sample, from 2728 m and 2703 m have much lighter values of -25.9 and -23.9‰ respectively, consistent with values from enclosing formations of the Tartan Formation recorded in other wells.

CHAPTER 7

Discussion

Discussion here of geochemical data from exploration wells investigated is based upon correlation to gamma ray (GR) logs (defining the lithological interval of the Tartan Formation), as these show differences between lithologic and geochemical boundaries over the intervals studied. Possible sources of organic matter are also discussed, as are the causes and timing of Tartan Formation deposition, and correlation to the Waipawa Formation. Data obtained during the present study are integrated with results from the study by Meadows (2008).

7.1 Geochemical correlation to Gamma Ray logs

GR logs covering the sampled interval, including the Tartan Formation interval, were derived from the original logs that are included in the relevant well completion and petroleum reports.

GR logs are lithology logs that measure the natural radiation of a formation. Sandstones and carbonates have low concentrations of radioactive material, and thus emit low levels of gamma radiation. Shales characteristically concentrate more radioactive material, thus emitting higher levels of gamma radiation than coarser sediments. Thus, as the shale content of a formation increases so to does the GR response (Asquith, 1983).

In the present study two wells from the Great South Basin (Rakiura-1 and Pukaki-1), and four wells from the Canterbury Basin (Resolution-1, Endeavour-1, Galleon-1, and Clipper-1) have been investigated. Four of these six wells contained Tartan Formation: Pukaki-1, Endeavour-1, Galleon-1, and Clipper-1. The GR logs for each of the wells are plotted against the geochemical data in Figure 7.1.

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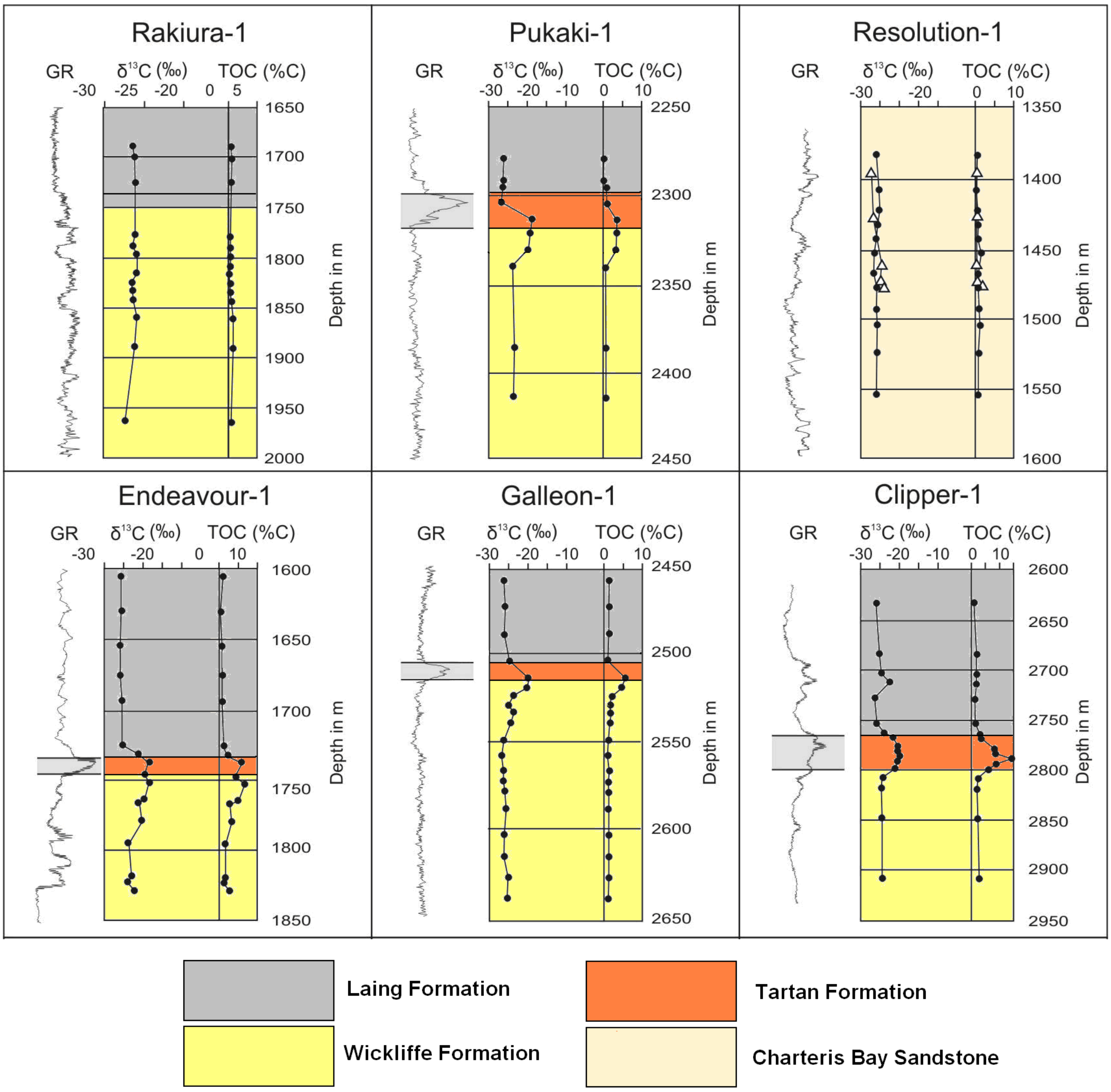

Figure 7.1 Geochemical comparisons to gamma ray log data (Shaded areas of the GR logs represent the Tartan Formation interval, solid points represent cuttings samples, and hollow points are sidewall core samples. Also note the variable depth and chemical scales for each well).

From this figure, it is evident that the GR response generally correlates to at least part of the geochemical excursions shown by the TOC and $\delta^{13}C$ records. It appears that, in wells where the Tartan Formation is present, the GR excursion occurs towards the top of the geochemical excursion, which often exceeds the limits of the GR excursion. This is a possible result of sample contamination from cuttings, where samples from higher depths are incorporated into samples received from deeper in the borehole; thus providing an offset indication of geochemical boundaries. However, it is likely that the depth differences between the GR and geochemical excursions in Pukaki-1, Endeavour-1, and possibly Galleon-1 are not caused solely by cuttings contamination from shallower samples. It appears that the deepest GR excursion finishes well above the deepest excursions of the geochemical data in these three wells. Small differences between GR and geochemical data can be attributed to cuttings contamination, but the larger variance observed is more likely controlled by the type of organic matter contained within the samples. As the GR log is a lithology log, changes in the properties of the strata encountered within the well influence its response depending upon the amount and distribution of the natural radiation present in a formation. The TOC and $\delta^{13}C$ values recorded in this study measure the quantity and type of organic carbon present in the formation. It is possible that the onset of the event associated with the geochemical changes began prior to the change in lithology, which would account for the differences in the data.

Meadows (2008) used the term "geochemical facies" to distinguish the differences between the GR response (as defining the formation boundaries) and the geochemical data over this interval. In light of the data obtained from the present study and further research into the global isotopic changes during the Paleocene, it appears that these geochemical changes prior to the recognised base of the Tartan Formation and the geochemical changes of the formation are associated with the Paleocene Carbon Isotope Maximum (PCIM) (see Chapter 3, Chapter 4, and Section 7.4).

7.2 Source of organic matter in samples from the Great South and Canterbury basins

C/N ratios from samples within the Tartan Formation interval (Figure 7.2) range from 22 to 38, and TOC contents range from 1.8 to 11.7%, with most samples having C/N ratios between 22 and 30, and TOC between 2 and 7%.

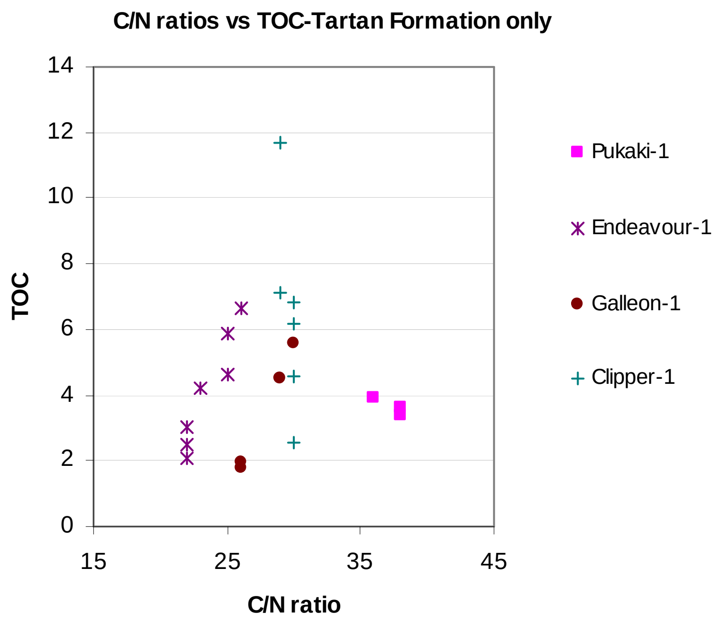

Figure 7.2 C/N vs. TOC for samples from the Tartan Formation.

Figure 7.2 displays the general trend of large increases in TOC content correlating positively with relatively small increases in C/N ratios. Only one sample examined within the Tartan Formation interval had a TOC value below 2% (Galleon-1; 2533 m, 1.8%), and all samples had C/N ratios above 20, indicating a predominantly terrestrial organic matter source with some possible marine plant contribution. There is greater terrestrial influence on organic matter with increasing TOC content, possibly as a result of enhanced organic matter preservation with increasing terrestrial composition. The elevated C/N ratios likely indicate reduced organic matter degradation associated with suboxic conditions within the water column. This would have led to preferential preservation of carbon-rich organic matter over nitrogenous components (Meyers *et al.* 2006). Microbial degradation under suboxic conditions by denitrification preferentially utilises nitrogenous compounds, such as amino acids (van Mooy *et al.* 2002) and proteinaceous matter, rather than carbon-rich compounds, such as carbohydrates (Verardo and MacIntyre, 1994) and C_3 and C_4 high-cellulose plants (Meyers, 1994). This leaves higher proportions of nitrogen-poor components in the sediments, resulting in higher C/N ratios. Data from this study suggest that similar conditions and events could have influenced the organic matter contained within Tartan Formation sediments, resulting in the high C/N, high TOC results observed.

Samples from the Tartan Formation are clearly distinct from samples from the enclosing formations (Fig. 7.3).

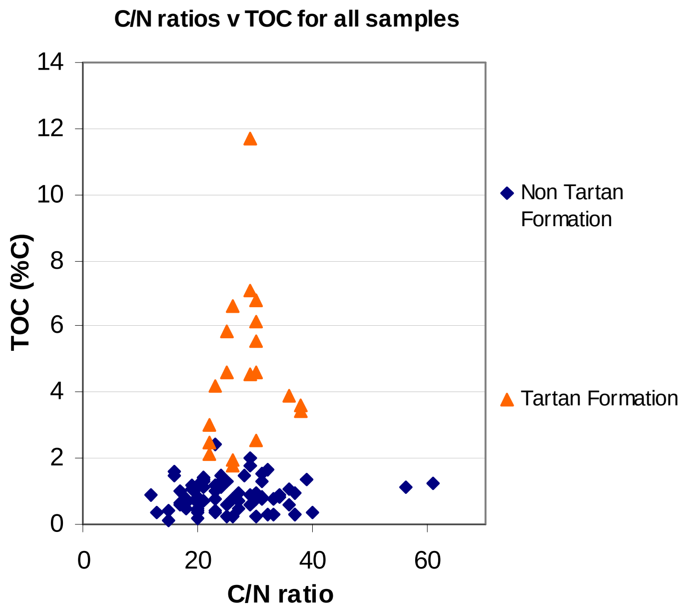

Figure 7.3 C/N vs. TOC for all samples analysed in this study.

From Figure 7.3, it is evident that there is much less variation in the C/N ratios of the Tartan Formation samples than from samples of adjacent formations. All but two samples from enclosing formations have TOC contents below 2%, and the trend of C/N vs. TOC is almost linear, whereas samples from the Tartan Formation typically display greater terrestrial influence on organic matter with increasing TOC content. This indicates that TOC has little effect on the C/N ratio of Tartan Formation samples compared to those from enclosing formations.

There are many samples from the underlying and overlying formations that have C/N ratios below 20, indicating a marine plant and algal or mixed marine/terrestrial source. There are also many samples that have C/N values at or above 20, indicating higher proportions of terrestrial components in the organic matter. The change in C/N ratio without a corresponding change in the TOC amongst samples from enclosing formations could be explained by the conditions surrounding preservation, and by differences in the extent of microbial activity degrading nitrogenous compounds of the organic matter (see below). Dumitrescu and Brassell (2006) suggest that samples with uniform C/N ratios could represent organic matter derived from a uniform source; this indicates that samples from the Tartan Formation (Fig. 7.2) have a much more uniform source of organic matter than adjacent formations (Fig. 7.3).

Examination of the individual data points for C/N ratios plotted against $\delta^{13}C$ values from each well from samples of the Tartan Formation (Fig. 7.4) shows a grouping of samples for each well (with the exception of Galleon-1, which is divided into two separate sub-clusters). The distinct grouping of samples in each well suggests that the organic matter supply was similar, and variability across wells suggests that preservation and organic matter supply varied from place to place.

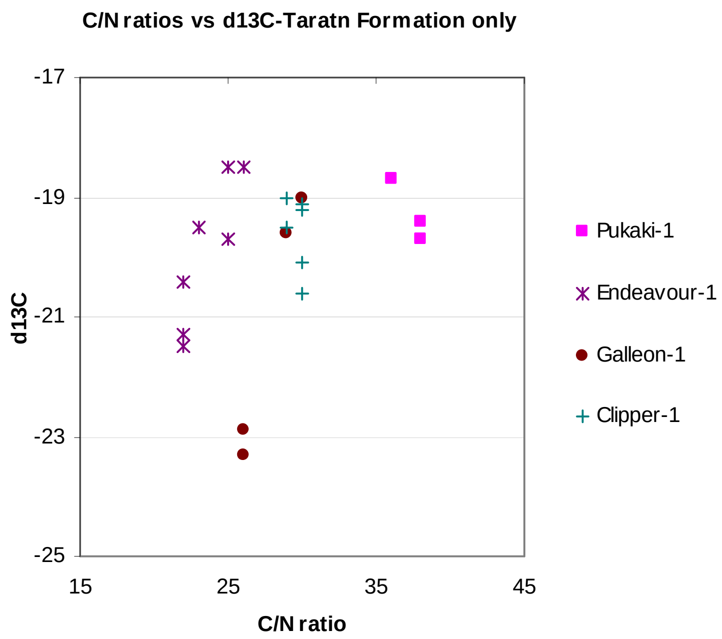

Figure 7.4 C/N vs. $\delta^{13}C$ data for samples from the Tartan Formation interval.

$\delta^{13}C$ ratios around -20‰ are typical of organic matter derived from C_3 marine plants/algae/bacteria (White, 2001), and heavier isotopic ratios of approximately -14‰ are characteristic of C_4 land plants (Meyers, 1994); however, it is unlikely that any C_4 land plant material would be present in samples from the Late Paleocene Tartan Formation as this plant type has been reported to have only developed around 25-30 Ma (Osborne and Beerling, 2006). Due to the high C/N ratios of samples within the Tartan Formation, it would appear that a terrestrial source of organic matter is likely. However, $\delta^{13}C$ analyses have given many isotopically heavy values, below -20‰, that tend to indicate a mixed marine and terrestrial source.

Figure 7.5 shows that samples of the Tartan Formation interval almost all lie between marine plant/bacterial, C_3 land plant and C_4 land plant compositions. Thus, it is likely that the organic matter of the Tartan Formation is derived from a mixture of sources, both marine and terrestrial, with the differences being produced by variations in the relative proportion of each type of source material. There are variations in both $\delta^{13}C$ and C/N ratios indicating changes in the source of organic matter throughout deposition, coupled with variable levels of preservation throughout the depositional period.

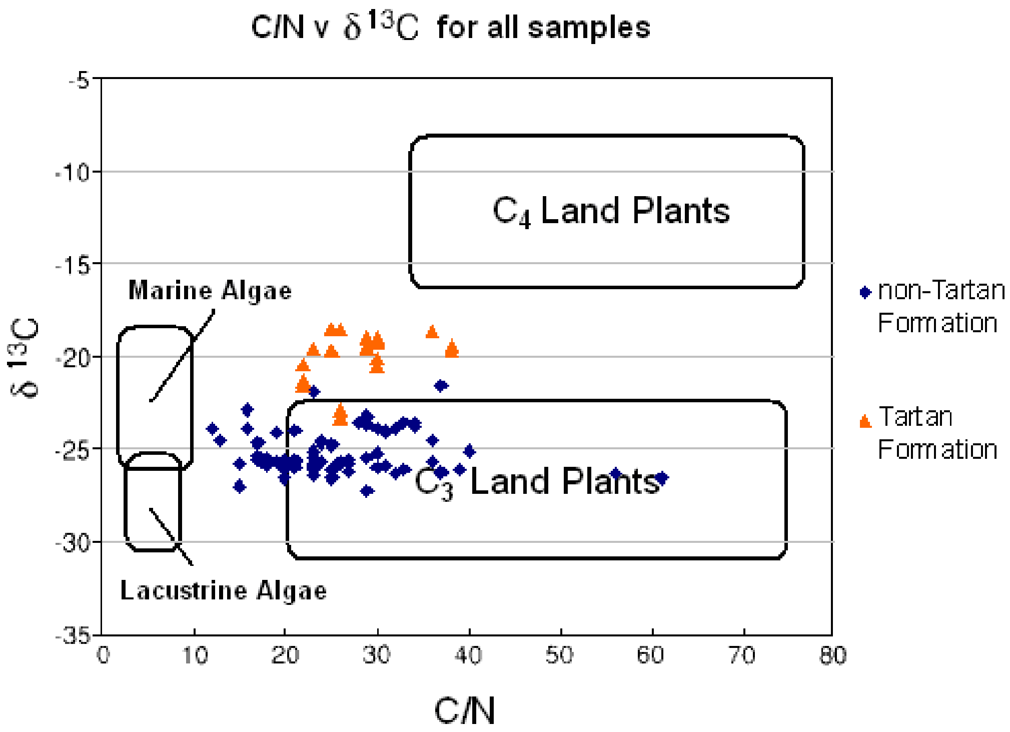

Figure 7.5 Comparison of C/N vs. $\delta^{13}C$ data from all samples analysed in this study, (including the above-mentioned Tartan Formation samples from Fig. 7.4) overlain onto a diagram modified from Meyers (1994; Fig. 1) The original diagram specified ranges for C/N and $\delta^{13}C$ values for different organic matter sources.

From Figure 7.5, Tartan Formation samples plot towards the lower C/N end-member for C_3 plants and towards the heavier $\delta^{13}C$ range for marine algae. There are several samples from the Tartan Formation interval that recorded $\delta^{13}C$ values towards the heaviest isotopic end-member range of marine algae. It is possible that these samples contain higher proportions of marine material than C_3 terrestrial organic matter, giving the heavy isotopic character which they exhibit.

Figure 7.5 also displays samples from the immediately adjacent Wickliffe and Laing formations. There is a distinct difference between samples from the Tartan Formation and those of the enclosing formations. These samples generally lie within the $\delta^{13}C$ range of -27 to -23‰, and most C/N ratios lie between 15 and 40. This indicates that there were several sources for organic matter (also shown in Figure 7.6), deposited with varying degrees of preservation. The majority of non-Tartan Formation samples plot towards the lower end-member for C/N ratios, and towards the middle and heavier end-member of the $\delta^{13}C$ range for C_3 land plants. Some of these samples appear to have a mixed terrestrial and marine character; such samples tend to plot on the lower end-member of the C/N ratio for C_3 land plants and the isotopically lighter end-member for $\delta^{13}C$ marine algae. The data in Figure 7.5 suggest that the organic matter of the enclosing formations of the Tartan Formation was derived from a combination of C_3 land plants and marine components, but predominantly contain terrestrial components.

In Figure 7.6 TOC data are compared to $\delta^{13}C$ data. Again, there is a clear distinction between samples from the Tartan and adjacent formations.

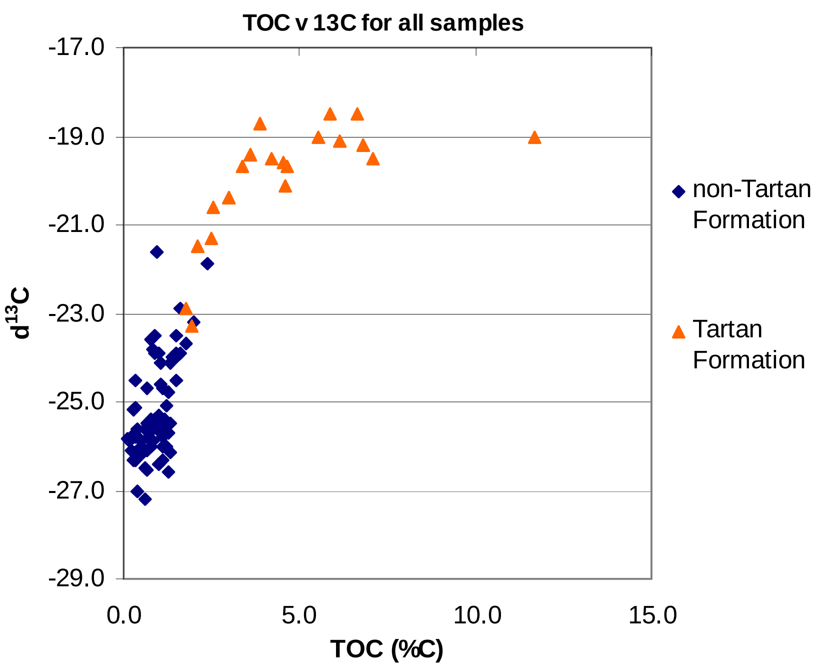

Figure 7.6 Comparison of TOC vs. $\delta^{13}C$ for Tartan and non-Tartan Formation samples.

The higher organic content samples correlate positively with heavier $\delta^{13}C$ values within the Tartan Formation. Figure 7.6 also demonstrates that the Tartan has variable preservation of organic matter between wells, probably due to both depositional environment and organic input. This is shown by variations in TOC content for Tartan Formation samples from 1.8 to 11.7%. Variations in $\delta^{13}C$ values across wells within the Tartan Formation indicate a change in the source of organic matter (also see Fig. 7.5 and corresponding discussion).

7.3 Correlation of latest geochemical data to Meadows (2008)

This section will compare the results from the present study of the Canterbury and Great South basins to previous work from the Great South Basin undertaken by the author. The previous work is included with this thesis as an electronic copy of Meadows (2008) as supplementary data.

In the present study six well from the Great South and Canterbury basins were investigated. The Late Paleocene Tartan Formation was present in four of these wells (Pukaki-1, Endeavour-1, Galleon-1, and Clipper-1). The Late Paleocene to Early Eocene section of five other wells from the Great South Basin have previously been investigated by the author; of which, four contained Tartan Formation (Kawau-1A, Hoiho-1C, Pakaha-1, and Toroa-1). In total, eight of eleven wells investigated contain Tartan Formation (five from the Great South Basin, and three from the Canterbury Basin). Table 7.1 displays peak geochemical values recorded from both studies for each well where Tartan Formation was identified.

Well	Peak $\delta^{13}C$ (‰)	Depth (m)	Peak TOC (%C)	Depth (m)
Meadows (2008)	Cuttings			
Kawau-1A	-17.4	2264	11	2264
Pakaha-1	-19.3	2551	6.5	2551
Meadows (2008)	Sidewall core			
Hoiho-1C	-15.8	1578	17.1	1578
Kawau-1A	-18.2	2240	9.3	2240
Pakaha-1	-20.7	2576	5.3	2576
Toroa-1	-21	2162	7.2	2162
Present study	Cuttings			
Pukaki-1	-18.7	2313	3.9	2313
Endeavour-1	-18.5	1752 & 1737	6.6	1752
Galleon-1	-19	2513	5.6	2513
Clipper-1	-19	2788	11.7	2788

Table 7.1 Peak $\delta^{13}C$ and TOC values recorded from this study and that by Meadows (2008).

The data presented in Table 7.1 displays highly organic rich and isotopically heavy $\delta^{13}C$ values for all wells containing the Tartan Formation. From well to well, peak TOC contents range from 3.9% in Pukaki-1, to a maximum of 17.4% in Hoiho-1C. $\delta^{13}C$ values range from -25‰ in Hoiho-1C, to -15.8‰, also in Hoiho-1C, whereas C/N ratios (see Appendix 3 and Appendix 4) range from 21 (Pakaha-1) to 44 (Hoiho-1C).

Tartan Formation samples from Pukaki-1 and Hoiho-1C contain the highest C/N ratios ranging from 35 to 44. C/N ratios within this range are indicative of plant material that has been derived from a predominantly terrestrial source. $\delta^{13}C$ data recorded from Tartan Formation samples in these wells range from -25‰ to -15.8‰ (both from Hoiho-1C), whereas the Pukaki-1 Tartan Formation samples range from -19.7‰ to -18.7‰. This range of $\delta^{13}C$ values are generally indicative of primarily marine sources of organic matter, such as algae, bacteria, and C_3 marine plants. The conflicting C/N and $\delta^{13}C$ data of the source of organic matter from Hoiho-1C and Pukaki-1C most likely indicate that organic matter was derived from mixed C_3 land plant, C_3 marine plant, marine bacterial, and algal sources (Fig. 7.7).

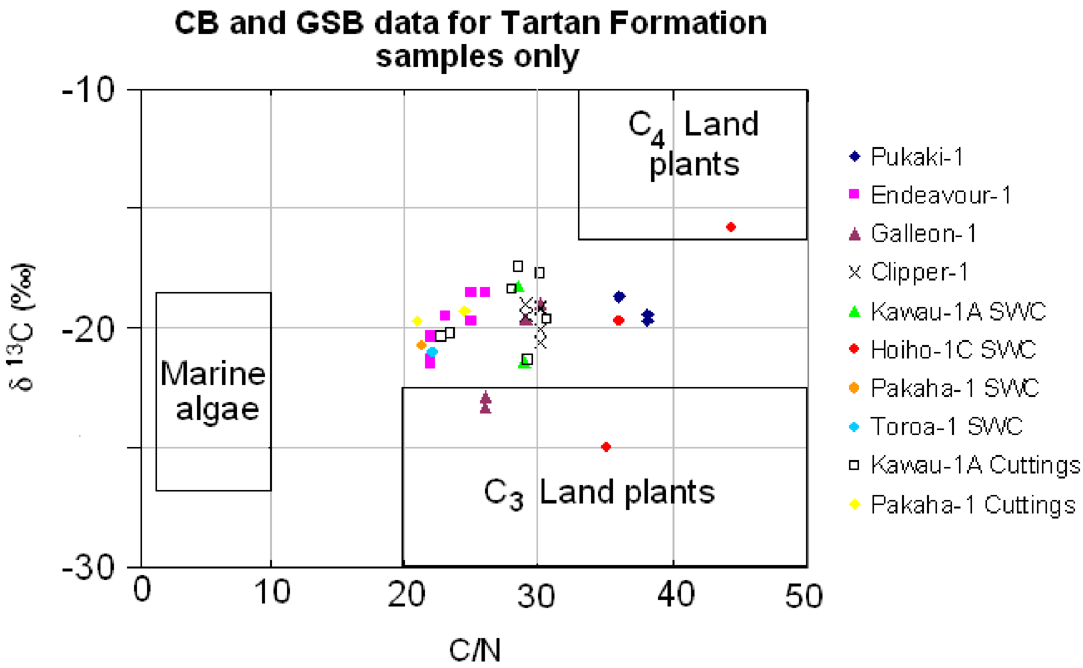

Figure 7.7 C/N and $\delta^{13}C$ data for all samples lying within the Tartan Formation (Figure modified from Meyers, 1994).

Differences in values for these samples are likely due to differing proportions of each type of organic matter present in samples.

Tartan Formation samples from Endeavour-1, Galleon-1, Clipper-1, Kawau-1A, Pakaha-1, and Toroa-1 contain relatively similar geochemical values. C/N ratios range from 21 to 31, TOC contents range from 1.8% (Galleon-1) and 11.7% (Clipper-1), while $\delta^{13}C$ values range from -23.3‰ (Galleon-1) to -17.4‰ (Kawau-1A).

C/N ratios that lie between 21 and 31 are generally considered to contain organic matter that has been derived from a predominantly terrestrial source (Fig. 7.7). $\delta^{13}C$ values between -23.3‰ and -17.4‰ are indicative of mixed marine and terrestrial plant sources (Fig. 7.6). As previously mentioned, differences in values between these Tartan Formation samples are likely due to differing compositions of marine and terrestrial components incorporated within the organic matter of a sample. The sample from Galleon-1 (-23.3‰) is likely to contain a high proportion of C_3 land plant material, whereas the sample from Kawau-1A (-17.4‰) is likely to contain a much higher ratio of marine derived plant material. Differences in the TOC content between samples indicate perturbations in factors affecting the preservation and accumulation of organic matter, such as; organic input, sedimentation rate, and sediment dilution, organic matter degradation by biological reworking, and other environmental factors.

Figure 7.8 is a well by well plot of C/N v. TOC for all wells containing Tartan Formation from the present study and the previous study by the author.

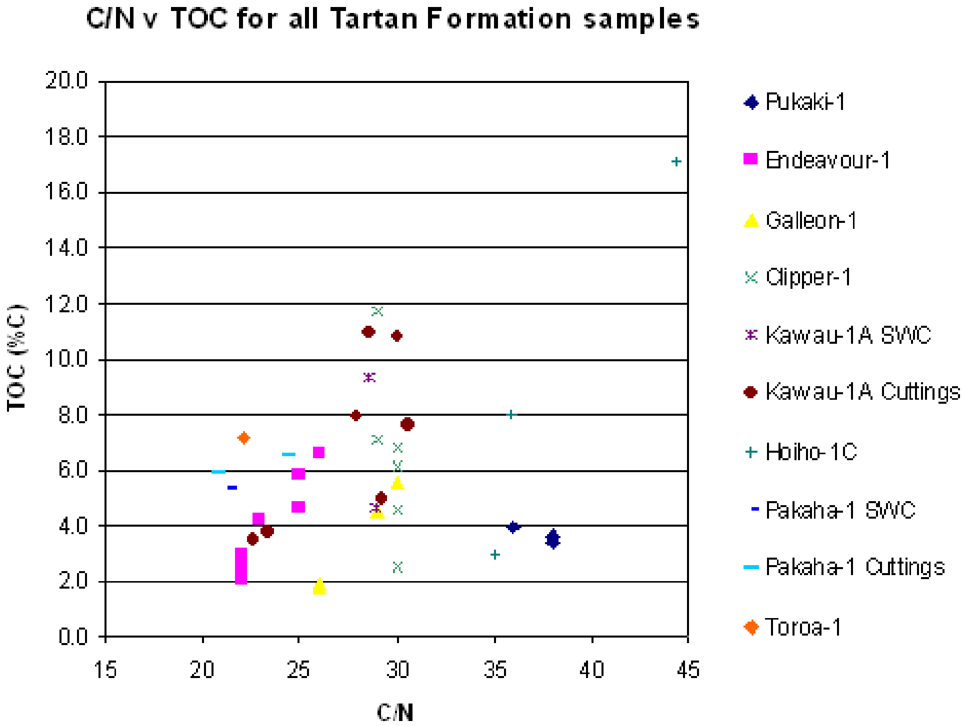

Figure 7.8 Well by well plot of Tartan Formation samples comparing C/N and TOC for all wells containing Tartan Formation.

The figure typically demonstrates grouping of data points for each well examined. The general trend of Figure 7.8 is for highly variable TOC contents correlating with relatively constant C/N ratios in any given well. This data suggests that there was a constant organic matter source with varying levels of preservation. The C/N ratio differences between wells are a likely reflection of varying types or proportions of organic matter sources between wells. From the work presented by Meadows (2008) C/N ratios appear to increase with distance from the inferred paleoshoreline, indicating greater terrestrial influence in the more distal well sites in the Great South Basin. Schioler and Roncaglia (2008) have reported a similar trend for the Tartan Formation using detailed palynological analyses. From their work, an increase in non-marine proxies was recorded in the three most distal wells of the Great South Basin (Hoiho-1C, Kawau-1A, and Pakaha-1), and was interpreted to be the result of deposition during a peak regression during the Thanetian (Late Paleocene) (see Sections 3.5 and 7.4 for further discussion).

Figure 7.9 demonstrates increasingly heavy $\delta^{13}C$ values correlating positively with increasing TOC contents amongst Tartan Formation samples for any given well. This trend indicates variable preservation between Tartan Formation samples in each well. The observed variations in $\delta^{13}C$ values across Tartan Formation samples in a given well indicate changing organic matter source components, with a likely more marine influence on the heavier $\delta^{13}C$ values and a mixed marine/terrestrial influence for the lighter $\delta^{13}C$ values. The higher organic content of the heavier $\delta^{13}C$ samples could suggest enhanced preservation of marine organic matter components over terrestrial components or a combination of greater preservation and accumulation of marine over terrestrial components.

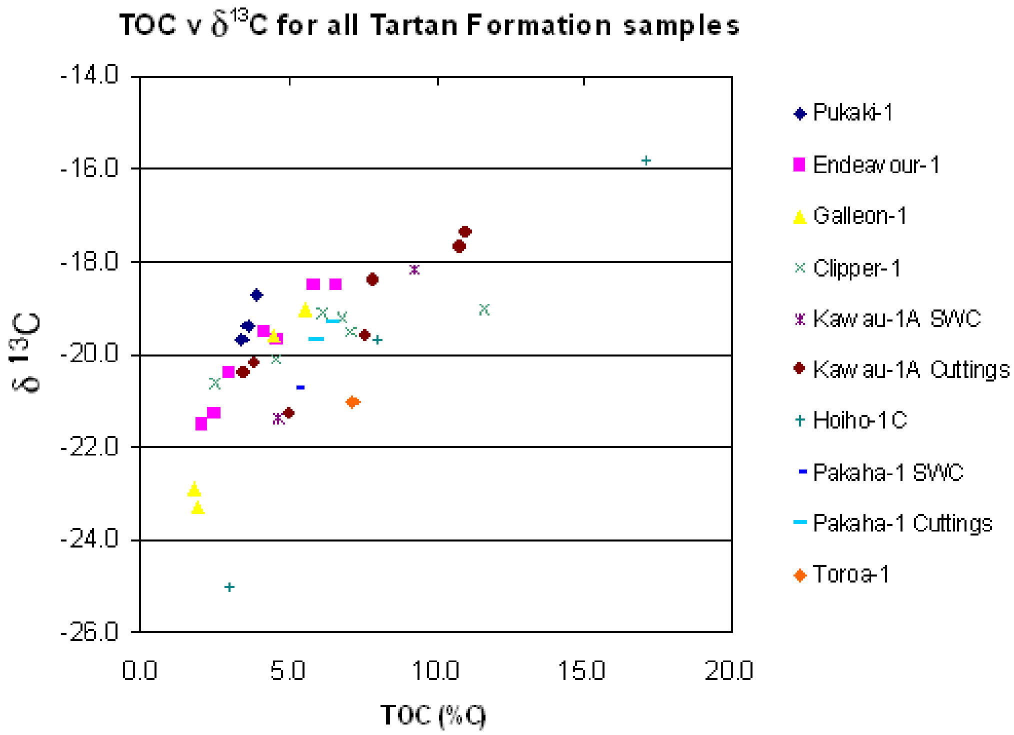

Figure 7.9 Well by well plot of Tartan Formation samples comparing TOC and $\delta^{13}C$ for all wells containing Tartan Formation.

Data comparing TOC and $\delta^{13}C$ for all Tartan Formation samples from both the present study and that by Meadows (2008) are presented in Figure 7.10.

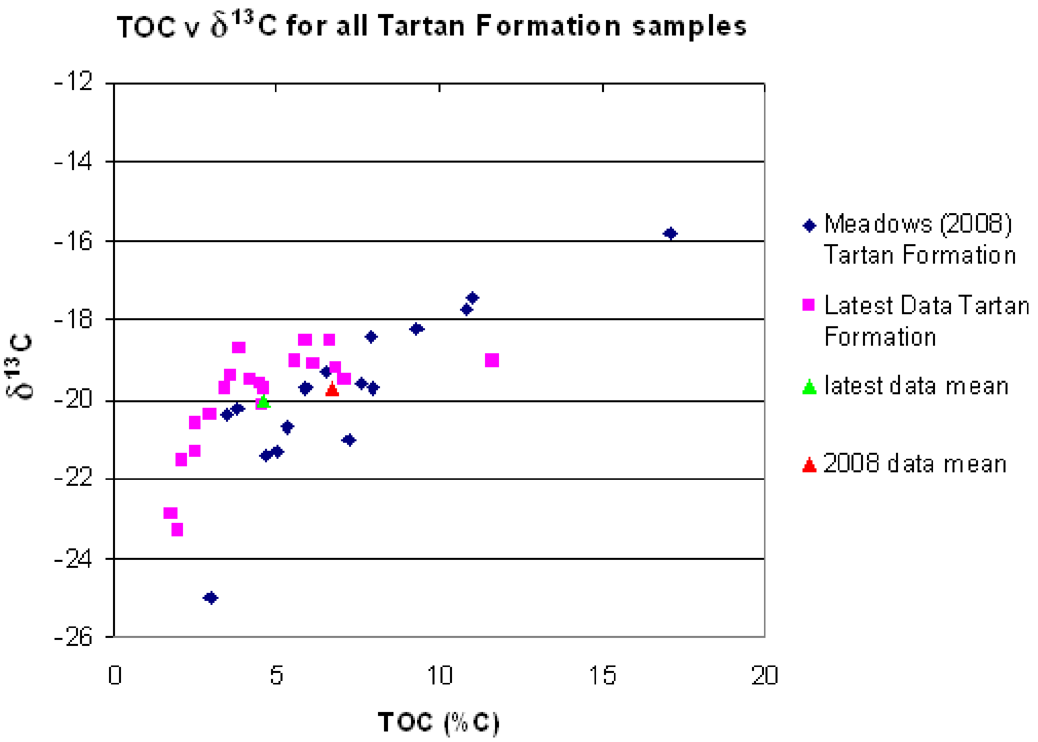

Figure 7.10 Comparison of latest data to the previous study of the Great South Basin by the author displaying differences in TOC and $\delta^{13}C$ for all Tartan Formation samples.

Although there is some overlap between the data from the present study and that by Meadows (2008) in Figure 7.10, it is evident that the data sets are distinct from one another. The figure demonstrates the differences between the two studies, with an overall mean value for each study. These single data points represent the average TOC and $\delta^{13}C$ values for all Tartan Formation samples in each study. The mean data point for the present study (TOC = 4.6%, $\delta^{13}C$ = -20‰) has a lighter $\delta^{13}C$ value and a lower organic content than that of the mean data point from the 2008 study (TOC = 6.7%, $\delta^{13}C$ = -19.7‰). While the bulk of the data points from both data sets share similar $\delta^{13}C$ values, it is evident from the figure that the samples from wells in the 2008 study of the Great South Basin generally contain higher TOC contents. The 2008 data also has much heavier $\delta^{13}C$ and TOC end-members, particularly those from Kawau-1A and Hoiho-1C.

Differences in paleoenvironmental conditions between the Great South and Canterbury basins are a likely cause for the observed trend in Figure 7.10. The Great South Basin would appear to have had, on average, greater organic matter input than that of the Canterbury Basin during deposition. If this is true, it was likely combined with greater organic preservation of deposited organic matter. These regional variations are the likely result of differences in the paleogeography of the area, and differences in the geochemistry reflect the extent in which the paleoenvironmental conditions influenced organic matter input, preservation, and accumulation. Causes for the variation in $\delta^{13}C$ values between well sites are further discussed below.

7.4 Comparison of the Tartan Formation to the Waipawa Formation and the PCIM

The enrichment of ^{13}C and the high TOC contents within the Tartan Formation of the Great South and Canterbury basins are consistent with that of the mid to Late Teurian Waipawa Formation elsewhere around New Zealand; however, samples from Hoiho-1C (1554 m; -15.8‰) and Kawau-1A (2264 m; -17.4‰) have $\delta^{13}C$ and TOC values that exceed those previously reported for the Waipawa Formation (Killops *et al.* 2000; Rogers *et al.* 2001; Hollis *et al.* 2006). Hollis *et al.* (2006) reported a $\delta^{13}C$ value of -17.5‰ for one Waipawa Formation sample from the mid-Waipara River outcrop (inland Marlborough) which is the heaviest recorded $\delta^{13}C$ value for the formation. From Killops *et al.* (2000), Rogers *et al.* (2001), and Hollis *et al.* (2006), the heaviest $\delta^{13}C$ values for Waipawa Formation (apart from the mid-Waipara River sample) generally range from -18.5‰ to -21‰, whereas values of -18.5‰ to -19‰ are common throughout Tartan Formation samples from the Great South and Canterbury basins.

The Tartan and Waipawa formations are defined by lithology. It is possible that the oceanographic environmental events that produced the geochemical changes associated with the deposition of the Tartan and Waipawa formations were synchronous; however, the age of the Waipawa Formation, (as reported by Killops *et al.* 2000; Rogers *et al.* 2001; Hollis *et al.* 2006), and the Tartan Formation (as reported by Schioler and Roncaglia, 2008) vary slightly depending on the basin each study focused on. Hollis *et al.* (2005) have mentioned the Waipawa Formation may represent a facies that developed during the Paleocene Carbon Isotope Maximum (PCIM) (see Chapter 4; Figure 4.1), but at different times and slightly different lithostratigraphic stages, depending on local conditions (such as: water depth, sediment supply, basin subsidence rates, nutrient levels, and biologic productivity). Thus, differences in apparent age of the Tartan/Waipawa Formation around New Zealand may be attributed to the influence of local conditions on the onset of deposition.

Carbon isotopic evidence presented by Killops *et al.* (2000) from East Coast Basin outcrops show that the start of the geochemical changes correspond to the lithological base of the Waipawa Formation. Rogers *et al.* (2001) give geochemical data for two East Coast Basin outcrops: Tawanui and Angora Stream. The Tawanui outcrop has no Waipawa Formation present; however, the Te Uri Member is present and is proposed as a Waipawa Formation equivalent. The Angora Stream section has Waipawa Formation present and no Te Uri Member is identified. In other outcrops, the Te Uri Member is overlain by Waipawa Formation (Moore 1988b, 1989). Rogers *et al.* (2001) concluded that the upper part of the Te Uri Member is a correlative to the Waipawa Formation.

However, geochemical data from some wells in the Great South and Canterbury basins demonstrate increases in TOC and isotopically heavy $\delta^{13}C$ values that appear below the recognised base of the Tartan Formation, in the upper Wickliffe Formation. It is possible that the geochemical change observed prior to the base of the Tartan Formation in some wells is caused by a similar geochemical change below the Waipawa Formation as documented in the East Coast Basin. This could indicate that the Tartan Formation (which is recognised by GR response) is only equivalent to the middle and upper parts of the Waipawa Formation, whereas the geochemical changes (characterised by TOC and $\delta^{13}C$ values) that occur below the recognised base of the Tartan Formation is related to the onset of the PCIM. This suggests that the termination of the PCIM was diachronous and differences in the lithostratigraphic expression of the Tartan and Waipawa formations could be the result of local environmental variations during deposition in the PCIM, affecting regions at slightly different times, and was more prominent in some areas. Thus, it is concluded here that differences in local conditions within the same overall framework define the variations between the Tartan and Waipawa formations.

$\delta^{13}C$ and TOC excursions typical of the Tartan Formation are not ubiquitous throughout the Great South and Canterbury basins, and the formation has variable thickness (and possibly age) throughout the basins. Schioler and Roncaglia (2008) reported that the Tartan Formation was absent from the three most proximal wells drilled in the Great South Basin (Takapu-1A, Tara-1, and Rakiura-1). Schioler and Roncaglia (2008) also mentioned that these three wells form a coast-parallel transect landward of the five wells where Tartan Formation is present, which is believed to have resulted in sediment bypass or erosion of the Tartan Formation in the three most proximal wells during a peak regression and coastline progradation during the Thanetian (see Chapter 3). Hollis *et al.* (2006) reported the presence of Waipawa Formation in outcrops at Black's Quarry and Whatuwhiwhi (Northland Basin), but the formation was absent from the nearby Price's Quarry outcrop. The Ariki-1 exploration well in the Taranaki Basin contains Tartan Formation (Killops *et al.* 2000), however is absent from other wells in the basin. As previously mentioned, the Waipawa Formation is present in many outcrops in the East Coast Basin (Te Hoe River, Angora Stream, Te Waeroa Stream) but is absent at Tawanui. From the present study, it is believed that the Tartan Formation is absent in the nearshore Resolution-1 (Canterbury Basin) exploration well; however, the formation is present in the more distal wells of the basin (Endeavour-1, Galleon-1, and Clipper-1).

The presence of the Tartan and Waipawa formations in some areas of a basin and the absence of it in other areas indicate local conditions influenced deposition. Great South and Canterbury basin wells that contain Tartan Formation also show positive $\delta^{13}C$ excursions, which indicate that the environmental changes during the PCIM affected these areas of the basins, whereas wells where the Tartan Formation is absent (unless eroded), the PCIM was not felt in that part of the basin, or was not intense enough to alter the $\delta^{13}C$ record. In some wells, the $\delta^{13}C$ excursion occurs below the recognised base of the Tartan Formation (see Fig 7.1 from this work, and Fig 7.2 from Meadows, 2008), which suggests that changes in the depositional environment occurred during the initial/early stages of the PCIM. Similar conditions are likely to have prevailed in the East Coast and Northland basins. The relatively short distances between the Tawanui (Waipawa Formation absent) and Angora Stream (Waipawa Formation present) outcrops, and the short distance between the Black's Quarry (Waipawa Formation present) and Price's Quarry (Waipawa Formation absent) outcrops suggest that the global environmental changes that resulted in the PCIM only influenced localised areas that were most favorable to organic matter preservation and accumulation. Hollis *et al.* (2005) suggested that the Waipawa Formation was deposited during the onset of the PCIM under an expanded oxygen minimum zone (OMZ) that is associated with condensed sedimentation. Thus, areas that did not experience this OMZ were unlikely to have been capable of accumulating and preserving a sufficient quantity of the organic matter containing enriched ^{13}C (that is representative of the PCIM) to noticeably alter the $\delta^{13}C$ record.

Kurtz *et al.* (2003) have stated that the PCIM likely represents a period of enhanced accumulation and burial of terrestrial organic matter, and Stott *et al.* (1996) mentioned that the isotopic changes that were recorded in the deep sea were transferred to the terrestrial carbon reservoirs via the atmosphere. In areas that were affected by the PCIM, the plant material that was deposited would be expected to contain a ^{13}C record of those changes. The author believes that the Tartan and Waipawa formations provide such a record, as organic carbon buried in sediment retains the carbon isotopic composition of its source, which reflects the isotopic record from the carbon reservoir from which it was derived.

As discussed earlier, the Tartan Formation coincides with part of the PCIM excursion. The observed diachrony of the Tartan Formation across the Great South and Canterbury basin, which the author believes to have been the result local variations across the area of deposition, is evidence of the Tartan Formation having been deposited at slightly different times during the PCIM. Variation in local conditions affecting the onset and duration of Tartan Formation deposition resulted in slightly different lithostratigraphic expressions of the Tartan Formation from one location to the next in the Great South and Canterbury basins. This reflects different representations (in timing) of the PCIM from one site to the next (where Tartan Formation is present). Thus, in a given well, the Tartan Formation's $\delta^{13}C$ excursion correlates to part of the PCIM, but variations in local conditions across the basins have determined which part of the PCIM is represented in a given site. The Great South Basin appears to have had higher organic input than the Canterbury Basin. This is likely coupled with conditions favoring greater preservation of deposited organic matter. These regional variations are the probable result of differences in the paleogeography of the area, and differences in the geochemistry reflect the extent in which paleoenvironmental conditions influenced organic matter input, source, preservation, and accumulation.

The data presented by Zachos *et al.* (2001; Figure 2) suggest that the PCIM event took place over approximately 4 Myr, between 59.5 and 55.5 Ma (mid to Late Paleocene). As discussed in Chapter 3, the depositional age of the Tartan and Waipawa Formations varies from approximately 58 to 55.5 Ma. The common $\delta^{13}C$ excursion of the Tartan and Waipawa formations span the duration of time in which a particular site's environment (where the Tartan or Waipawa formations were deposited) was influenced by the changing organic matter of the PCIM. From the information available to the author at present, no precise time constraints can be placed on the deposition of the Tartan Formation. Estimates from the present information can only constrain the deposition of the Tartan Formation (and similarly the Waipawa Formation) to within part of the PCIM period (of which the author believes the effects of vary between sedimentary basins and also between sites within those basins). Based on these considerations, the author believes that the Tartan Formation is a correlative of the Waipawa Formation but that it is premature to synonymise the two.

It maybe that the peak $\delta^{13}C$ excursions observed in Kawau-1A and Clipper-1 (both of which are well sampled wells that have a smooth set of data points both leading up to and following the peak $\delta^{13}C$ value) reflect the peak of the PCIM (approximately 57 to 56 Ma). It may also represent a period where the environmental conditions were most augmented in that area. Hoiho-1C recorded the heaviest $\delta^{13}C$ value (-15.8‰) of all wells examined, possibly indicating that the PCIM had the greatest influence around Hoiho-1C during deposition. This sample from Hoiho-1C also considerably exceeds all previously reported $\delta^{13}C$ values for the Waipawa Formation, suggesting that the environmental changes during the PCIM were greater around the Hoiho-1C area than elsewhere around New Zealand where the Tartan and Waipawa formations were deposited.

CHAPTER 8

CONCLUSIONS

- There is no geochemical evidence for the presence of the Tartan Formation in Rakiura-1, Takapu-1A, and Resolution-1.

- Geochemical studies of the six wells examined here, and five other wells from the previous study show that, in general, the Tartan Formation is distinct from enclosing formations and can be recognised by enrichments in TOC and ^{13}C, with C/N ratios above 20. These changes agree well with the top of the formation as defined by its lithology.

- The high organic richness of the Tartan Formation with respect to the relatively low organic richness of adjacent formations establishes that there was a profound change in the conditions under which the Tartan Formation was deposited.

- In some wells geochemical changes appear below the recognised lithological base of the Tartan Formation, in the upper part of the underlying Wickliffe Formation. This is attributed to the onset of oceanographic environmental changes during the Paleocene Carbon Isotope Maximum (PCIM) that featured from the mid-Paleocene to the Late Paleocene, below the Paleocene-Eocene boundary.

- TOC data from Clipper-1 and Kawau-1A (the most comprehensively sampled wells) provide evidence for more favorable preservation and/or accumulation of organic matter during the mid stages of deposition of the Tartan Formation than during the initial and final stages. Further, TOC data for enclosing formations suggest that conditions for the preservation and accumulation of organic matter were more favorable prior to the deposition of the Tartan Formation than following it.

- All samples within the Tartan Formation have C/N ratios above 20, with little variation. There appears to be a greater terrestrial influence on organic matter with increasing TOC content, possibly as the result of enhanced organic matter preservation with increasing terrestrial composition, and depressed organic matter degradation associated with suboxic conditions in the water column.

- It is probable that organic matter within samples of the Tartan Formation is composed of a mixture of C_3 land plant and marine bacterial/plant/algal material, with the isotopically heavier samples containing a predominance of marine components and the lighter samples containing higher proportions of terrestrial source components. The organic matter within enclosing formations appears to have been derived primarily from C_3 terrestrial plants sources.

- Samples from enclosing formations show a wide range of C/N values. Many samples have C/N ratios below 20, indicating a marine bacterial/plant/algal or mixed marine and terrestrial source. Many others that have C/N ratios of 20 and above indicate a significant terrestrial composition. There is little variation in the TOC contents within these formations, with most samples having values below 2%. This indicates that there were varying degrees of preservation of organic matter within these formations.

- Tartan Formation samples within a given well show a relatively close clustering of isotopic values, indicating a similar source of organic matter throughout deposition; however, it is evident that there are slight variations in the isotopic range between wells. This indicates that preservation and organic matter sources were variable across the areas where the Tartan Formation was deposited. Further evidence for varying degrees of preservation across Tartan Formation samples is provided by the positive correlation of increasingly heavy $\delta^{13}C$ values corresponding to increasing TOC contents.

- The Great South Basin appears to have had higher organic input than the Canterbury Basin. This is likely coupled with conditions favoring greater preservation of deposited organic matter. These regional variations are the probable result of differences in the paleogeography of the area, and differences in the geochemistry reflect the extent in which paleoenvironmental conditions influenced organic matter input, source, preservation, and accumulation.

- Tartan Formation deposition coincides with the mid to Late Paleocene Waipawa Formation deposited elsewhere around New Zealand; however, TOC and $\delta^{13}C$ values for the Tartan Formation exceed those previously reported for the Waipawa Formation.

- Geochemical changes below the lithological base of Tartan and Waipawa formations are contemporaneous with the PCIM, and represent different lithostratigraphic expressions of that event. Termination of the PCIM around New Zealand appears to have been diachronous and differences between the stratigraphic position of the Tartan and Waipawa formations are attributed to local geographical variations during deposition.

- It is concluded here that the Tartan and Waipawa formations are correlatives. However, two separate names are used for the formation as they are widely separated and no unequivocal relationship can be made between the formations based solely on the data from this study.

- TOC and $\delta^{13}C$ enrichments associated with the Tartan Formation are not ubiquitous, and the formation has variable thickness throughout the Great South and Canterbury basins. This indicates that the environmental changes during the PCIM were more prominent in some areas than others, depending on local conditions. Thus, Tartan Formation deposition reflects different representations of part of the PCIM, depending on where and when each area was influenced by the event.

- TOC and $\delta^{13}C$ enrichments associated with the Tartan Formation span the time in which that area was affected by the PCIM. Peak values in Clipper-1 and Kawau-1A (the most comprehensively sampled wells) may correspond to the peak effect of the PCIM in those wells. The enrichment of TOC and ^{13}C are greatest in Hoiho-1C, suggesting that the environmental changes during the PCIM influenced this area more than any other region where the Tartan Formation was deposited.

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Dylan Meadows, 2009.

Appendices

Dylan Meadows, 2009.

Appendix 1

INTERNATIONAL			NEW ZEALAND				
Era	**Period**	**Epoch**	**Series**	**Stage**	**Symbol**	**Age of base (Ma)**	**Duration (Ma)**
CENOZOIC	**Quaternary**	**Holocene**	Wanganui Series	Haweran	Wq	0.34	0.34
		Pleistocene		Castlecliffian	Wc	1.63	1.29
				Nukumaruan	Wn	2.4	0.77
	Neogene	**Pliocene**		Mangapanian	Wm	3.03	0.63
				Waipipian	Wp	3.6	0.57
				Opoitian	Wo	5.28	1.68
		Miocene	Taranaki Series	Kapitean	Tk	6.5	1.22
				Tongaporutuan	Tt	11.0	4.5
			Southland Series	Waiauan	Sw	13.2	2.2
				Lillburnian	Sl	15.1	1.9
				Clifdenian	Sc	16.0	0.9
			Pareora Series	Altonian	Pl	19.0	3
				Otaian	Po	21.7	2.7
			Landon Series	Waitakian	Lw	25.2	3.5
	Paleogene	**Oligocene**		Duntroonian	Ld	27.3	2.1
				Whaingaroan	Lwh	34.3	7
		Eocene	Arnold Series	Runangan	Ar	35.8	1.5
				Kaiatan	Ak	37.0	1.2
				Bortonian	Ab	43.0	6
			Dannevirke Series	Porangan	Dp	46.2	3.2
				Heretaungan	Dh	49.5	3.3
				Mangaorapan	Dm	53.0	3.5
				Waipawan	Dw	55.5	2.5
		Paleocene		Teurian	Dt	65.0	9.5
MESOZOIC	**Cretaceous**		Mata Series	Haumurian	Mh	84.5	19.5
				Piripauan	Mp	86.5	2
			Raukumara Series	Teratan	Rt	89.0	2.5
				Mangaotanean	Rm	92.0	3
				Arowhanan	Ra	95.0	3
			Clarence Series	Ngaterian	Cn	100.0	5
				Motuan	Cm	103.0	3
				Urutawan	Cu	108.0	5
			Taitai Series	(Korangan)	Uk	(117)	9

International and New Zealand Geochronological Timescales. Modified from Geological and Nuclear Sciences (2003).

Appendix 2

Biostratigraphy of the Tartan Formation in Canterbury and Great South basin wells

Resolution – 1

The following is a brief summary of the biostratigraphy of Paleocene and Eocene strata in Resolution-1 as described by Hornibrook *et al.* (1975) in Milne (1975).

The interval between 1380 m and 1415 m is characterised by a mid-Eocene (Bortonian, Ab) microfauna.

The Bortonian index foraminiferan species, *Gaudryina proreussi*, appears in cuttings from 1380-85 m, and is common in later cuttings samples. The Bortonian species, *Plectina aggrestior*, is present in cuttings from 1400-05 m and 1410-15 m (together with *Marginulinopsis spinobesa*).

Between 1396 m and 1415 m, the Lower Bortonian form, *Euuvigerina wanzea*, is present. The interval 1415 m to 1465 m contains some Bortonian foraminifera which are present due to cavings in cuttings samples. Hornibrook *et al.* (1975) stated that the appearance of *Elphidium hampdenense* in the cuttings sample from 1410-15 m is a definite indicator of Heretaungan age. This form is also present in sidewall cores from 1428 m and 1443 m. Another species present in the sidewall core from 1443 m is *Globorotalia crater*, which is a Heretaungan (Dh) to Mangaorapan (Dm) species.

The interval from 1465 m to 1490 m was analysed from one sidewall core sample from 1474.5 m. This sample contained a shallow water assemblage of agglutinated foraminifera. The interval was assigned a Teurian age based on the appearance of *Bolivinopsis compta* and *Bolivinopsis spectabilis*.

Palynological analyses of the sidewall core sample from 1478 m identified *Nothofagus waipawaenesis* and *Triorites minor*. *T. minor* is considered to be more frequent in the Dannevirke Series than in the Haumurian Series, while *Nothofagus waipawaenesis* is regarded as a Teurian index species (Hornibrook *et al.* 1975).

Endeavour – 1

The following description of the biostratigraphy of Endeavour-1 focuses on Paleocene and Eocene strata as discussed by Wilding and Sweetman (1971).

The interval between 1494 m and 1576 m has been assigned a Heretaungan age based on the appearance of *Elphidium hampdenensis*, which is considered to be a typical Heretaungan marker, and is common throughout this interval. Other species of the Dannevirke Series common within this interval include *Vaginulinopsis marshalli* and *Nuttallides carinotrumpyi*.

Planktonic species that appear for the first time within this interval are *Globigerina triloculinoides* and *Globorotalia aequa rex*. Benthonic species appearing for the first time within this interval include *Buliminella browni*, which is associated with the Waipawan to Heretaungan, and *Bulimina subbortonica*.

Elphidium hampdenensis is not found between samples from 1576 m to 1615 m. Its absence here and lower downhole has been used as an indicator for the top of the Mangaorapan Stage (Wilding and Sweetman, 1971).

Faunas within the interval 1615 m and 1975 m are dominated by *Haplophragmoides* spp. and *Trochammina* spp. Other species commonly found include *Cyclammina elegans*, *Bolivinopsis compta*, *Karrerulina aegra*, and *Thalmannammina subturbinata*. There is a lack of prominent forms that clearly indicate the boundary between the Waipawan and the Teurian (Wilding and Sweetman, 1971).

Palynological analyses of samples between 1719 m and 1734 m show the first appearances of *Proteacidites hakeoides,* and *P. annularis*, both of which are known to first appear in the Waipawan. Between these samples, the Teurian species *Clavifera triplex* and *Nothofagidites waipawaensis* disappear from the fossil record. Based upon this information the Waipawan-Teurian boundary is inferred to lie between these two samples (Wilding and Sweetman, 1971).

The sample from 1737 m has been found to contain several species, all of which indicate an age no older than Teurian. These species include *Nothofagidites waipawaensis*, *Tricolpites secarius* and *Engelhardtioidites minisculus*.

Galleon – 1

The following is a brief summary of the biostratigraphy of Paleocene and Eocene strata in Galleon-1 as described by Gibbons and Fry (1986).

Dannevirke Series strata (Porangan to Teurian) in Galleon-1 are present from a depth of 1914.6 m to 2675 m.

The characteristic Porangan (Dp) *Globigerina boweri* Biozone is represented at 1914.5 m. The interval between 1950 m and 2595 m is dominated by agglutinated foraminifera. The upper part of this interval (down to 2320.8 m) is believed to be of Heretaungan age (Dh). Below this, to around 2402 m, the age is thought to be Mangaorapan (Dm) to Waipawan (Dw). Poor and sparse faunal assemblages limit accurate distinction of the Dm-Dw boundary (Gibbons and Fry, 1986).

Palynological analyses of the sample from 2402 m constrain the *Apectodinium homomorphum* Biozone to the Early Waipawan (and possibly Late Teurian) at this depth.

The Teurian Stage is represented from 2474.6 m to 2675 m in this well. Palynological evidence places the *Palaeocystodinium australinum* Biozone, which is characteristically of Teurian age, between 2474.6 m and 2624 m.

The *Bolivinopsis spectabilis* Biozone is represented between 2603 m and 2624 m. Hornibrook (1968) stated that the presence of *Bolivinopsis spectabilis* indicated an age no younger than Teurian. There are some foraminiferal forms present that Moore (1988b) suggested are characteristic forms commonly identified with the Waipawa Formation, such as *Bathysiphon* sp. The occurrence of *Globigerina triloculinoides* within this biozone suggests an age of Teurian (Dt) to Waipawan (Dw), or possibly Heretaungan (Dh). This interval differs from the overlying Agglutinate Interval in the presence of *Bolivinopsis spectabilis*, *Buliminella creta*, *Conotrochammina whangaia*, and also the reduced abundance and diversity of species.

Below the *Bolivinopsis spectabilis* Biozone is the *Globigerina pauciloculata* Biozone (2672 m). This interval differs from the overlying *Bolivinopsis spectabilis* Biozone in the presence of *Globigerina pauciloculata* (Gibbons and Fry, 1986).

Clipper – 1

A description of the biostratigraphy of Dannevirke Series strata in Clipper-1, as written by Crux *et al.* (1984), is summarised below.

The Porangan Stage (Dp) is represented between 2410 m and 2460 m in Clipper-1. The sidewall core from 2410 m contains *Globigerapsis index* and *Globigerina frontosa boweri*, which is indicative of a Porangan age. Benthonic foraminifera in this sample include *Bulimina subortonica*, which is a known Dannevirke species around New Zealand (Crux *et al.* 1984).

The sample from 2455 m contains *Elphidium saginatum*, a benthonic index for the Porangan. The presence of the nannofossils *Cyclococcolithus formosus* and *Reticulofenestra umbilica* at 2410 m suggests an age of no lower than mid-Eocene, as internationally these species do not range below the mid-Eocene.

The Mangaorapan Stage is present from 2460 m to approximately 2560 m. The occurrence of the nannofossil *Chiasmolithus biden*, at 2460 m indicates an Early Eocene to Paleocene age, with Eocene confirmed by the co-occurrence of the Eocene restricted species, *Neococcolithes dubius*. Foraminiferal assemblages within this interval contain a mixture of agglutinated and calcareous benthonic forms. No planktonic index taxa are present; however, a Mangaorapan age to 2540 m is confirmed by the presence of *Vaginulinopsis marshalli* (Crux *et al.* 1984).

The interval between 2560 m and 2694.5 m did not yield age diagnostic taxa; however, based upon evidence from above and below this interval, an age of Mangaorapan to Waipawan is inferred.

The interval between 2694.5 m and 2790 m is believed to be of Early Waipawan to Late Teurian age. The top of this interval is characterised by the first downhole appearance of the dinoflagellete cyst genus *Apectodinium*, including *A. homomorphum* in the sidewall core from 2694.5 m. This species is associated with the Waipawan-Teurian boundary, with a bias towards the Teurian (Wilson, 1984).

The Teurian Stage is represented from 2790 m to 3175 m. A cuttings sample from 2790 m contains an abundant, low diversity, agglutinated microfauna which comprises common deformed *Haplophragmoides* sp., *Cyclammina grangeri*, and *Karreriella* sp. Hornibrook (1968) has described a similar assemblage from the Teurian. The first downhole occurrence of the benthonic form, *Gaudryina whangia*, at 2895 m confirms a Teurian age.

The sidewall core at 2800 m contains the first downhole occurrence of the dinoflagellete cyst genus *Palaeocystodinium*, which is persistent from this depth, and includes forms close to *P. australinum*. Wilson (1984) stated that this species has an age that is no younger than Teurian around New Zealand. Wilson (1984) also recorded the same upper range limit for *Palaeoperidinium pyrophorum*, which appears for the first time at 3100 m.

The first appearance of *Trithyrodinium evittii* at 3150 m suggests an Early Paleocene age, whilst the appearance of *Isabelidinium druggii* at 3175 m indicates an earliest Teurian age. *Isabelidinium druggii* is associated with the Cretaceous-Tertiary boundary in New Zealand (Crux *et al.* 1984).

Rakiura – 1

The following is a brief summary of the biostratigraphy of Teurian to Waipawan strata in Rakiura-1 as described by Raine *et al.* (1993).

Teurian strata in this well are present from a depth of 1660 m to 2167(?) m, followed by Waipawan strata from 1560 m to 1660 m. Moderate to poor foraminiferal faunas were commonly recovered from lower Dannevirke strata (Teurian to Waipawan). Cuttings samples of mid-Late Teurian age contain tentatively identified *Cibicides hampdenensis* (Dw-Ak). Lower Teurian samples are barren to sparsely fossiliferous, with only agglutinated assemblages present, of which, benthic taxa dominate. *Budashevaella multicamerata* (Mh-Dt) is the principle species to indicate ages in this interval. *Cyclammina amplectans* (Dt-Ar) is also present and is the only other species with a reasonably well known range identified from this interval.

Dinoflagellate assemblages from a sample taken from 1755.6 m include *Palaeocystodinium golzowense*, *Spiniferites septatus* (Dt-Dh) and *Cerodinium* cf. *medcalfii*, which tend to indicate the *P. golzowense Zone* (Teurian age). Based on the presence of *Palaeoperidinium pyrophorum*, *Cerodinium speciosum*, *Spiniferites septatus* (Dt-Dh), and *Palambages* cf. *morulosa* from the sample taken from 1737.4 m, the apparent age is Teurian.

The Waipawan/Teurian boundary was placed midway between samples dated by dinoflagellates at 1591.1 m and 1737.4 m (Raine *et al.* 1993).

Pukaki – 1

Schioler and Roncaglia (2008) recognised the top of the Tartan Formation in this well to be at a depth of 2297.5 m and the base at 2316.2 m. Raine *et al.* (1993) stated that the Teurian Stage (Dt) occurs between 2400(?)-2790 m, followed by an unconformity or condensed interval between 2350-2450 m (the interval was defined by 2350 m being the lowest Porangan sample and 2450 m being the highest likely Teurian sample). Overlying the 2350 m sample are strata of Porangan (Dp) age [1825-2400(?) m].

Due to the possibility that an unconformity is present between Porangan and Teurian strata, it is conceivable that several hundred meters of strata may have been eroded. No fossil evidence is present in this 2350 m to 2450 m interval to indicate the presence of the Heretaungan (Dh), Mangaorapan (Dm) or Waipawan stages (Dw) (Raine *et al.* 1993). If there is an unconformity due to erosion within this interval, it is probable that any fossil record from these stages would have been removed during the erosive event.

Comparison of data from both Schioler and Roncaglia (2008) and Raine *et al.* (1993) suggests that the Tartan Formation was deposited between the latest Teurian and the earliest Porangan. More accurate constraints on the age of the Tartan Formation in this well are not possible based on current knowledge.

Teurian foraminifera identified by Raine *et al.* (1993) include *Bolivinopsis spectabilis*, *Haplophragmoides* cf. *teuria*, *H.* sp., and *Thalmannammina* sp. Faunas recovered that are likely to be of latest Teurian age were of poor quality and consisted entirely of agglutinated taxa.

The biostratigraphy and age of the Tartan Formation from exploration wells examined by Meadows (2008) are also included here.

Toroa – 1

The top of the Tartan Formation in the Toroa-1 petroleum exploration well was reported to be at 2137 m and the base at 2200 m by Cook *et al.* (1999). This implies that most of the Tartan Formation was deposited during the Late Teurian with a small portion having been deposited during the earliest Waipawan Stage. The Teurian interval occurs between 2150 m-2863 m and the Waipawan interval between 1350 m-2150 m in Toroa-1 (Raine *et al.* 1993).

A sidewall core from 2206.8 m, approximately the depth that Cook *et al.* (1999) give as the base of the Tartan Formation, shows a moderately rich dinoflagellate assemblage with the first appearance of *Palaeocystodinium golzowense*, indicating the Late Teurian *P. golzowense Zone*. The same sidewall sample contains *Phyllocladidites mawsonii*-dominated assemblages of miospores, in which some restricted Cenozoic taxa, including *Nothofagus waipawaensis* (which is restricted to the Teurian), occur.

Palynofloras and foraminifera agree in giving a Teurian age at around 2200 m, but above this level there is some doubt of the age, due to the occurence of the foraminifera *Bolivinopsis spectabilis* in a sidewall sample taken from 1847 m. *B. spectabilis* is of Waipawan age, above the limits of the upper Teurian. The dinoflagellete *Apectodinium homomorphum* from 2094 m also suggests Waipawan age (Raine *et al.* 1993).

Cyclammina spp. is a characteristic Waipawa Black Shale species, and has been identified from about 2150 m through 2260 m. Below 2260 m, faunas are still dominated by a

Cycalmmina-Budashevaella association, indicating a Late Teurian age, but there is a tendency for declining abundance (Raine *et al.* 1993).

Pakaha – 1

Cook *et al.* (1999) reported the top of the Tartan Formation in the Pakaha-1 petroleum exploration well to be at a depth of 2503 m and the base at a depth of 2551 m. Raine *et al.* (1993) designated the interval 2055 m-2485 m to belong to the Waipawan Stage, while the Teurian Stage occurs between 2485 m and 3167 m. Comparison of the data from both Cook *et al.* (1999) and Raine *et al.* (1993) shows that deposition of the Tartan Formation occurred during the latest Teurian.

A sidewall core from 2252 m contains a dinoflagellate-dominated palynoflora with an *A. homomorphum* or *W. spinulosa Zone* assemblage, of Early to mid-Waipawan age. Another sidewall sample from 2473 m was dated from nannofossils to be of upper Teurian to basal Waipawan age (Hornibrook and Edwards, 1977).

The approximate positioning of the top of the Teurian is suggested by the occurrence of the foraminifera *Bolivinopsis spectabilis* at 2463 m. *Bulimina kickapooensis*, *Alabamina creta* and *Anomalinoides piripaua* have the highest occurrence in the sidewall core from 2554 m, and are considered to be more definitive species for the determination of the upper boundary of the Teurian Stage (Raine *et al.* 1993).

A sidewall core examining dinoflagellates from 2505 m contains fairly abundant *Palaeocystodinium golzowense* and rare *Cassidium fragile*, indicating Late Teurian.

Raine *et al.* (1993) stated that the Teurian/Waipawan boundary lies between sidewall samples at 2505 m and 2474 m, with a depth of 2485 m being chosen to represent the boundary.

The upper Teurian is characterised by a Waipawa Black Shale lithofacies, primarily comprising agglutinated foraminiferal fauna typified by *Budashevaella multicamerata* and *Cyclammina elegans*, with minor calcareous benthics, in particular *Bulimina kickapooensis* and *Alabamina creta* (Raine *et al.* 1993).

Kawau – 1A

The top of the Tartan Formation as published by Cook *et al.* (1999) is at a depth of 2220 m, while the base is reported to be 2264 m. Raine *et al.* (1993) state that the Teurian interval is between 2140 m and 2850 m. Thus the Tartan Formation in Kawau-1A is entirely of upper Teurian age.

The top of the Teurian was placed by Raine *et al.* (1993) at the highest occurrence of the foraminifera *Cyclammina elegans*, in a cutting sample taken from 2140 m.

The foraminiferal fauna primarily consists of agglutinated forms. Principle taxa are *Cyclammina elegans*, *Budashevaella multicamerata* and *Haplophragmoides* sp. (Raine *et al.* 1993).

Hoiho – 1C

The top of the Tartan Formation in Hoiho-1C is placed at 1545 m, while the base is at a depth of 1592 m (Cook *et al.* 1999). Raine *et al.* (1993) placed the Teurian Stage between 1545 m and 1735 m. Thus the Tartan Formation here was deposited during the very latest Teurian. The top of the Teurian Stage is placed at the highest occurrence of *Bolivinopsis spectabilis* together with the tentatively identified *Cyclammina elegans*, in a fauna from a cuttings sample from 1545 m. The highest occurrence of the typical Teurian foraminiferan *Budashevaella multicamerata* was identified in a cuttings sample from 1554 m.

All samples are characterised by sparse to moderately abundant, low diversity assemblages consisting primarily or entirely of agglutinated taxa. No planktics were observed. Agglutinated taxa are dominated by *Bolivinopsis*, *Cyclammina elegans*, *Budashevaella multicamerata*, *Haplophragmoides* spp., and *Karreriella aegra* (Raine *et al.* 1993).

Appendix 3

Full list of geochemical data from Meadows (2008) analyses

Well	Depth(m)	Depth(ave)	$\delta^{13}C$	TOC	%N	C/N
Takapu-1A	485-94	490	-25.8	3.3	0.06	64
Takapu-1A	530-40	535	-26.7	1.1	0.04	31
Takapu-1A	585-95	590	-26.1	0.8	0.04	23
Takapu-1A	631-40	636	-27.8	1.4	0.05	33
Takapu-1A	686-95	691	-26.2	1.1	0.05	26
Takapu-1A	695-704	700	-26.4	1.1	0.05	26
Takapu-1A	704-13	709	-27	1.3	0.05	30
Takapu-1A	759-65	762	-25.6	2.3	0.06	45
Takapu-1A	805-14	810	-26.8	0.9	0.04	26
Takapu-1A	860-69	865	-25.2	1.4	0.03	54
Kawau-1A	2030-2037	2034	-27	0.2	0.02	12
Kawau-1A	2076-2085	2081	-27.3	0.3	0.02	18
Kawau-1A	2140-2149	2145	-26.4	1.6	0.05	37
Kawau-1A	2177-2186	2182	-26.3	0.9	0.03	35
Kawau-1A	2232-2241	2237	-21.3	5	0.2	29
Kawau-1A	2241-2250	2246	-19.6	7.6	0.29	31
Kawau-1A	2250-2259	2255	-17.7	10.8	0.42	30
Kawau-1A	2259-2268	2264	-17.4	11	0.45	29
Kawau-1A	2268-2277	2273	-18.4	7.9	0.33	28
Kawau-1A	2277-2287	2282	-20.2	3.8	0.19	23
Kawau-1A	2287-2296	2292	-20.4	3.5	0.18	23
Kawau-1A	2302	2302	-26	1.7	0.1	20
Kawau-1A	2357	2357	-25.1	1.9	0.13	17
Kawau-1A	2405-2415	2410	-26.9	1.2	0.08	18
Kawau-1A	2451-2460	2456	-26.6	1.0	0.05	23
Kawau-1A	2506-2515	2511	-27.6	1.1	0.05	26

Kawau-1A	Actual SWC	2107	-27.9	1.0	0.03	39
Kawau-1A		2180	-26.6	0.8	0.03	31
Kawau-1A		2193	-28.5	0.4	0.02	23
Kawau-1A		2201	-25.6	0.7	0.03	27
Kawau-1A		2218	-24.5	0.4	0.02	23
Kawau-1A		2240	-18.2	9.3	0.38	29
Kawau-1A		2263	-21.4	4.7	0.19	29
Kawau-1A		2301	-27.3	1.2	0.05	28
Kawau-1A		2376	-27.6	1.3	0.05	30
Kawau-1A		2387	-27.2	1.3	0.20	8
Hoiho-1	Actual SWC	1524	-27.1	0.6	0.02	35
Hoiho-1		1536	-26.6	1.5	0.05	35
Hoiho-1		1554	-26.3	0.5	0.02	29
Hoiho-1		1558	-25	3	0.1	35
Hoiho-1		1578	-15.8	17.1	0.45	44
Hoiho-1		1582	-19.7	8	0.26	36
Hoiho-1		1614	-26.6	1.3	0.06	25
Hoiho-1		1646	-26.4	0.7	0.02	41
Pakaha-1	2372-81	2377	-23.6	1.9	0.07	32
Pakaha-1	2473-82	2478	-25.5	1.5	0.08	22
Pakaha-1	2491-2500	2496	-26.4	0.7	0.07	12
Pakaha-1	2546-55	2551	-19.3	6.5	0.31	24
Pakaha-1	2555-64	2560	-19.7	5.9	0.33	21
Pakaha-1	2701-10	2706	-26.1	1.4	0.14	12
Pakaha-1	2756-65	2761	-26.8	0.9	0.09	12
Pakaha-1	2802-11	2807	-25.8	1.2	0.1	14
Pakaha-1	Actual SWC	2253	-27.9	0.4	0.04	11
Pakaha-1		2474	-27.7	0.4	0.05	10
Pakaha-1		2505	-26.4	1.1	0.09	14
Pakaha-1		2576	-20.7	5.3	0.29	21

Pakaha-1		2639	-25.9	1.5	0.12	15
Pakaha-1		2659	-27.0	1.6	0.15	12
Pakaha-1		2838	-26.0	1.5	0.13	13
Toroa-1	1957-66	1962	-27.3	0.5	0.02	29
Toroa-1	2012-21	2017	-26.9	0.4	0.02	20
Toroa-1	2067-76	2072	-26.7	0.7	0.03	25
Toroa-1	2113-22	2118	-26	1.0	0.04	28
Toroa-1	2241-50	2246	-24.5	1.4	0.06	27
Toroa-1	2341-51	2346	-26	0.2	0.01	27
Toroa-1	2378-87	2383	-26.3	0.4	0.02	23
Toroa-1	2433-42	2438	-27.4	0.3	0.01	30
Toroa-1	**Actual SWC**	2079	-26.2	0.1	0.02	4
Toroa-1		2124	-26.6	0.1	0.03	4
Toroa-1		2160	-26.2	0.2	0.04	7
Toroa-1		2162	-21	7.2	0.38	22
Toroa-1		2207	-25.9	1.6	0.1	19
Toroa-1		2233	-27	0.9	0.06	18
Toroa-1		2235	-26.8	0.5	0.04	15
Toroa-1		2260	-25.5	1.9	0.09	25

Appendix 4

Full list of geochemical data from the present study

Well	Depth(m)	Depth(Avg)	$d^{13}C$	TOC	%N	C/N
Rakiura-1	1683-92	1688	-26.1	0.4	<0.1	23
Rakiura-1	1698-1701	1700	-26	0.5	<0.1	20
Rakiura-1	1720-29	1725	-25.9	0.5	<0.1	18
Rakiura-1	1774-84	1779	-25.9	0.2	<0.1	20
Rakiura-1	1784-93	1789	-26.1	0.3	<0.1	33
Rakiura-1	1793-1802	1798	-25.8	0.2	<0.1	26
Rakiura-1	1802-11	1807	-26.3	0.3	<0.1	37
Rakiura-1	1811-20	1816	-25.8	0.1	<0.1	15
Rakiura-1	1820-29	1825	-26.3	0.3	<0.1	37
Rakiura-1	1829-39	1834	-26.1	0.2	<0.1	25
Rakiura-1	1838-48	1843	-26.2	0.5	<0.1	27
Rakiura-1	1856-66	1861	-25.7	0.7	<0.1	26
Rakiura-1	1884-93	1889	-26.0	0.8	<0.1	30
Rakiura-1	1963-65	1964	-27.2	0.6	<0.1	29
Pukakai-1	2274-83	2279	-26.3	0.3	<0.1	32
Pukakai-1	2284-99	2292	-25.8	0.3	<0.1	23
Pukakai-1	2290-2300	2295	-26.3	1.1	<0.1	56
Pukakai-1	2300-08	2304	-26.6	1.3	<0.1	61
Pukakai-1	2308-17	2313	-18.7	3.9	0.1	36
Pukakai-1	2317-25	2321	-19.4	3.6	0.1	38
Pukakai-1	2325-35	2330	-19.7	3.4	0.1	38
Pukakai-1	2335-44	2340	-23.8	0.8	<0.1	34
Pukakai-1	2381-90	2386	-23.5	0.9	<0.1	34
Pukakai-1	2410-18	2414	-23.6	0.8	<0.1	33
Resolution-1	Actual SWC	1396.5	-27.0	0.4	<0.1	15
Resolution-1		1428	-26.5	0.6	<0.1	25
Resolution-1		1462.5	-24.5	0.3	<0.1	13
Resolution-1		1474.5	-24.7	0.7	<0.1	17
Resolution-1		1478	-23.9	1.6	<0.1	32
Resolution-1	1380-85	1383	-25.74	0.3	<0.1	20
Resolution-1	1405-10	1408	-25.18	0.3	<0.1	30
Resolution-1	1420-25	1423	-25.14	0.3	<0.1	40
Resolution-1	1430-35	1433	-25.63	0.6	<0.1	36
Resolution-1	1440-45	1443	-25.77	0.7	<0.1	27

Resolution-1	1450-55	1453	-26.14	1.3	<0.1	39
Resolution-1	1465-70	1468	-26.56	0.7	<0.1	20
Resolution-1	1475-80	1478	-25.88	0.8	<0.1	31
Resolution-1	1490-95	1493	-25.89	0.8	<0.1	23
Resolution-1	1500-10	1505	-25.6	0.9	<0.1	27
Resolution-1	1520-30	1525	-25.5	0.7	<0.1	21
Resolution-1	1550-60	1555	-26.12	0.7	<0.1	20
Endeavour-1	1604-06	1605	-25.5	0.7	<0.1	18
Endeavour-1	1628-31	1630	-25.6	0.6	<0.1	17
Endeavour-1	1652-55	1654	-26.0	0.8	<0.1	20
Endeavour-1	1674-76	1675	-25.9	0.8	<0.1	20
Endeavour-1	1692-95	1694	-25.4	0.8	<0.1	18
Endeavour-1	1723-26	1725	-25.3	1.0	<0.1	17
Endeavour-1	1729-32	1731	-21.5	2.1	0.1	22
Endeavour-1	1735-38	1737	-18.5	5.9	0.3	25
Endeavour-1	1744-47	1746	-19.5	4.2	0.2	23
Endeavour-1	1750-53	1752	-18.5	6.6	0.3	26
Endeavour-1	1762-65	1764	-19.7	4.6	0.2	25
Endeavour-1	1765-68	1766	-21.3	2.5	0.1	22
Endeavour-1	1777-80	1779	-20.4	3.0	0.2	22
Endeavour-1	1793-96	1795	-23.9	1.5	0.1	16
Endeavour-1	1817-20	1819	-22.9	1.6	0.1	16
Endeavour-1	1820-23	1822	-23.9	0.9	<0.1	12
Endeavour-1	1826-29	1828	-21.9	2.4	0.1	23
Galleon-1	2455-60	2458	-25.7	1.2	<0.1	19
Galleon-1	2470-75	2473	-25.5	1.4	<0.1	21
Galleon-1	2485-90	2488	-25.5	1.2	<0.1	20
Galleon-1	2500-05	2503	-24.1	1.1	<0.1	19
Galleon-1	2510-15	2513	-19.0	5.6	0.2	30
Galleon-1	2515-20	2518	-19.6	4.5	0.2	29
Galleon-1	2520-25	2523	-23.3	2.0	<0.1	26
Galleon-1	2525-30	2528	-24.5	1.5	0.1	24
Galleon-1	2530-35	2533	-22.9	1.8	<0.1	26
Galleon-1	2535-40	2538	-24	1.4	0.1	21
Galleon-1	2545-50	2548	-25.8	1.1	0.1	20
Galleon-1	2555-58	2557	-26.4	1.0	0.1	23
Galleon-1	2564-67	2566	-26	1.1	0.1	21
Galleon-1	2570-73	2572	-26	1.2	0.1	23
Galleon-1	2576-79	2578	-25.4	1.2	<0.1	23
Galleon-1	2585-88	2587	-25.1	1.2	0.1	23
Galleon-1	2600-03	2602	-25.7	1.3	0.1	24

Galleon-1	2612-15	2614	-25.7	1.3	0.1	21
Galleon-1	2624-27	2626	-24.7	1.1	<0.1	24
Galleon-1	2636-39	2638	-24.8	1.3	0.1	25
Clipper-1	2630-35	2633	-25.6	0.4	<0.1	20
Clipper-1	2680-85	2683	-24.6	1.0	<0.1	36
Clipper-1	2700-05	2703	-23.9	1.0	<0.1	30
Clipper-1	2710-15	2713	-21.6	0.9	<0.1	37
Clipper-1	2725-30	2728	-25.9	0.8	<0.1	31
Clipper-1	2750-55	2753	-25.4	0.9	<0.1	29
Clipper-1	2760-65	2763	-23.2	2.0	0.1	29
Clipper-1	2765-70	2768	-20.6	2.5	0.1	30
Clipper-1	2775-80	2778	-19.1	6.2	0.2	30
Clipper-1	2780-85	2783	-19.2	6.8	0.3	30
Clipper-1	2785-90	2788	-19.0	11.7	0.5	29
Clipper-1	2790-95	2793	-19.5	7.1	0.3	29
Clipper-1	2795-2800	2798	-20.1	4.6	0.2	30
Clipper-1	2805-10	2808	-23.5	1.5	0.1	28
Clipper-1	2815-20	2818	-24.1	1.3	<0.1	31
Clipper-1	2845-50	2848	-24.0	1.5	<0.1	31
Clipper-1	2905-10	2908	-23.7	1.8	<0.1	29