**STUDIES ON THE GLACIOVOLCANIC
AND MAGMATIC EVOLUTION OF
RUAPEHU VOLCANO, NEW ZEALAND**

by

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ABSTRACT

This thesis undertakes a detailed case study of the processes and timescales of arc andesite-dacite magma generation and lava flow emplacement at a continental composite volcano. This has been achieved through the collection and integration of high-resolution field, geochronological and geochemical datasets for lava flows that form the edifice of Ruapehu.

The influence of syn-eruptive lava-ice interaction on the distribution and preservation of lava flows on glaciated composite volcanoes is investigated by characterising the morphology and fracture characteristics of effusive products at Ruapehu. Ice-bounded and ice-dammed lava flows display over-thickened (50–100 m-high) margins adjacent to or within glaciated valleys, are intercalated with till and have lateral margins that are pervasively fractured by quench-contraction cooling joints. These characteristics can be accounted for by impoundment and chilling of lava flows that were emplaced against large flank glaciers. In contrast, lava flows located within valleys have minimal moraine cover and glacial striae and are characterised by fracture networks indicative of only localised and minor interaction with ice/snow. These lavas were emplaced onto a relatively ice-free edifice following glacial retreat since ~18 ka.

New high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages and whole-rock major element geochemistry for lava flows are interpreted in the context of geologic mapping, volcano-ice interaction processes and previous chronostratigraphic studies. This provides a high-resolution eruptive history and edifice evolution model for Ruapehu. Sub-glacial to ice-marginal effusive eruption of basaltic-andesite and andesite constructed the northern portion of the exposed edifice between ~200 and 150 ka (Te Herenga Formation) and the wide south-eastern planèze as well as parts of the northern, eastern and western flanks of Ruapehu between ~166 and 80 ka (Wahianoa Formation). No ages were returned for lava flows for the period from 80–50 ka, indicating one or a combination of: an eruptive hiatus; subsequent erosion and burial of lavas; or syn-eruptive glacial conveyance of lava flows to the ring-plain. The greater part of the modern edifice was constructed via effusion of lava flows of the syn-glacial Mangawhero Formation (50–15 ka) and post-glacial Whakapapa Formation (<15 ka). Syn-glacial edifice growth occurred primarily via effusion of andesite-dacite lava flows that formed ice-bounded ridges adjacent to valley-filling glaciers. Post-glacial summit cones were constructed in the presence of remnant

upper flank glaciers between 15 and 10 ka. Debuttressing of two northern summit cones and a southern summit cone as ice underwent continued post-glacial retreat resulted in two major Holocene sector collapses and deposition of debris avalanche deposits on the northern and south-eastern flanks of Ruapehu, respectively. The northern collapse scar was infilled by a new cone comprising <10 ka lava flows that form the modern upper northern and eastern flanks of the volcano. Late Holocene to historic eruptive activity has occurred through Crater Lake, which occupies the site of the collapsed southern cone.

New whole-rock major and trace element compositions for lavas and their mineral and melt inclusion geochemical characteristics are evaluated within the context of the improved chronostratigraphic framework. The new constraints are combined with existing whole-rock isotopic data to establish the long-term development of the magma generation system beneath Ruapehu. Basaltic-andesite lavas erupted between ~200 and 150 ka contain low-K₂O (2–3 wt. %) melt inclusions and have whole-rock compositions characterised by low incompatible element (K, Rb, Ba, Th, U) abundances and high ¹⁴³Nd/¹⁴⁴Nd-low ⁸⁷Sr/⁸⁶Sr when compared to younger eruptive products. In particular, basaltic-andesite to dacite lavas that were erupted between 50–35 ka define a high-K/Ca trend over a range of ~8 wt. % SiO₂ as well as elevated incompatible trace element contents when compared to all other documented eruptive products from Ruapehu. Rhyodacitic to rhyolitic melt inclusions, interstitial glass and melt pockets in partially fused feldspathic xenoliths contained within the dacite lavas from this latter period contain high K₂O (5–6 wt. %) and Rb contents (250–280 ppm). The whole-rock and glass characteristics of 50–35 ka lavas reflect the generation and assimilation of partial melts of the greywacke-argillite basement within the magma system beneath Ruapehu during this period. Selective partial melting and assimilation of fertile, K- and Rb-rich mineral phases (e.g. biotite) within the meta-sedimentary mineral assemblage is inferred to explain the enriched nature of these melts. A reversion to progressively less silicic and less potassic lavas with lower incompatible element abundances erupted since 26 ka is matched by the recurrent incorporation of crystals that trapped low-K₂O melt inclusions. The trend is interpreted to reflect the exhaustion of fertile phases within assimilated continental source rocks as the crust was progressively heated during long-term thermal conditioning of the arc lithosphere beneath Ruapehu.

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Publications arising from this thesis

Journal articles

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- Eaves, S.R., Anderson, B.M., Mackintosh, A.N., Doughty, A.M., Townsend, D.B., Conway, C.E., Winckler, G., Schaefer, J.M., Leonard, G.S., and Calvert, A.T., (2016b), The Last Glacial Maximum in central North Island, New Zealand: paleoclimate inferences from 2D glacier modelling: *Climate of the Past*, v. 12, p. 943-960.
- Greve, A., Turner, G.M., Conway, C.E., Townsend, D.B., and Calvert, A.C., (2016 manuscript under review), Secular variation and new paleomagnetic age constraints on lava flows from the Tongariro Volcanic Centre, New Zealand: *Geophysical Journal International*, Manuscript ID: GJI-S-15-0993.

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CHAPTER 1

1. INTRODUCTION

1.1. BACKGROUND TO THIS STUDY

Andesite-dacite composite volcanoes are the surficial emblems of arc-related subduction zone magmatism that occurs along Earth's continental convergent margins. On one hand, these volcanoes are the sites of frequent, unpredictable and hazardous volcanic phenomena, and on the other hand they represent valuable windows into the subduction factory that destroys oceanic crust and generates continental crust. In both cases, constraining the processes and timescales of magma generation and eruption remains at the centre of research efforts to understand how and why arc volcanoes erupt. Establishing high-resolution volcanic stratigraphies is vital to such research because they reveal the tempo and types of past eruptive behaviour. Within these frameworks, a comprehensive story of a volcano's growth and degradation can be achieved and modelling the petrogenesis and evolution of magmas can be undertaken with confidence.

Composite volcanoes are complex entities that are shaped by an interplay between volcanic, magmatic, tectonic and climatic processes. Many have lofty heights and are located along volcanic arcs at mid- to high-latitudes (e.g. Cascade and Andean arcs) that have sustained substantive ice volumes in past glacial periods as well as at present. Glacial erosion of composite volcanoes provides exposure through eruptive sequences that would otherwise be hidden on the flanks of composite volcanoes. However, in addition to sector collapse, glaciation is a key agent for disturbing conformable or continuous eruptive stratigraphies, through eroding primary volcanic deposits and burying them under till (e.g. Singer et al., 1997).

For settings with coeval eruptive and glacial histories, the presence of ice on edifice flanks imposes a major influence on the preservation and distribution of effusive products during eruptions because glaciers can deflect and impound lava flows (Lescinsky and Sisson, 1998; Edwards et al., 2013). Because local ice volumes fluctuate over timescales of tens of kyr in response to global climate cycles (Denton and Hughes, 1983; Lisiecki and Raymo, 2005), complex stratigraphic relationships between lava flows of different age are produced (e.g. Lescinsky and Fink, 2000). To ensure the fidelity of eruption histories in such settings, accurate radiometric age dating of comprehensive sample suites

needs to be undertaken within frameworks that take into account the stratigraphic consequences of volcano-ice interaction.

Magmas erupted at arc volcanoes represent the final products of multi-stage melting, mixing, fractionation and assimilation processes that begin in the asthenosphere and continue throughout the lithosphere (e.g. DePaolo, 1981; Hildreth and Moorbath, 1988; Gamble et al., 1999). Flux melting of the mantle wedge adjacent to subduction zones due to dehydration of the downgoing slab and its sediment cover is most widely regarded as the origin of primary arc magmas (e.g. McCulloch and Gamble, 1991), although direct derivation from slab and sediment melting is also feasible in some settings (e.g. Defant and Drummond, 1993).

Magmas subsequently pass through the crustal filter of arc lithosphere and are differentiated by crystal fractionation and crustal anatexis as they ascend toward Earth's surface. Despite a global correlation between continental convergent margins and andesites with crust-like compositions (Gill, 1981; Rudnick and Gao, 2003), the wide variation of the lithological characteristics and dynamics of the slab, mantle wedge and overlying arc lithosphere at individual subduction zones makes it difficult to define a consensus model for the generation of their source magmas. This is further compounded by the complexity of sequences of volcanic rocks within eruption episodes ranging from timescales of <1–20 yr (Clynne, 1999; Coombs et al., 2000) to >10 kyr (Gamble et al., 2003; Frey et al., 2004). Thus, whereas whole-rock geochemical and isotopic constraints enable the identification of a crustal signature in arc andesite volcanic rocks (e.g. Hildreth and Moorbath, 1988; Sisson et al., 2013), micro-scale investigations of discrete mineral and melt populations allows interrogation of the origin of this signature, and the nature and timescales of magma assembly and eruption processes (Davidson et al., 2005).

Located in the central North Island of New Zealand, Ruapehu is a typical large, mid-latitude, continental arc volcano, which has been constructed throughout a >200 kyr lifetime with coeval eruptive and glacial histories. Ruapehu has been New Zealand's most active volcano in historical time, with notable magmatic or phreatomagmatic explosive episodes in 1895, 1945 and 1995–6. The latter of these eruptions resulted in widespread tephra dispersal that affected tourism, aviation, agriculture, and electricity generation industries in central North Island, New Zealand (Cronin et al., 1998; Johnston et al., 2000). The location of Ruapehu within the Tongariro National Park, a World Heritage

Site that attracts ~800,000 visitors annually, underlines the importance of having well-constrained temporal frameworks of eruptive behaviour at this active volcano.

Furthermore, Ruapehu presents an ideal candidate for establishing a high-resolution eruptive chronology that integrates volcano-ice interactions and allows investigation of the compositional evolution of a productive arc magma system. Three key shortcomings of previous research have precluded the generation of a detailed geological map, eruption history and edifice evolution model for Ruapehu volcano:

1) Oversight of the effects of syn-eruptive lava-ice interaction on the preservation and distribution of eruptive products. Although glaciation of the edifice has been widely cited to explain stratigraphic unconformities (e.g. Hackett and Houghton, 1989), only one previous study recognised that lava flows interacted with glacial ice during effusive eruptions on Ruapehu (Spörli and Rowland, 2006). The complex stratigraphic relations resulting from volcano-ice interaction has made the relative sequencing of lavas with disparate distributions difficult.

2) Sparse geochronology data to constrain the timing and duration of periods of effusive growth of the volcano. Existing radiometric age data for lavas have relatively large uncertainties that make discrimination of effusive eruption phases difficult and only limited data have been collected for post-50 ka lavas (Gamble et al., 2003).

3) Fragmentary sampling of the edifice. Comprehensive sampling of accessible parts of Ruapehu has been undertaken (e.g. Waight et al., 1999), however, there is a conspicuous lack of petrological and geochemical data for lava flows from the more remote western and southern portions of the edifice.

The net result of these limitations is that current models of edifice growth and magma system evolution (e.g. Price et al., 2012) rely on an incomplete chronostratigraphic framework. This PhD research is motivated by the need to overcome these limitations in order to advance the contemporary understanding of continental arc volcanism and the development of composite volcanoes in New Zealand and globally.

1.2. THESIS OBJECTIVES AND STRUCTURE

The aim of this PhD research is to generate a high-resolution lava flow chronological framework in order to document the magmatic and glaciovolcanic evolution of Ruapehu volcano. Detailed geological and glaciovolcanic mapping and high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data are combined with whole-rock geochemical data acquired from lava flows. This allows investigation of the long-term morphological and magmatic evolution of this prototypical arc volcano. Micro-analytical techniques are utilised to define the textural and chemical characteristics of crystal and melt components within andesite-dacite lava flows to unravel the processes that have operated within Ruapehu's magma generation system over the last ~200 kyr.

Key questions I address in this thesis include:

- Were ridge-top lava flows eroded by glaciers or emplaced against ice at Ruapehu?
- Can ice-marginal lava flows be used to inform paleoclimate reconstructions of former glacier extents?
- Did Ruapehu grow via discrete episodes of construction punctuated by erosion, or are apparent eruptive hiatuses biased by non-preservation of volcanic products?
- What are the ages of the oldest and youngest lava flows exposed on the edifice, and can the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer be applied to andesite flows as young as the Holocene?
- What processes controlled the timing of two major Holocene sector collapse events?
- Has edifice erosion, sector collapse and deglaciation since ~20 ka cause elevated eruption rates?
- How has the varying magma flux through the lithosphere influenced the composition of erupted products over time?
- Are high-magnesian andesites the products of elevated meta-igneous crustal contamination, primary mantle-derived magmas or mafic-felsic interaction?

These questions relate to the broader topics of glaciovolcanism, geochronology and magmagenesis that form central themes to current global volcanological research, and are addressed within 5 main chapters in this thesis:

Chapter 1 introduces the motivation for carrying out this research. Key questions and objectives of the study are outlined. The geological context and previous research carried out on Ruapehu are presented to highlight the reasons for undertaking this PhD research.

Chapter 2 describes the morphology and fracture characteristics of effusive products resulting from the interaction between lava flows and former glaciers at Ruapehu volcano. Methods used to measure lava flow morphologies and fractures are described and processes of lava flow emplacement and fracture generation are discussed. This chapter has been published in the *Bulletin of Volcanology* (Conway et al., 2015).

Chapter 3 presents a high-resolution lava flow chronology for Ruapehu volcano within the context of new geological mapping and pre-existing chronostratigraphic studies. Analytical techniques used for the measurement of $^{40}\text{Ar}/^{39}\text{Ar}$ ages and whole-rock major element compositions of lava flows are defined here. These new geochronological and geochemical data are used to define eruptive packages within previously defined chronostratigraphic formations. Ages for ice-marginal lava flows are used to constrain the timing and extent of former glaciation on the volcano, and overall time-composition relationships for lava flows are outlined. A new interpretation is presented for the generation of Holocene sector collapse events at Ruapehu based on the post-glacial debuttressing and failure of originally ice-bounded summit cones. This chapter has been prepared as an article to be submitted to the *Journal of Volcanology and Geothermal Research*.

Chapter 4 characterises the magmatic and crustal sources and processes that have generated arc andesite-dacite lava flows at Ruapehu within the chronostratigraphic framework established in Chapter 3. Analytical techniques used to determine whole-rock and in-situ mineral and melt compositions are described herein. The revised chemical chronology of effusive products reveals wide magma composition diversity at ~50–35 ka. High-magnesian andesites and dacites that contain potassic melt inclusions and glass hosted in xenoliths erupted during this time reflect contamination of stalled magmas by enriched partial melts (high-K and -Rb) derived from continental crust and interaction with recharging mafic magmas. The progressive reversion to less silicic, potassic and radiogenic isotope compositions of lavas erupted since 26 ka reflects decreasing levels of crustal assimilation in derivative andesite magmas below Ruapehu. This chapter has been prepared as an article to be submitted to the *Journal of Petrology*.

Chapter 5 integrates the datasets and key findings presented in the three previous chapters. Key questions introduced in Chapter 1 are answered and future research objectives are suggested.

Chapters 2, 3 and 4 are written in the style of stand-alone journal articles with individual abstract, introduction, methods, results and discussion sections, but their formats adhere to the overall thesis style. Additional descriptions of analytical techniques and sample information for this thesis are presented in the appendices. Geological, geochemical and geochronological data collected during this study contributed directly to, and are also presented within, the publication of a GNS Science volcanic geology map and bulletin (Townsend et al., 2016). Levels of input consistent with normal requirements for co-authorship for journal articles have been provided by supervisors and co-authors throughout the term of this PhD. G. Leonard and A. Calvert operated the mass spectrometer and collected $^{40}\text{Ar}/^{39}\text{Ar}$ data at the U.S. Geological Survey geochronology laboratory in Menlo Park, CA. D. Townsend digitised boundaries of eruptive packages in ArcGIS that were modified by C. Conway in the drafting of map figures in Chapters 2 and 3.

1.3. ORIGIN AND IMPORTANCE OF COMPOSITE VOLCANOES WITHIN CONTINENTAL ARCS

Composite volcanoes (also termed compound volcanoes, stratovolcanoes and composite cones) are polygenetic constructional volcanic edifices formed by repeated eruptions from single or multiple vents that are related to a common magma system (Davidson and de Silva, 2000). If progressive eruption of lavas and pyroclastic deposits occurs throughout the lifetime of the volcano from a persistent summit vent, a conical and steep-sided edifice will be constructed (Thouret, 1999). Eruptive vents or centres commonly migrate over time or are synchronously active at spatially discrete foci, however, which results in the formation and juxtaposition of overlapping edifices and a complex intercalation of volcanic products (e.g. Hobden et al., 1996). Composite volcanoes formed in this way often resemble asymmetric cones, broad massifs or ridge-like edifices.

Composite volcanoes are the typical volcanic landform associated with convergent continental margins due to: (1) the persistence of subduction zones that supplies a steady

source of magma and results in long-lived polygenetic eruptive centres; and (2) the intermediate composition and viscosity of typical arc andesite-dacite magmas, which results in construction of steep edifices with conical morphologies. Continental arc volcanoes are dominant sites of subaerial volcanism on Earth and represent the interface between the atmosphere and subduction zone-derived magmas and volatile elements. As such they hold key importance for regulating the global climate and the flux of elements through Earth's mantle and crust. Moreover, they present significant natural hazards to human populations due to their frequent, unpredictable and often violent eruptions and potential to generate lahars and catastrophic sector collapse events.

This section introduces (1) the tectonic setting and significance of convergent continental margins, (2) key petrogenetic models for how intermediate magmas are generated in these settings, (3) how understanding the tempo and types of eruptive activity at composite volcanoes is informed by studying long-term eruption histories, and (4) basic principles of glaciovolcanism that are relevant to temperate-latitude composite volcanoes.

1.3.1. Convergent continental margins and the global subduction zone system

Subduction zones are regions on Earth where the convergence of tectonic plates results in the descent of dense oceanic crust beneath the opposing and overriding plate and into the underlying asthenosphere. In the case of convergent continental margins, the overriding plate is composed of continental crust. Convergent continental margins are located around most of the Pacific Ocean and along the southern margin of Eurasia (Fig. 1.1).

Subducted plates consist of upper mantle lithosphere, altered oceanic crust and sediment (von Huene and Scholl, 1991). During descent, altered oceanic crust and sediments are heated and release H₂O-rich fluids and melts into the overlying mantle wedge, which consequently lower the solidus temperature of mantle peridotite by several hundred °C and triggers partial melting (McCulloch and Gamble, 1991; Gaetani and Grove, 1998; Grove et al., 2012). The zone of melting is generally located where the subducted plate is at a depth of 100–130 km (Gill, 1981; Tatsumi, 1986; Syracuse and Abers, 2006). The derivative basalts contain high H₂O contents (of up to 6 wt. % compared to <0.5 wt. % in mid-ocean ridge basalt; Sobolev and Chaussidon, 1996; Grove et al., 2002; Wallace, 2005) and fluid-mobile trace elements (K, Rb, Ba, Sr, U, Pb) that are sourced from

subducted sediments and altered oceanic crust (McCulloch and Gamble, 1991; Plank and Langmuir, 1998).

Figure 1.1. Location of composite volcanoes associated with continental convergent margin magmatism that are referred to in this thesis. Grey lines represent major subduction zone plate boundaries. Red triangles are locations of the labelled volcanoes.

Due to their high H_2O contents, the basaltic melts are highly buoyant and rise into hotter portions of the mantle wedge, where further melting occurs. The basaltic magmas from this zone are only very rarely erupted at the surface within arc settings to provide information about the mantle conditions in which they equilibrated. This is because the magmas must first transit through the lithosphere of the overriding plate where they invariably stall and are consequently differentiated. The lithospheric processing of arc magmas is introduced below in section 1.3.2.

1.3.2. Characteristics and petrogenesis of intermediate composition arc magmas

Andesite typifies the intermediate composition (~58–63 wt. % SiO_2) of volcanic products erupted at continental arc volcanoes, and closely resembles that of the continental crust (Taylor and McLennan, 1995; Rudnick and Gao, 2003). Constraining the genesis of andesite magmas is therefore important for understanding the origin of Earth's crust and processes of element recycling at subduction zones (e.g. Carmichael, 2002). Andesite magmas are proposed to originate via four main end-member models: direct partial

melting of a hydrous mantle source (e.g. Grove et al., 2012); partial re-melting of altered basaltic crust (e.g. Jackson et al., 2003); crystal fractionation of arc basalts in the crust (e.g. Pichavant et al., 2002); and mixing between mafic and felsic composition magmas and/or crust (e.g. Kent, 2013). For continental arc settings it is evident that crustal filtering of primary magma occurs and, thus, composite scenarios that combine these interrelated melting, mixing, crystallisation and assimilation processes are invoked to explain the genesis of intermediate compositions magmas (e.g. Hildreth and Moor bath, 1988; Dungan et al., 2001; Price et al., 2012; Sisson et al., 2013).

Many studies of andesite petrogenesis implicate the base of the crust above the zone of mantle melting associated with subduction as an important staging site of magma differentiation because it is progressively intruded by ascending basaltic magmas, which stall, cool and crystallise (Dufek and Bergantz, 2005). Subduction zones prevail over timescales of Myr, thereby facilitating progressive intrusion of basalt into the crust and the development of a 'hot zone' (Annen and Sparks, 2002). It is here that the mafic magmas transfer heat and volatiles to the crust, leading to melting. In such settings the lower crust represents a mix of partially crystallised basalt, partially melted crust and its refractory residue, and H₂O released from basalt crystallisation (Annen et al., 2006). Conductive zones in the crust or uppermost mantle that have been mapped by geophysical imaging are consistent with the presence of molten material and significant volumes of liberated H₂O (e.g. Cascades, Stanley et al., 1990; Andes, Brasse et al., 2002; New Zealand, Heise et al., 2010). Fractionated magmas will tend to ascend toward the upper crust, where further textural and chemical modification takes place.

Upper crustal magma systems beneath andesitic arc volcanoes are envisioned as complex networks of interconnected melt and mush bodies (e.g. Gamble et al., 1999; Humphreys et al., 2006). These volcanic plumbing systems allow dynamic interaction between magma and melt batches of varied composition. Widespread documentation of disequilibrium petrographic textures in andesite lavas (Eichelberger, 1978; Gamble et al., 1999; Coombs et al., 2000; Dungan and Davidson, 2004; Reubi and Blundy, 2008; Ruprecht et al., 2012; Millet et al., 2014 among many) and the dominant bimodality of basaltic and dacitic-rhyolitic compositions of mineral-hosted melt inclusions (Reubi & Blundy, 2009) indicates that mixing between mafic and silicic end-member components is an important process within individual eruptive products and over the lifetime of a volcano.

In contrast, some recent compilations of global datasets for arc volcanic rocks surmise that, despite the irrefutable evidence for magma mixing, the general chemical systematics of andesite-dacites are primarily governed by (1) the composition of melts extracted from the mantle (Turner and Langmuir, 2015) and (2) high-pressure crystal fractionation of hydrous basalts (Lee and Bachmann, 2014). While a consensus model is unlikely to be applicable to all arc settings due to their individual tectonic and geodynamic characteristics, resolving the source signatures of arc magmas and the genesis of andesite remains a critical debate in volcanology now as it did 65 years ago (Tilley, 1950).

1.3.3. Reconstructing eruption histories and magma flux rates at composite volcanoes

Eruptive behaviour at arc composite volcanoes ranges from effusive eruption of lava flows and domes through to explosive eruptions that generate pyroclastic flow and fall deposits. Eventual effusive or explosive eruption will ultimately be governed by the final volatile budget and degassing history of the derivative magma as well as the crustal stress regime and conduit conditions (e.g. Martel et al., 1998; Szramek et al., 2006; Pardo et al., 2014). Diverse eruptive styles may therefore occur simultaneously or vary over long timescales at composite volcanoes due to the complex crustal conditioning of arc magmas (see section 1.3.2). Interactions between eruptive products and water/snow/ice at the summit, in the subsurface or on the flank of a volcano can also produce phreatic or phreatomagmatic eruptions and generate lahars. Summit and flank zones of composite volcanoes comprise intercalated lava flows and pyroclastic material that have been emplaced proximal to vents. Sequences of pyroclastic fall and volcaniclastic deposits are better-preserved on surrounding ring plains that provide a record of the explosive activity and degradation of a volcanic edifice. Complete eruption histories incorporate records from both the edifice and ring plain, however, sequences of lava flows and associated breccias provide the best possible in situ record of edifice growth.

Eruption ages for andesite-dacite lava flows at Quaternary composite volcanoes are most commonly determined by the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer (Singer et al., 1997; Hildreth et al., 2003; Frey et al., 2004; Fierstein et al., 2011). This technique has almost entirely replaced the K/Ar method due to its ability to provide information on the volume and compositions of argon gas released throughout cumulative heating of a sample. In this

way, the effects of alteration can be identified and mitigated. Developments to high-precision instrumentation (e.g. Coble et al., 2011), improved understanding of the behaviour of argon in volcanic glass (e.g. Clay et al., 2015), and methods to counter argon recoil processes that affect fine-grained rocks (e.g. Fleck et al., 2014) have established $^{40}\text{Ar}/^{39}\text{Ar}$ dating as a means for determining accurate eruption ages for Pleistocene and, potentially, Holocene volcanic rocks. Comprehensive geological mapping accompanied by accurate high-resolution geochronological and geochemical datasets can be used to constrain detailed constructional histories of composite volcanoes (e.g. Dungan et al., 2001; Hildreth et al., 2003; Escobar-Wolf et al., 2010). Defining the rates of eruption and the durations of cone-building phases helps to interpret the longevity of magma reservoirs in the crust as well as fundamental relationships between subduction zone parameters (plate convergence rate, age of subducted slab, crustal thickness) and magma flux (e.g. Frey et al., 2004; Turner and Langmuir, 2015).

1.3.4. Volcano-ice interactions

Interactions between volcanism and glaciation represent an important part of the eruptive histories of many composite volcanoes globally, particularly those high-elevation examples located at mid- to high-latitudes, which hosted significant accumulations of ice during past glacial periods (e.g. Mt Baker, Hildreth et al., 2003). Observations from historical eruptions and analogue experiments have indicated the ability of ice to impound and deflect lava flows (Edwards et al. 2013). As a result, volcanism in the presence of ice (i.e. glaciovulkanism; cf. Kelman et al. 2002) produces distinct lava morphologies and has a primary impact on the spatial distribution of effusive products.

The general model for ice-marginal effusive volcanism on composite volcanoes invokes the emplacement of lava flows onto ridges adjacent to the lateral margins of valley-filling glaciers on the flanks of a volcano following an eruption from the summit (Lescinsky and Sisson, 1998). Lava is excluded from the valley by the glacier mass and is confined between the glacier margin and the adjacent ridge, resulting in thickening of the flow as it fills the available space. Retreat of the ice during an interglacial period results in exposure of ridge-bounded overthickened flows and subsequent lavas will be emplaced at lower elevations within the ice-free valley. This has two general implications: (1) eruptive histories for glaciated composite volcanoes must incorporate the effects that the former

presence of valley glaciers and ice caps have on the spatial and stratigraphic position of lava flows (e.g. Stevenson et al. 2006); and (2) glaciovolcanic deposits are useful paleoclimate proxy indicators that can be used in combination with glacial moraine distributions to infer the former presence, extent, and thickness of terrestrial ice (e.g. Smellie, 2008). Detailed mapping and dating of effusive glaciovolcanic products at composite volcanoes has been undertaken in few studies to date (Mee et al., 2009; Lachowycz et al., 2015), but glaciovolcanism is often inferred to have had general influences on the long-term eruption histories and morphological development of composite volcanoes (e.g. Schmidt and Grunder, 2009).

1.4. RUAPEHU VOLCANO

Ruapehu is the largest currently active volcano in New Zealand, with an estimated volume of $\sim 150 \text{ km}^3$ for the modern edifice (Gamble et al., 2003). Ruapehu attracts national attention because of its frequent historical explosive eruptions coupled with its growing popularity as a tourist destination. To the international community, Ruapehu represents a long-lived composite volcano and a site to investigate the development of a productive magma system in a continental arc setting. This section introduces the geologic setting and volcanic and glacial histories of Ruapehu, and reviews published material on the composition and genesis of its eruptive products.

1.4.1. Arc setting and basement geology

Ruapehu volcano is located at the southern end of the Taupo Volcanic Zone (TVZ), an active continental rifted-arc in central North Island, New Zealand (Fig. 1.1). Volcanism in the TVZ is associated with westward subduction of oceanic crust of the Pacific Plate beneath continental crust of the Australian Plate along the Hikurangi Trench system (Cole, 1979; Reyners et al., 2006). The subduction front is located $\geq 100 \text{ km}$ southeast of the North Island along the Hikurangi Trough, where the Pacific Plate is currently moving obliquely westward at $\sim 45 \text{ mm yr}^{-1}$ relative to the Australian Plate (DeMets et al., 2010). The southernmost portion of the TVZ includes the Tongariro and Ruapehu composite volcanoes, which are the dominant edifices within the Tongariro Volcanic Centre (TgVC; Grindley, 1960; Cole, 1978). Extension in the TgVC occurs at a direction of $\sim 115^\circ$ and a

rate of $2.3 \pm 1.2 \text{ mm yr}^{-1}$ (Villamor and Berryman, 2006a). The tectonic structure that is manifested by this motion is the 40 km-wide Mount Ruapehu Graben, which is bound by the Rangipo and Raurimu faults to the east and west, respectively, and by the Karioi and Ohakune fault sets to the south (Fig. 1.2; Villamor and Berryman, 2006a).

Figure 1.2. Regional setting of Ruapehu volcano within the Tongariro Volcanic Centre (TgVC) at the southern end of the Taupo Volcanic Zone (TVZ) in central North Island, New Zealand (inset). Major faults and townships within the TgVC are labelled in the main figure. Recently active and peripheral vents of the Tongariro and Ruapehu composite volcanoes are labelled.

The Ruapehu and Tongariro composite volcanoes of the TgVC are constructed on late Tertiary sediments and Mesozoic basement. The latter comprises the predominantly

Jurassic Torlesse Supergroup greywacke sequence that outcrops along the ranges east of the Rangipo fault. To the west of the Tongariro Domain, the ranges are composed of Jurassic Waipapa Terrane rocks, derived from more mafic sources (Adams et al., 2009; Price et al., 2015). Although poorly constrained, the Kaweka Terrane is inferred to extend westwards from the Axial Ranges under Ruapehu volcano (Sissons and Dibble, 1981; Rowland et al., 2010). The crustal thickness beneath Ruapehu is interpreted to be 40 km (Villamor and Berryman, 2006a; Salmon et al., 2011).

1.4.2. Volcanic and glacial histories

Earliest geological mapping of the Tongariro region in the 1920s and 1930s led to the recognition of Ruapehu as a multiple-vent composite volcano with a complex growth history that involved erosion of an older edifice and subsequent emplacement of young lava flows that constructed steeper portions of the upper cone (Grange and Hurst, 1929). Later workers incorporated ring plain and glacial deposits into the geological history of the volcano (Gregg, 1960; Topping, 1973). Hackett (1985) undertook the first detailed geologic study of Ruapehu volcano and established a chronostratigraphic framework for the growth history of the edifice, which was aided by sparse pre-existing whole-rock K/Ar radiometric age data (Stipp, 1968).

The growth history was later constrained by $^{40}\text{Ar}/^{39}\text{Ar}$ geochronological data acquired primarily for pre-100 ka lava flows (Gamble et al., 2003). Volcanic products are grouped within the Te Herenga (250–180 ka), Wahianoa (160–115 ka), Mangawhero (60–15 ka) and Whakapapa (<15 ka) formations, which represent the eruptive products of four main phases of edifice growth (Fig. 1.3; Hackett, 1985). Ages and durations of the phases were constrained by $^{40}\text{Ar}/^{39}\text{Ar}$ ages for lava flows from the Te Herenga Formation (3 samples), Wahianoa Formation (11 samples) and Mangawhero Formation (7 samples) by Gamble et al. (2003). Their dating study concentrated on the clear stratigraphic sequence of Wahianoa Formation lava flows exposed within the deeply glaciated Wahianoa and Whangaehu valleys on the southeast flank of Ruapehu.

Figure 1.3. Schematic maps of the distribution of effusive eruptive products (a) and glacier extents (b) for Ruapehu volcano. Abbreviations and age ranges are shown for the Te Herenga (TH), Wahianoa (WA), Mangawhero (MA), and Whakapapa (WH) formations. Map modified from Hackett and Houghton (1989) and Price et al. (2012). Idealised ice extents are modified from McArthur and Shepherd (1990) and Eaves (2015) are displayed for the Last Glacial Maximum (LGM) and present-day (PD).

Lavas of the Mangawhero Formation were inferred to have been erupted during discrete pulses of effusive activity centred on ~45 and ~22 ka (Gamble et al., 2003). Complex stratigraphic relationships between lavas of this and the subsequent Whakapapa Formation were interpreted as the result of rapid transitions between construction and intense degradation of the edifice (Hackett and Houghton, 1989). A chronostratigraphic model of rapid and discrete constructional phases of growth separated by erosion formed the basis of numerous petrochemical investigations that were summarised by Price et al. (2012) in a review of the magma system evolution.

The ring plain holds a thick apron of stacked pyroclastic and volcanoclastic material consisting of debris flow, debris avalanche and hyperconcentrated stream flow deposits interbedded with local andesitic tephra and distal rhyolitic tephra sourced from farther north in the TVZ (Cronin and Neall, 1997; Lecointre et al., 1998; Donoghue and Neall, 2001). Aggradation has likely been rapid following eruptive phases (Hackett and Houghton, 1989) and during glacial periods (Cronin and Neall, 1997), while large-scale sector collapse events may have occurred following the transition from glacial to interglacial periods (Tost et al., 2014). The explosive eruptive history of Ruapehu since ~27 ka has been documented for the tephrostratigraphic record preserved on the eastern

flank and ring plain of Ruapehu (Donoghue et al., 1995a). A series of Plinian eruptions occurred during the period from ~22 to 10 ka, while coeval but volumetrically minor pyroclastic flow deposits are also preserved on the eastern flank of the edifice (Donoghue et al., 1995a; Pardo et al., 2012). The past 2 kyr of volcanic activity at Ruapehu have been characterised by low-volume ($<0.05 \text{ km}^3$) but frequent (25–30 yr periodicity) phreatomagmatic eruptions through Crater Lake (Donoghue et al., 1997), with additional phreatic eruptions as often as annually. The lake drains into the Whangaehu River valley, which is the principal modern lahar drainage pathway (Cronin et al., 1997).

Past glaciation of Ruapehu is evident from the deep U-shaped valleys that indent the flanks of the edifice as well as the presence of large lateral moraines and striated lava flow surfaces (McArthur and Shepherd, 1990; Waight et al., 1999). The most recent period of major glaciation of the edifice occurred at ~31–17 ka, which coincides with the global Last Glacial Maximum, when the termini of valley glaciers were advanced greatly compared to modern ice extents (Fig. 1.3; Eaves, 2015). The impact of pre-historical glaciation of Ruapehu between phases of eruptive activity has been recognised as having generated major stratigraphic unconformities (Hackett and Houghton, 1989). The timing of emplacement of Mangawhero Formation lavas (60–15 ka) and glaciation during the last glacial cycle (71–15 ka; Lisiecki and Raymo, 2005) suggests that syn-eruptive interaction between lava and ice was also an important aspect of the edifice growth history (Spörli and Rowland, 2006). Glaciers have retreated rapidly in historical times (Heine, 1963), and only sparse accumulations of permanent ice are now present around the uppermost western, southern and eastern flanks, and over the broad ice-filled northern portion of the summit area (Fig. 1.3).

1.4.3. Petrology, composition and magma genesis of eruptive products

Edifice-forming lava flows from Ruapehu are most succinctly defined as complex lithic and crystal cargoes hosted within dacitic or rhyolitic melts (Price et al., 2012). The effusive products contain diverse mineral assemblages of plagioclase, orthopyroxene, clinopyroxene, olivine, and ubiquitous but volumetrically minor oxide phases (Graham and Hackett, 1987). Oscillatory and reverse zoning patterns are ubiquitous throughout the cargo of crystals, and evidence of reaction and resorption suggests a complex suite of processes operate within Ruapehu magma storage systems (Price et al., 2005). Rather

than being true phenocrysts that were grown within the host magma, most crystals instead represent antecrysts derived from previously cooled magmas or xenocrysts incorporated from disaggregated wall rocks (Davidson et al., 2007; Price et al., 2012). Lava groundmasses comprise felted microcrystalline aggregates of plagioclase, pyroxene and magnetite, with minor relative volumes of brown glass that have dacite to rhyolite bulk compositions (Price et al., 2012). Hornblende is extremely rare and where present is bordered by reaction coronas (Price et al., 2012).

Whole-rock compositions range from medium-K basaltic-andesites to high-K dacites, and one basalt flow has been sampled (Fig. 1.4; Cole, 1978; Price et al., 2012). Lava flow compositions have become progressively more evolved with time, as constrained by existing radiometric age data (Gamble et al., 2003; Price et al., 2012). However, the composition of the youngest Ruapehu lavas assigned to the Whakapapa Formation and historic eruptive products apparently also define a wide compositional range equivalent to that defined by all older eruptive products (Gamble et al., 1999).

Figure 1.4. Compositional data for Ruapehu volcanic rocks. (a) SiO₂ vs. K₂O diagram for Ruapehu lavas. Data are grouped into fields relating to edifice-forming formations; abbreviations are the same as in Fig. 1.3. (b) ¹⁴³Nd/¹⁴⁴Nd vs. ⁸⁷Sr/⁸⁶Sr diagram for lava flows from Ruapehu volcano. Both figures are modified from Price et al. (2012).

The broad major and trace element compositional trends are reflected in isotopic data. Basaltic-andesites of the Te Herenga Formation display relatively low ⁸⁷Sr/⁸⁶Sr values at high ¹⁴³Nd/¹⁴⁴Nd compared to the wide range toward elevated ⁸⁷Sr/⁸⁶Sr values at relatively low ¹⁴³Nd/¹⁴⁴Nd for post-Te Herenga Formation lava flows that indicate assimilation of continental crust (Figure 1.4; Price et al., 2005, 2012). Compositional data for Te Herenga Formation eruptive products suggest that their derivative magmas were minimally contaminated by continental crust in contrast to the elevated levels of intracrustal

processing inferred for post-160 ka magmas (Price et al., 2012). Superimposed on the broad long-term compositional trends are non-systematic geochemical variations detailed for eruptive products sampled at the scale of an intra-formation lava flow sequence (1–10 kyr) or historic eruptive phase (~50 years; Waight et al., 1999; Gamble et al., 2003; Price et al., 2012; Kilgour et al., 2013). The short-term compositional variability indicates that magmas are tapped from a complex plumbing system, which is invoked to represent a plexus of dispersed reservoirs through which magmas pass at varying timescales and follow unique fractionation and mixing histories (Gamble et al., 1999; Nakagawa et al., 2002).

1.5. SUMMARY

From initial accumulation and differentiation to the eventual emplacement and cooling of the derivative lava flows on the volcano's flanks (Fig. 1.5), the major processes in the lifetime of arc magmas are scrutinised and sequenced in a high-resolution stratigraphy for Ruapehu in this PhD thesis. The following chapters each deal with three major themes for current global volcanological research:

1. Glaciovolcanism: The morphology and fracture characteristics of effusive glaciovolcanic products have been defined for the Ruapehu edifice. This provides a detailed case study for lava-ice interaction processes at other glaciated composite volcanoes with comparable eruptive and glacial histories.

2. Geochronology: The $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer has been applied to a comprehensive sample suite of andesite-dacite lava flows in order to establish a high-resolution eruption history for Ruapehu. Ages for ice-bounded lava flows are used to constrain the timing and extent of former glaciers. The reliability of the dating technique has been proven for Holocene age andesite lavas in this study and has aided interpretation of the causes of sector collapse events.

3. Magma genesis: Whole-rock major and trace element geochemistry and micro-scale mineral and melt compositions for lava flows have been placed within the chronostratigraphic framework established in this study. Time-composition trends for Ruapehu lavas reveal the broad evolution of this productive magma system over the last ~200 kyr, and indicate modes of crustal magmatism.

Figure 1.5. Summary cartoon of the regions of lava flow emplacement and magma generation at Ruapehu that are the subject of investigation in this thesis. Numbers refer to the major themes outlined above.

CHAPTER 2

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2. LAVA-ICE INTERACTION ON A LARGE COMPOSITE VOLCANO: A CASE STUDY FROM RUAPEHU, NEW ZEALAND

ABSTRACT

Ice exerts a first-order control over the distribution and preservation of eruptive products on glaciated volcanoes. Defining the temporal and spatial distributions of ice-marginal lava flows provides valuable constraints on past glacial extents, and is crucial for understanding the eruptive histories of such settings. Ice-marginal lava flows are well-displayed on Ruapehu, a glaciated andesite-dacite composite cone in the southern Taupo Volcanic Zone, New Zealand. Flow morphology, fracture characteristics and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronological data indicate that lavas erupted between ~51 and 15 ka interacted with large valley glaciers on Ruapehu. Ice-marginal lava flows exhibit grossly overthickened margins adjacent to glaciated valleys, are intercalated with glacial deposits, display fine-scale fracture networks indicative of chilling against ice, and are commonly ridge-capping due to their exclusion from valleys by glaciers. New and existing $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages for ice-marginal lava flows indicate that glaciers descending to 1300 m above sea level were present on Ruapehu between ~51–41 ka and ~27–15 ka. Younger lava flows located within valleys are characterised by blocky flow morphologies and fracture networks indicative of only localised and minor interaction with ice and/or snow, mainly in their upper reaches at elevations of ~2600–2400 m. An $^{40}\text{Ar}/^{39}\text{Ar}$ eruption age of 9 ± 3 ka (2σ error) determined for a valley-filling flow on the northern flank of Ruapehu indicates that glaciers had retreated to near-historical extents by the time of emplacement for this lava flow. The applicability of $^{40}\text{Ar}/^{39}\text{Ar}$ dating to ice-marginal flows on glaciated andesite-dacite composite volcanoes makes this technique an additional proxy for paleoclimate reconstructions.

2.1. INTRODUCTION

Interactions between volcanism and glaciation represent an important part of the eruptive histories of many volcanoes globally. The elevations reached by composite volcanoes means that snow and ice accumulation can be significant, even in equatorial regions at the present day (Major and Newhall, 1989; Cullen et al., 2006), and were important aspects of volcano histories during past glacial periods. Many styles of volcanic activity are influenced strongly by interactions between molten rock and ice/water, whether in the form of magma-water interactions in explosive volcanism (e.g. Houghton et al., 1999) or in controlling the morphology and distribution of effusive products (Lescinsky and Fink, 2000). Observations from historical eruptions and analogue experiments have indicated the ability of ice to impound and deflect lava flows (Edwards et al., 2013). As a result, volcanism in the presence of ice (i.e. glaciovolcanism; cf. Kelman et al., 2002) produces distinct lava morphologies, which can be recognised in pre-historic volcanic products and used to infer the past extent and thickness of ice (e.g. Lescinsky and Fink, 2000; Smellie, 2008).

Eruptive histories for composite volcanoes with glacial histories need to acknowledge the impact that valley glaciers and ice caps have on the spatial and stratigraphic position of lava flows (e.g. Stevenson et al., 2006). Understanding the glaciovolcanic evolution of a volcano provides information on the spatial and temporal relationships between volcanism and glaciation (Kelman et al., 2002). This leads to three fundamental questions: (1) can glaciovolcanic research aid paleoclimate reconstructions?; (2) are there feedback mechanisms between deglaciation and volcanism?; and (3) what are the hazards associated with the disruption of snow/ice during volcanic eruptions? Here the first of these questions is investigated through a case study of lava-ice interaction on a large, mid-latitude, glaciated composite volcano.

A detailed study of the morphologies and fracture characteristics is presented for lava flows erupted during the last 60 kyr at Ruapehu, New Zealand. The observations provide new insights into flow emplacement environments and fracture mechanisms during effusive eruptions on ice-clad volcanoes. In combination with geochemical and geochronological data, the mapped distribution of ice-marginal flows provides valuable constraints on past glacial extents in central New Zealand.

2.2. GEOLOGICAL SETTING AND GLACIAL HISTORY OF RUAPEHU

Ruapehu is situated within the Ruapehu graben at the southern termination of the Taupo Volcanic Zone (TVZ) in the central North Island, New Zealand (Fig. 2.1; Villamor and Berryman, 2006a). The TVZ is a region of high heat flow, extension and volcanism associated with westward subduction of the Pacific plate beneath the Australian plate along the Hikurangi Trench (Fig. 1; Cole and Lewis, 1981). Ruapehu (2797 m) is New Zealand's largest active andesite volcano with a $\sim 150 \text{ km}^3$ edifice surrounded by a volcanoclastic ring plain of similar volume (Hackett and Houghton, 1989). The volcano presently hosts several small ($< 1 \text{ km}^2$) summit glaciers and is seasonally covered (May to November) with snow down to elevations of $\sim 1500 \text{ m}$ above sea level (a.s.l.).

The edifice has been constructed over the last $\sim 250 \text{ kyr}$ by episodes of voluminous lava effusion punctuated by periods of erosion, sector collapse, and lower intensity volcanic activity (Hackett and Houghton 1989). Edifice-forming deposits consist primarily of blocky lava flows and autobreccias with few dikes and minor pyroclastic fall and laharcic deposits (Hackett and Houghton 1989). Effusive eruption of low-K basaltic andesite from $\sim 250\text{--}60 \text{ ka}$ constructed the oldest exposed parts of the Ruapehu edifice, located on the northern and south-eastern flanks (Gamble et al., 2003; Fig. 2.1). Effusive eruption of basaltic-andesite to dacite with accompanying explosive activity has predominated since 60 ka and has built the majority of the modern edifice-forming flanks (Pardo et al., 2012; Price et al., 2012).

Edifice growth since 60 ka has coincided with marine isotope stages (MIS) 3 and 2, when global terrestrial ice cover was relatively extensive (Lisiecki and Raymo, 2005). In New Zealand, large glaciers were hosted along the Southern Alps throughout the Quaternary, although on North Island apparently only the Tongariro and Ruapehu composite cones and south-facing basins of the Tararua Ranges were glaciated (Brook, 2009). Ruapehu edifice displays diagnostic evidence for past glacial activity, including large U-shaped valleys and glacial deposits (till) that cover large areas on all flanks of the volcano (Fig. 2.1). Based on geomorphological mapping of moraines, McArthur and Shepherd (1990) reconstructed a $\sim 140 \text{ km}^2$ ice mass on Ruapehu consisting of a cap that covered the summit and fed valley glaciers that descended to $\sim 1200 \text{ m a.s.l.}$ Two advances of valley glaciers between ~ 60 and 14 ka have been inferred from regional paleoclimate climate studies and geomorphological mapping (McArthur and Shepherd, 1990).

Figure 2.1. Simplified geologic map of Ruapehu. Lava flows are defined as pre-60 ka (ol), syn-glacial (60–15 ka; sgl), and post-glacial (< 14 ka; pgl). Glacial deposits are shown in green (older till and outwash; ot). Young till (t) is delineated only for the north-western flank for the purposes of a later figure (see Fig. 12). Older (orp) and younger (yrp) volcanoclastic deposits are categorised for the ringplain. Older lavas of Hauhungatahi volcano (Hv) are situated on exposed Neogene sediments (Ns). Locations of the Taupo Volcanic Zone (TVZ), Taranaki Ranges, Southern Alps, and Taranaki volcano are shown in the inset figure. The Hikurangi Trough marks the seafloor expression of westward subduction of the Pacific plate (PAC) beneath the Australian plate (AUS). Extent of the geologic map of Ruapehu is shown by the red box.

One study to date has reported evidence for interaction between lava and ice on southeast Ruapehu during this time period (Spörli and Rowland, 2006). Throughout New Zealand,

terrestrial evidence from fluvial terraces, loess and paleosol sequences, and paleovegetation patterns indicates that the climate of North Island ameliorated rapidly from ~18–16 ka (Newnham et al., 2003). This inference is consistent with the wholesale retreat of South Island glaciers between ~17.8 and 15.7 ka in response to climatic warming that accounted for ~86% of the net temperature rise between ~20 ka and the early Holocene (Putnam et al., 2013a). A pollen sequence from a core located ~150 km northeast of Ruapehu indicates that the trend of warming was interrupted by a cold climate reversal from 13.6–12.6 ka, but later resumed from 12 ka into the Holocene (Hajdas et al., 2006).

2.3. METHODS

2.3.1. Fieldwork

Fieldwork campaigns from 2012 to 2014 were dedicated to delineating and describing effusive glaciovolcanic features over the entire Ruapehu edifice, as part of a wider study into the evolution of the volcanoes of Tongariro National Park led by GNS Science (Townsend et al., 2016). Initial sites of interest, particularly steep ridges and bluffs, were identified from digital terrain models (DTMs) and aerial photographs, and subsequently reconnoitred. Lava flow morphology, internal structure, and lithology were described at exposures. Fracture types were classified for lava flows that displayed fracture patterns indicative of cooling due to contact with ice, snow or water (see section 2.4.1). Ice-marginal flow margins were mapped with ArcGIS using field evidence and inferences from DTMs based on gross flow morphology that indicated likely interaction between lava and ice. Detailed sections were measured at these localities and fracture plane orientations, and striation spacing and height were recorded. Locations of observed fracture types and their measurements are available in Appendices A1 and A2.

2.3.2. Geochemistry

Samples were collected for geochemical analysis from relevant lava flows where their geomorphology was important in constraining the geographical extent of lava-ice interaction. Whole-rock samples were cut using a diamond saw to remove weathered

parts, crushed using a Rocklabs Boyd crusher, and powdered using a Rocklabs agate or tungsten-carbide ring mill at Victoria University of Wellington. Powders were made into fused lithium metaborate glass discs and analysed for major oxide concentrations by X-Ray Fluorescence (XRF) following the methods of Ramsey et al., (1995). Disc-making and analyses were carried out at the Open University, Milton Keynes, U.K. Internal standards WS-E (Whin Sill dolerite) and OU-3 (Nanhoron microgranite) were analysed to monitor precision and accuracy of the results. Major oxide analyses were accurate to within 2.0 relative % of the recommended values for the internal standards. Analytical precision (2σ) was 1.5 relative % or better for all elements with concentrations >0.3 wt. %.

2.3.3. Geochronology

Radiometric $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages for three lava flows are presented here in order to provide temporal constraints for ice-marginal and post-glacial flows. The ages are a subset of the data presented in Chapter 3. Analysis of crystalline groundmass separates from andesite lava flows has been shown to produce the most reliable results (Hildreth and Lanphere, 1994), and such textures were observed in the interior of thick lava flows at Ruapehu (Gamble et al., 2003). Sufficient K concentrations for analysis require minimum groundmass plagioclase crystal widths of $10\text{ }\mu\text{m}$ and a groundmass glass abundance of $<5\%$. Samples selected for dating were crushed using a Rocklabs Boyd crusher and sieved to retain the $250\text{--}350\text{ }\mu\text{m}$ size fraction. An LB-1 Barrier type Frantz was used to remove phenocrysts and xenoliths from grains of groundmass in the crushed rock fraction via magnetic separation. To remove altered and adhered material, groundmass separates were washed in water for up to 20 hours in an ultrasonic bath, then washed in acetone to remove any hydrocarbons from grain surfaces, and then rinsed in deionized water. Finally, any remaining grains with adhering phenocrysts, xenoliths or areas of glass were removed by hand-picking. Samples were irradiated at the USGS-TRIGA reactor in Denver, Colorado and isotopic analyses were undertaken at the US Geological Survey Geochronology Laboratory in Menlo Park, California following the methods of Calvert et al., (2005).

2.4. EVIDENCE FOR LAVA-ICE INTERACION AT RUAPEHU

2.4.1. Lava flow fracture types

Upon contact with a glacier, lava flows conductively transfer heat to the ice, which results in the production of meltwater (Wilson and Head, 2007). As the lava rapidly cools against the ice and water to form glass, the rate of heat transfer slows, the glacier resists further melting and the flow becomes confined against its margin (Lescinsky and Sisson, 1998). Fractures form when the tensile strength of a lava flow is exceeded due to thermal contraction (Lore et al., 2000), and propagate perpendicular to the maximum thermal gradient, i.e. away from the cooling surface (DeGraff and Aydin, 1987). Intermittent propagation produces ‘striations’ on the fracture plane, which represent the fracture tip stalling in plastic lava, before advancing once the tensile strength is exceeded due to further cooling. Wider spacing between striations and greater striation height (i.e. protrusion from the fracture plane) indicates slower fracture propagation (Lore et al., 2000). In this way, striation spacing and height can be used in ancient lavas to infer the direction and rate of cooling. The anatomies of five fracture types generated by interaction between lava and ice/meltwater are described below and summarised in Table 2.1. These types were arrived at by combining previous studies with our new observations from lava flows at Ruapehu. Existing type names are used for continuity with previous work and the term ‘fracture’ is employed to describe related features and processes.

2.4.1.1. Column-forming joints

The most widely-studied of the fractures produced by lava-ice interaction are column-forming joints. Intersecting fracture planes that form arrays of horizontally-oriented columns are interpreted as explicit evidence for contact between lava and ice, because the lateral margin of a glacier presents a vertical cooling surface (e.g. Lescinsky and Sisson, 1998). Column-forming joints on lava flow margins at Ruapehu intersect to form 4, 5, or 6-sided polygons in cross-section with diameters of 10–20 cm (Fig. 2.2). Striations (also known as “chisel marks”) on the column faces (i.e. fracture planes) are invariably oriented perpendicular to the column axis, spaced at distances <5 cm and protrude above the fracture planes by up to 5 mm. Where measurable, striations indicate that fractures propagated inward from the margins of lava flows. Greatest column-forming joint lengths

extend continuously for up to 30 m and have orientations that are predominantly near-vertical, but vary in the form of short wavelength (<1 m) undulations of amplitude <2 cm, or longer wavelength (2–10 m) fanning patterns.

Figure 2.2. Fracture types indicative of interaction between lava and ice at Ruapehu. Refer to text and Table 2.1 for full descriptions of fracture characteristics.

2.4.1.2. Pseudopillow fractures

The term ‘pseudopillow fracture’ is used to describe a pattern in lavas that is produced by two distinct generations of fracturing (Watanabe and Katsui, 1976; Forbes et al., 2012). Pseudopillow fractures consist of curvilinear ‘master’ fractures spaced at distances of >50 cm, and ‘subsidiary’ fractures oriented perpendicular to the master fracture and spaced at distances of <50 cm (Fig. 2.2).

Table 2.1. Summary of fracture type characteristics and their proposed genesis.

Fracture type	Components	Dimensions	Occurrence	Genesis
Column-forming joints	Fracture planes intersect to form 4–6-sided polygons (i.e. columns). Striations mark fracture planes at orientations perpendicular to the column axis	Spacing (column diameter): 10–30 cm, Average length: ~1 m, max length 30 m. Striations: <5 cm spacing with mm-scale relief	Glassy margins of lava flows	Cooling-induced fracture propagation from lava-ice interface, or from basal/upper contact with till/atmosphere
Pseudopillow fracture	Sub-vertical, curvilinear master fractures; sub-horizontal, column-forming subsidiary fractures that propagate from the master fracture	Master fractures: Spacing <5 m; Length <20 m. Subsidiary fractures: Spacing <20 cm; Length: <2 m	Glassy margins of lava flows	Cooling-contraction of flow with primary vertical fracture propagation, followed by secondary fracturing perpendicular to master fracture plane due to ingress of coolant (meltwater/steam)
Kubbaberg joints	Curvilinear fractures intersect chaotically in hackly pattern	Length <20 cm Spacing <20 cm Striations: <5 cm spacing with mm-scale relief	Glassy upper, lateral and basal margins of lava flows; prominent in sub-glacial flows	Rapid quenching and fracturing of lava in contact with ice and/or meltwater
Crease structure	Pair of opposing fracture planes separated by a central valley. Each fracture plane is marked by striations aligned sub-parallel to central valley orientation	Spacing: <50 cm Length: <200 cm Apical angle: <30° Striations: < 5 cm spacing with <1 cm relief	Glassy lateral margins of lava flows; common in basal zones of flows	Cooling-induced contraction of lava and intermittent fracture propagation due to contact with ice/water/steam
Platy joints	Curvilinear fractures intersect at low angles to form overlapping platy joints; microcrystalline groundmass	Spacing: <10 cm Length: <100 cm	Interior zones of lava flows; exposed via erosion of outer glassy margins	Endogenous flow and shearing inward of, and parallel to, lava-ice margin; heat retained behind the outer quenched margin of the flow

Subsidiary fractures are interpreted to form due to the ingress of water or steam through the initial master fracture, which induces cooling and contraction of the host lava (e.g. Tucker and Scott, 2009). Therefore, the transformation of ice to meltwater is a necessary step in generating this fracture type. Pseudopillow fractures in lava flows on Ruapehu consist of <20 m-long sub-vertical and curvi-planar master fractures. Master fractures are arranged sub-parallel to each other and spaced at distances of 0.5–5 m where they are present as networks along the margins of lava flows. Master fracture planes are occasionally corrugated by sub-horizontal striations, which indicate that fracture propagation was sub-vertical, although directions could not be unambiguously determined due to erosion of the fine-scale features. Subsidiary fractures are oriented approximately perpendicular to master fractures, and intersect the master fracture plane to form polygons with diameters <10 cm adjacent to the master fracture and >20 cm at distances >1 m from the master fracture (Fig. 2.2).

2.4.1.3. Kubbaberg joints

Rapid quenching of a lava flow in the presence of water produces an irregular network of arcuate intersecting fractures, called ‘kubbaberg’ joints. Kubbaberg is an Icelandic term meaning cube-jointed lava or entablature (e.g. Sæmundsson, 1970; Williams, 1995; Forbes et al., 2014). Kubbaberg jointing occurs exclusively in very glassy zones within the lateral, upper or basal margins of lava flows on Ruapehu. Fractures are spaced <15 cm apart and cross-cut each other chaotically (Fig. 2.2). Striations on kubbaberg joint planes are spaced at <5 cm and are often curved.

2.4.1.4. Crease structures

Crease structures are fractures that form as a result of lateral spreading and thermal contraction of the outer surface of a lava dome or flow (Anderson and Fink, 1992). Tensile stress is concentrated perpendicular to the axis of spreading, which results in tearing of the outer surface of the lava. Ductile lava beneath the crust is then exposed to the ambient atmospheric temperature, and intermittent fracture propagation ensues. Fine-scale crease structures have not previously been recognised as resulting from lava-ice interaction, but occur in close association with column-forming joints, pseudopillow

fractures and kubbaberg joints in the glassy marginal zones of lava flows on Ruapehu. Crease structures in Ruapehu lava flows are fractures that are defined by opposing planes spaced <20 cm apart at the flow margin, but taper towards each other to intersect at an apical angle of $<30^\circ$ in a central valley inward of the flow's margin (Figs. 2.2, 2.3). Thus, crease structures form open cavities at their open edges on lava flow margins. Central valley directions show no preferential orientation, i.e. can be any angle from vertical to horizontal, but are always sub-parallel to the flow margin.

Figure 2.3. Representative images of crease structures in ice-marginal lava flows at Ruapehu. Refer to Figure 2.4 for locations of photographed sites. (a) Lobe of glassy, ice-bounded andesite on western Ruapehu, pervasively cut by closely spaced crease structures inferred to have formed at the original lava-ice contact. (b) Close-up of crease structure located in box outlined in (a). Wall offsets (wo) cut across striations (st), which strike parallel to the central valley (v) and are spaced at ~ 1 cm. (c) View into a horizontal crease structure shows a ruptured lava bridge consisting of matching wall offsets (wo) on opposing faces of an opened fracture plane. Divisions on pencil are 1 cm. (d) Sheared glassy and spinose lava in the central valley of a crease structure.

Individual crease structures extend along flow margins for 10–200 cm laterally and 5–50 cm into the lava (Fig. 2.3). Crease structures, spaced at distances of 2–50 cm and aligned sub-parallel to each other, occur in groups that pervasively fracture flows over areas <5 m² (Fig. 2.3a). Each fracture plane is marked by striations that are aligned sub-parallel to

the central valley and are spaced at distances of 1–5 cm with individual reliefs of <1 cm (Figs. 2.2, 2.3b). Each striation has a correspondent on the opposite wall of the fracture, such that the planes are approximately symmetrical about the axis of the central valley. Thin bridges of lava (<1 cm-thick, <5 cm-wide) with sigmoidal morphology often connect the opposing planes. These lava bridges were observed as intact, incipiently broken, or completely ruptured (Fig. 2.3c). Where the broken bridges merge with the fracture plane, they form <1 cm-high wall offsets that trend perpendicular to, and cut across single or several, striations on each plane (Figs. 2.2, 2.3b). Striations form as the crease structure intermittently propagates into the flow and the opposing fracture planes spread apart about the central valley and form a cavity (Fig. 2.2). Ruptured lava bridges represent the lateral propagation of the crease structure (Fig. 2.2). Lava within the central valley of crease structures is very glassy and often finely spinose (Fig. 2.3d), which indicates that ductile shearing of viscoelastic lava occurred during fracture propagation.

2.4.1.5. Platy joints

Platy joints are common in subaerial lavas of intermediate-silicic composition (e.g. Bonnicksen and Kauffman, 1987), but have also been recognised for lava flows that have interacted with ice (Lescinsky and Fink, 2000). The exposed interior zones of thick (10–100 m) lava flows at Ruapehu are characterised by curvilinear fractures that intersect at low angles to form overlapping plates with lengths of ~1 m and thicknesses of <10 cm (Fig. 2.2). Platy jointed zones of flows are composed of lava with groundmass textures comprising microcrystalline plagioclase and pyroxene (5–30 μm microlite crystal width) and minimal glass (<10 volume %). Platy joints are dominantly sub-horizontal in the lower 5–30 m of thick flows, although orientations are locally variable and can change by 90° over lengths of 2 m. The lateral margins of lavas commonly expose vertical plates, whereas the front noses of flows are characterised by platy joints arranged in patterns that curve in a concave pattern from the top (sub-vertical plates) to the base (sub-horizontal plates) of the flow. Approximately vertical fractures (>5 m-long with >1 m-spacing) cut across platy joints.

2.4.2. Lava flow morphology

Ruapehu lava flows studied here are categorised into four types based on their distribution relative to glaciated valleys, dimensions, and fracture types. Their mapped distributions are shown in Figure 2.4.

Figure 2.4. Hill-shaded DTM of Ruapehu showing distribution of ice-marginal lava flow types and moraine ridges. Locations of geochemistry and geochronology samples with eruption age ranges are shown, as well as locations of photographed sites in other figures.

2.4.2.1. Ice-bounded flows

Lava flows perched on the tops or sides of ridges and heads of glaciated valleys are located adjacent to all major valleys of the volcano and are especially prominent on the eastern, western and southern flanks between 1300–2100 m a.s.l. (Fig. 2.4). Flows are thinnest on the crests of ridges and thicken towards the adjacent valleys often as discrete

knuckles of lava, but terminate abruptly to form cliffs 5–50 m-high (Fig. 2.5). Lava flows are intercalated with moraines, which together form valley sides up to 200 m-high. Contacts below the lava with moraines are commonly concealed by autoclastic talus derived from the over-steepened flows (Fig. 2.6a), and above by degradation of overlying moraine material.

Figure 2.5. Example of ice-bounded lava flows from eastern Ruapehu. Note the fine-scale jointing on the vertical face of this ~30 m-thick flow (below the NZ Alpine Club Hut; circled in red). Note also the thin ridge-top flow (near skyline), that thickens downslope and terminates in a small, perched knuckle. Refer to Figure 2.4 for location of flow.

Where observed, lava basal contacts are planar and often marked by overhangs and cavities. Basal contacts are characterised by glassy groundmass textures and very fine kubbaberg or column-forming joints (<5 cm spacing). Where glacial till is exposed at the basal contact of a flow, two common features are observed: (1) quenched lobes and clasts

of lava identical to the overlying flow are present in the adjacent till; (2) gradational contacts between lava with kubbaberg or column-forming joints and till (containing clasts of lava from the adjacent flow) are present (Fig. 2.6b). The observations indicate that the till was deposited prior to (or coeval with) emplacement of the flow. Ridge-top, valley axis-parallel lava flows that display overthickened margins, relationships with till that are indicative of interaction with ice, and lava-ice interaction fracture types (see below) are classified here as ice-bounded flows (cf. Lescinsky and Sisson 1998).

Figure 2.6. Fracture characteristics of ice-bounded lava flows at Ruapehu. Locations of photographed sites are shown in Figure 2.4. (a) Column-forming joints on the margin of an ice-bounded flow on western Ruapehu range in orientation from horizontal (lower margins) to vertical (top of flow). (b) Gradational contact (dashed line) between ice-bounded flow with column-forming joints (co; right) and sheared till containing clasts of the adjacent lava (left). (c) Range of fracture types observed in ice-bounded lava flow on south-western Ruapehu: pseudopillow fractures (pp); platy joints (pl); column-forming joints (co) and crease structures (cr). Glassy zones (gl) are also present throughout the flow. Person (seated) for scale. (d) Side view of ice-bounded flow on eastern Ruapehu. Platy joints (pl) of variable orientation exposed throughout the flow. Note the capping till and talus apron that typically obscure flow contact relationships.

Column-forming joints define the quenched margins of ice-bounded flows and are oriented horizontally on the sides and vertically on the tops of flows (Fig. 2.6a). Small volume ($<10 \text{ m}^3$) lobes of lava perched on valley walls that can be traced upward to major

ridge-capping lava flows are composed of fanning arrays of sub-vertical column-forming joints. Column-forming joints occur in close association with pseudopillow fractures, which are arranged in sets of sub-parallel master fractures spaced <5 m apart and oriented sub-vertical (Fig. 2.6c).

Kubbaberg joints occur at the basal contact or top surface of ice-bounded flows, and are sometimes preserved along the lateral margins of flows (Fig. 2.6c). Fine-scale crease structures (<20 cm-long) are located on glassy lobes of ice-bounded flows, where they are commonly oriented sub-vertical and spaced <10 cm apart such that they pervasively fracture glassy zones of <2 m² (Fig. 2.3a). Crease structures with greater lengths (>1 m), wider spacing (>20 cm) and dominantly sub-horizontal orientations are present in the lower 10 m of thick ice-bounded flows (Fig. 2.6c).

Flow interiors displaying ubiquitous platy joints have been exposed for ice-bounded flows that are missing their outermost quenched carapaces, which have collapsed or been eroded. The lower 5–10 m of ice-bounded flows display regularly arranged horizontal plates ~ 100 cm-long and <10 cm-thick. Middle to upper levels of ice-bounded flows display concentric platy jointing that is sub-horizontal at the top of the flow and sub-vertical on the margins of the flow (Fig. 2.6d).

Colonnades are here represented by ~ 35 m-high outcrops of lava exposed along ice-bounded flow margins that behead or divert valley drainages. Basal contacts of colonnades are composed of glassy lava fractured by closely spaced kubbaberg or column-forming joints and are commonly marked by overhangs (Fig. 2.7). Above this lowermost zone of colonnades, lava is fractured by broad, approximately vertical, column-forming joints at >50 cm spacing that extend for 1–3 m into the flow. The upper 20–30 m of colonnade outcrops expose fine-scale (10–20 cm diameter) column-forming joints in association with pseudopillow fractures and kubbaberg joints. Column-forming joints are dominantly oriented sub-vertically and display wavy undulations with amplitudes of 1–10 cm over wavelengths of 20–210 cm. Arrays of columns that fan from vertical to horizontal over distances of <10 m are common at colonnade outcrops (Fig. 2.7).

Figure 2.7. Glassy colonnade of an ice-bounded flow overlying till on south-western Ruapehu. Location of flow is shown in Figure 2.4.

2.4.2.2. Ice-dammed flows

Lavas forming cliffs of heights >50 m that are located within glaciated valleys at Ruapehu are classified here as ice-dammed flows. Flows have flat tops and thicken downslope toward their frontal terminations, which form near-vertical cliffs up to 100 m-high and 600 m-wide oriented perpendicular to the axes of the valleys below them (Fig. 2.8). Fans of autoclastic debris that formed through gravitational collapse and erosion of the over-steepened terminal bluff fringe the flow fronts and typically obscure their basal contacts such that the true thicknesses of flows are unknown. Ice-dammed flows at Ruapehu are located on the north-eastern, north-western, and western flanks between 1560–1880 m a.s.l. (Fig. 2.4).

Figure 2.8. Ice-dammed flow on north-western Ruapehu. Location of photographed site is shown in Figure 2.4. Height of front margin is ~80 m. Full compositional data for flows with SiO₂ contents displayed are shown in Table 2.2.

Glassy and massive lava with associated autobreccia comprise the upper 10 m of flows (Fig. 9a, b). The lower 20–40 m of flows are characterised by <15 cm-thick and 30–100 cm-long sub-horizontal plates bounded by regularly spaced and oriented fractures (Fig. 2.9a, b). Vertical fractures spaced at distances of 2–5 m and continuous over lengths of 40–60 m extend through platy and glassy zones in ice-dammed flows (Fig. 2.9a); platy joints are cut by the vertical fractures. Fine-scale, horizontal column-forming joints are present commonly on the lateral margins of ice-dammed flows and, rarely, on the front in close association with pseudopillow fractures, kubbaberg joints and crease structures (Figs. 2.9c, d). The different fracture networks often merge without distinguishable boundaries, resulting in compound arrays and geometries of the joints.

Figure 2.9. Fracture characteristics of ice-dammed lava flows at Ruapehu. Locations of photographed sites are shown in Figure 2.4. (a) Glassy (gl) and platy jointed (pl) lava exposed in terminal face of ice-dammed flow on north-eastern Ruapehu. Flow thickness is ~50 m. (b) Front margin of ice-dammed flow on western Ruapehu exhibits horizontal platy joints (pl) in the lower ~20 m of the flow, and glassy lava (gl) in the upper zones of the flow. Person for scale circled in red. (c) Left lateral margin of ice-dammed flow on western Ruapehu exhibits a range of fracture types: column-forming joints (co); pseudopillow fractures (pp); glassy lava (gl); kubbaberg joints (kb). Person for scale circled in red. (d) Transition(dashed line) between sub-vertical pseudopillow fractures (pp) and horizontal column-forming joints (co).

Pseudopillow fractures display approximately vertical, curvilinear master fractures with horizontal striations that formed due to intermittent fracture propagation in a vertical direction. Pseudopillow subsidiary fractures intersect each other to form sub-horizontally oriented columns. Crease structures are most common on the lateral margins of ice-dammed flows and display sub-vertical central valley orientations.

2.4.2.3. Sub-glacial flows

Valley-floor lava flows with sinuous morphological forms and height-to-width ratios $>1:1$ are observed at three locations at Ruapehu (Figs. 2.4, 2.10a). The flows are located on

gentle slope gradients on the south-western flank at 1620 m and south-eastern flank at 1750 m. The lavas exhibit glassy groundmass textures and display fine-scale kubbaberg joints spaced at distances of <20 cm in the upper levels of the flows, indicative of rapid cooling in the presence of water (Figs. 2.10c, d).

Figure 2.10. Sub-glacial lava flows on Ruapehu. (a) Sinuous, valley-floor flow on south-western Ruapehu exhibits kubbaberg joints (kb) and glassy lava (gl). It was probably emplaced within a meltwater channel beneath a glacier. Flow thickness is ~10 m. (b) Concentric platy joints (pl) on lateral margin of sub-glacial flow on south-western Ruapehu. Flow height is ~5m. (c and d) Lateral margin of a sub-glacial flow on south-western Ruapehu, exposing kubbaberg joints (kb) and a lower glassy zone (gl). Full compositional data for the lava flow are shown in Table 2.2. Refer to Figure 2.4 for location of photos.

Middle to lower zones have broad column-forming joints and conchoidal fractures spaced at distances of >1 m (Figs. 2.10c, d). Concentric platy joint orientations in the lavas replicate flow margin morphologies where the outer glassy carapace has been removed by erosion (Fig. 10b). There is no evidence to suggest that these flows were erupted from a vent source beneath ice (i.e. no hyaloclastite breccia or pillow lavas were observed). These flows are classified here as sub-glacial flows and are analogous to the ‘esker-type’ flows described by Lescinsky and Fink (2000), albeit on a smaller scale.

2.4.2.4. *Post-glacial flows*

Lava flows located within valleys on Ruapehu that have relatively little moraine cover and display minor or no glacial striae are classified as post-glacial flows (i.e. erupted since 14 ka during MIS 1, as defined by Lisiecki and Raymo, 2005). This inference is based on paleoclimate indicators elsewhere in central North Island that the LGM climatic conditions had ameliorated and large-scale retreat of glaciers had occurred by ~14 ka (e.g. Newnham et al., 2003). Post-glacial lavas have relatively low height-to-width ratios (<1:10) and mantle older ice-marginal flows on the upper slopes of the edifice, in association with autobreccias, welded spatter and pyroclastic flow deposits. Several of the flows are rootless and many are diverted away from glacial catchments on the upper flanks. Post-glacial flows form blocky flow fields that onlap older moraines and lavas on gentle slope gradients within valleys or at lower flank elevations (<1700 m a.s.l.; Fig. 2.11). Lavas display evidence for minor and localised interaction with glaciers or snow: column-forming joints and pseudopillow fractures are present only rarely on flow margins. Column-forming joints have the same dimensions as those in ice-marginal lavas, but are restricted to exposures within areas of <10 m². Pseudopillow fractures display relatively small master fracture lengths (<2 m) and close subsidiary fracture spacings (<10 cm). No post-glacial flows display gross overthickening or impoundment at their margins.

2.5. AGES AND COMPOSITIONS OF LAVA FLOWS

A subset of relevant eruption age and compositional data are presented for this study that are presented in full in Chapter 3. High-precision ⁴⁰Ar/³⁹Ar eruption ages were determined for an ice-dammed flow on the north-western flank (43 ± 2 ka; all errors reported as 2σ) and an ice-bounded flow on the south-western flank of Ruapehu (21 ± 3 ka; Table 2.2; Fig. 2.4). Based on its geomorphology and near-identical major element chemistry, a sub-glacial flow located 600 m to the west is inferred to have been erupted and emplaced coevally with the 21 ± 3 ka ice-bounded flow.

Figure 2.11. Post-glacial lava flows on north-western Ruapehu. These flows are typically <5 m-thick, drape over topography and have little or no till cover. Distance to skyline is ~1.5 km. Refer to Figure 2.4 for location of photo. Full compositional data for flows, with SiO₂ contents displayed, are shown in Table 2.2.

⁴⁰Ar/³⁹Ar eruption ages of 46 ± 5 ka and 21 ± 6 ka were determined by Gamble et al., (2003) for lava flows that are here identified as being ice-bounded (Table 2.2; Fig. 2.4). The crystalline interior of a post-glacial lava flow exposed in the valley floor on northern Ruapehu yielded an eruption age of 9 ± 3 ka. Post- glacial eruption ages are inferred for lava flow samples CC195, CC335 and CC447 due to their valley-floor locations. Ruapehu lava flows studied here display a 58.3–64.3 wt. % range in SiO₂ content (Table 2.2). Post-glacial lavas have compositions intermediate of this range, from approximately 58–60 wt. % SiO₂, whereas lavas that were erupted from ~51–41 ka generally have higher SiO₂ contents.

Table 2.2. $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages and major element geochemistry of dated lava flows.

Sample	CC313	CC415	CC364	CC408	CC135	CC335	CC195	CC447	CC279
Type	ice-dammed	ice-bounded	ice-bounded	ice-bounded	sub-glacial	post-glacial	post-glacial	post-glacial	post-glacial
Age $\pm 2\sigma$	43 $\pm$ 2 ka	46 $\pm$ 5 ka*	21 $\pm$ 6 ka [#]	21 $\pm$ 3 ka	21 $\pm$ 3 ka ⁺	<14 ka	<14 ka	<14 ka	9 $\pm$ 3 ka
SiO ₂	64.34	63.84	58.33	60.93	61.01	58.6	59.79	59.08	58.85
TiO ₂	0.57	0.75	0.7	0.78	0.79	0.73	0.73	0.66	0.75
Al ₂ O ₃	15.53	15.11	16.09	17.29	17.55	17.11	17.26	16.71	17.26
Fe ₂ O ₃	4.99	5.12	7.57	6.43	6.15	7.52	7.03	6.92	7.43
MnO	0.09	0.08	0.12	0.1	0.09	0.12	0.11	0.11	0.12
MgO	3.37	3.17	5.22	2.65	2.46	3.96	3.27	4.51	3.82
CaO	4.72	4.82	7.35	6.03	6.18	7.17	6.51	6.92	6.89
Na ₂ O	3.76	3.35	3	3.75	3.85	3.22	3.39	3.38	3.25
K ₂ O	2.42	3.04	1.54	1.97	1.88	1.57	1.73	1.63	1.63
P ₂ O ₅	0.15	0.18	0.14	0.17	0.16	0.14	0.14	0.14	0.14
LOI	0.06	0.54	-0.07	-0.1	-0.12	-0.15	0.04	-0.06	-0.14

Eruption ages and uncertainties (2σ) are rounded to the nearest 1 kyr. Dated samples used here to provide ages for geochemistry samples from the same flow are: T5-11 (*) and X1/6 (#), which were analysed by Gamble et al., (2003); and CC408 (+), which was analysed in this study. Post-glacial ages are inferred for samples CC335 and CC195 from valley-floor lava flows. Compositions are values of weight % and are normalised to totals of 100. Loss on ignition (LOI) values are included.

2.6. DISCUSSION

2.6.1. Ice-marginal lava flow emplacement

The general model for ice-marginal effusive volcanism on composite volcanoes considers the emplacement of andesite-dacite lava onto ridges adjacent to the lateral margins of valley-filling glaciers on the flanks of a volcano following an eruption from the summit (Lescinsky and Sisson, 1998). Lava is excluded from the valley by the glacier mass. Steep-walled channels are formed at the margins of glaciers due to the production and drainage of meltwater resulting from thermal erosion of the ice (Wilson and Head, 2007). Confinement of lava within the channel between the glacier's margin and the adjacent ridge causes the flow to grow thicker as it fills the available space. Ice-marginal flows on Ruapehu display characteristics previously described for those from other locations (e.g. Lescinsky and Fink, 2000): ridge-top locations; over-thickened margins adjacent to glaciated valleys; intercalation with till; and fine-scale cooling fractures and glassy textures.

The morphology of lava flows at Ruapehu provides additional insight into processes of ice-marginal flow emplacement, and the northwest flank of the volcano provides an ideal case study of the different flow types and processes (Fig. 2.12). Lava knuckles (Fig. 2.5) and colonnades (Fig. 2.7) are common features of ice-bounded flows at Ruapehu. Knuckles form thick bluffs adjacent to valleys, and are the product of lava having ponded in discrete void spaces along the lava-ice interface (Fig. 2.12). Lava colonnades were formed where lava was impounded against thick walls of ice along the margins or heads of glacial valleys. The resultant flows solidified as >20 m-high cliffs of lava that preserve exceptional exposures of column-forming joints (Fig. 2.7).

Lava able to flow into small channels at the margin of the glaciers is now perched on the sides of valleys below ridge-bounded flows as low-volume lobes, or flowed through and cooled within meltwater channels in glaciers to form sub-glacial flows (Figs. 2.10, 2.12). One aspect of effusive glaciovulkanism that is still not well understood is the volume of lava that is erupted supra-glacially and presumably transported to the ringplain (Fig. 2.12). These deposits have not previously been recognised in the geological record at Ruapehu, or for that matter at other glaciated composite cones from New Zealand (e.g. Tongariro) or globally (e.g. Mt. Rainier), but may be able to be identified if their clasts display fracture types indicative of interaction with ice (Fig. 2.2).

Figure 2.12. Relationships between ice-marginal flows, glaciated valley and post-glacial flows. Aerial photograph (top panel; taken in August 2009) and 3-D view with draped geology (centre panel) of the north-western flank of Ruapehu (view direction shown in Fig. 4). For reference the summit peak is marked with a black triangle, Whakapapa Hut is circled in red, and the snowline is ~1700 m in this image. Lower left: block diagram at ~42 ka showing inferred mechanism of emplacement of ice-marginal flows and relationship to the glacier (gl), old till (ot), young till (t), old and young ringplain deposits (orp and yrp), and pre-60 ka lava (ol). Ice-bounded flow (b, on right) formed knuckles (k) and colonnades (c) with associated fracture types where lava was emplaced along the glaciers' margin. Kubbaberg joints (kb) formed where lava interacted with meltwater generated at the lava-ice interface. Ice-dammed flows (d) were impounded within the valley by the glacier mass. An unknown volume of supra-glacial lava (s) travelled through meltwater channels on top of the glacier and was transported to the ringplain. Lower right: present-day setting of the valley showing the distribution of ice-marginal flows and their talus (grey), post-glacial flows (young lava; pgl) and post-42 ka moraines (young till; t) and young volcanoclastic ringplain deposits (yvp).

Moreover, the comprehensive geochemical database for Ruapehu should make it possible to correlate these distal deposits to temporally-constrained eruptive formations on the edifice and incorporate them into eruption volume estimates. The brief geochemistry dataset presented here shows that ice-marginal flows range in composition from andesite to dacite, whereas post-glacial flows are exclusively andesites. The effusion of dacite between ~51 and 41 ka can be linked to the long-term magmatic evolution of Ruapehu (Price et al., 2012).

The different type, spacing and orientation of fractures reflect different emplacement environments, cooling rates and directions in lava flows, and they inform our understanding of flow emplacement processes at glaciated composite cones (Lodge and Lescinsky, 2009). Five distinct fracture types in lavas at Ruapehu that were produced via interaction with ice have been identified and described (Fig. 2.2). Compound arrays of column-forming joints, pseudopillow fractures and kubbaberg joints observed for ice-marginal flows (Figs. 2.6c, 2.9c) are interpreted to reflect the rapid quenching, and variable fracture propagation directions and rates within lava emplaced in the presence of ice and associated meltwater. Production, movement and removal of meltwater during and following emplacement of lava against glacial margins created variable cooling directions and consequent fracture propagation directions within flows. The presence of fanning polygonal column patterns in ice-bounded colonnade flows (Fig. 2.7) indicates that a complex arrangement of cooling directions existed between lava and ice-meltwater within a dynamic emplacement environment. The ingress of meltwater (and/or steam) through master fractures induced subsidiary fracture propagation in pseudopillow fractures (Lescinsky and Fink, 2000).

Heat loss to adjacent glaciers from the interior of ice-bounded flows was buffered by their quenched outer rinds (Wilson and Head, 2007). Microcrystalline groundmass textures with microlite lengths of $>5\ \mu\text{m}$ indicate that cooling rates for platy jointed zones were significantly slower than for glassy zones. In lava flows where the quenched margins have been eroded, the exposed platy joints are horizontal and regular at lower zones of the flow (Fig. 2.9b), and sub-vertical and concave at upper and marginal zones (Fig. 2.10b). The observed patterns indicate that platy joints formed parallel to (a) flow direction and (b) cooling surfaces (i.e. perpendicular to the direction of cooling and confinement; Fig. 2.2). Platy joints are interpreted as resulting from late-stage shearing of lava due to their flow-parallel orientation, position inwards of the lava flow margin and crystalline

groundmass textures (Lescinsky and Fink, 2000). The interiors of ice-marginal lava flows at Ruapehu underwent continued endogenous movement parallel to the outer carapace of the flow after they were impounded by glaciers and as they slowly cooled.

The presence of valley-filling ice of thickness ~50–150 m was required to impede the advance, generate the extraordinary thicknesses, and produce the chilled margins of ice-dammed lava flows (Fig. 2.12). The pervasive and contiguous fracture patterns in ice-dammed flows and lack of internal contacts (Figs. 2.9a, b) indicate that they were emplaced as large volume single flows and fractured throughout as cohesive bodies of cooling lava. A high effusion rate (combined with a suitable glacier-valley-ridge geometry) is the probable reason why these lava flows were able to thermally erode such a substantial amount of ice. The north-western ice-dammed flow is a dacite (Table 2.2), and the high viscosity of the lava may also have contributed to its impoundment. There is a notable similarity between Ruapehu ice-dammed flows and The Barrier, a ~200 m-high vertical face of an ice-marginal andesite flow resulting from glacial impoundment downslope of Mt. Price in Canada's Garibaldi Volcanic Arc (Fig. 20 in Hickson, 2000).

2.6.2. Origin of crease structures in ice-marginal flows

Fine-scale crease structures are present in the glassy lateral and basal margins of ice-dammed and ice-bounded lava flows on Ruapehu, and are closely associated with kubbaberg joints, column-forming joints and pseudopillow fractures (Fig. 2.6c). These observations are interpreted as evidence that crease structures can form as a result of interaction between lava and ice, a correlation made here for the first time. Prior to this study, the occurrence of crease structures was limited to subaerial lava flows and domes (e.g. Anderson and Fink, 1992). The key features on the fracture planes of crease structures in Ruapehu lavas are (1) striations, which represent the inward propagation of the fracture tip and central valley-normal opening of the fracture and (2) wall offsets, which represent the lateral propagation of the fracture trace parallel to the central valley (Figs. 2.2, 2.3). Crease structures reported here differ from those described for subaerial lavas (Anderson and Fink, 1992) in that they have significantly shorter central valley lengths, shorter flow margin-to-central valley lengths, and more closely-spaced striations. The finer scale of ice-marginal crease structures may be the result of a higher thermal gradient compared with atmospherically-cooled subaerial lavas. The morphology of

crease structures closely resembles that of spreading cracks in pillow lavas, which also consist of opposing faces that are marked by striations and are approximately symmetrical across a central valley (Goto and McPhie, 2012).

The origin of pillow lava spreading cracks and subaerial lava flow crease structures is evaluated herein to understand how crease structures were formed in ice-marginal flows at Ruapehu. Crease structures in subaerial lava flows form as a result of thermal contraction and lateral spreading of their upper skin, and are therefore located on the top surfaces of flows (Anderson and Fink, 1992). For pillow lavas, spreading cracks must overcome the pressure of the overlying water column in order to fracture. The continued supply of magma allows rupturing and spreading of the chilled outer crust of the pillow to occur (Goto and McPhie, 2012). In contrast to subaerial lava flows and submarine pillow lavas, crease structures in ice-marginal flows at Ruapehu are located at the lateral margins of overthickened lavas (Fig. 2.6c), indicating that they formed adjacent to a vertical and confining cooling surface. The force imposed by the overlying mass of lava had to be overcome in order to achieve fracture opening, particularly for horizontal crease structures. Steam produced from lava-ice interaction (e.g. Edwards et al., 2013) likely played a key role in opening the crease structures in these environments, if it was trapped at the lava-ice interface and/or if it was being generated faster than it could escape, through creating high pressure within the fractures and/or locally lowering the lava viscosity. Fracture expansion may also have been facilitated by bulging of flow margins and continued flow advancement or inflation as ice was melted and meltwater was drained to create void space at the glacier-lava interface. The identification of crease structures on the lateral margins of andesite-dacite lava flows may therefore also be useful to infer interaction between lava and ice at other volcanoes.

2.6.3. Implications for paleoclimate reconstructions

Glaciovolcanic deposits are useful paleoclimate proxy indicators that can be used to infer the former presence, extent, and thickness of terrestrial ice (e.g. Smellie, 2008). Evidence for the impoundment of lava flows by valley-filling glaciers at Ruapehu has been presented based on flow morphology and fracture characteristics. The boundaries of ice-marginal lava flows therefore represent former extents of glacial ice and provide valuable paleoclimatic information. The absolute temporal and spatial distributions of ice-marginal

flows determined in this study are compared with previous glacier reconstructions for Ruapehu. During the Last Glaciation (71–14 ka), advances of valley glaciers on Ruapehu are tentatively proposed to have occurred between 40–32 ka and 25.5–22.5 ka, based on geomorphological mapping and inferences of regional climate (McArthur and Shepherd 1990). Glaciers reached 1200 m a.s.l. with equilibration line altitudes (ELAs) of 1500 m a.s.l. during the earlier and greater of the two inferred advances (McArthur and Shepherd, 1990).

The advent of high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ age determination for young intermediate-composition volcanic rocks (e.g. Fierstein et al., 2011) is particularly applicable to ice-marginal lava flows at glaciated volcanoes. Glacial impoundment results in the slow cooling of overthickened lavas, which produces crystalline groundmass textures favourable for dating in flow interiors that are exposed via erosion of oversteepened, fractured flow margins. A limited $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology dataset is presented here for two purposes: (1) to identify that ice-marginal lava flows were erupted and emplaced during past glacial periods and (2) to provide some preliminary constraints on the timing of past glaciation at Ruapehu.

Figure 2.13. Graph of $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages (diamonds, with bars indicating 2σ uncertainties) for selected Ruapehu lava flows. Global $\delta^{18}\text{O}$ fluctuations and marine isotope stages (MIS; data from Lisiecki and Raymo, 2005) are plotted to indicate the coincidence of ice-marginal lava flow eruptions during former glacial periods (higher $\delta^{18}\text{O}$ values, MIS 3–2) and eruption of a valley-floor lava flow during the post-glacial period (lower $\delta^{18}\text{O}$ values, MIS 1).

The implications regarding paleoclimate reconstructions are elaborated on in Chapter 3 using the complete geochronologic dataset. New and existing $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages determined for ice-marginal lava flows provide absolute temporal constraints on past

glacial extents at Ruapehu: large valley-filling glaciers were present at 47 ± 4 ka, 46 ± 5 ka, 43 ± 2 ka, 21 ± 6 ka, and 21 ± 3 ka. Accounting for uncertainties, the range in older eruption ages (51–41 ka) falls within MIS 3 (Fig. 2.13). The range of younger eruption ages (27–15 ka) broadly overlaps timing of the latter glacial advance inferred to have occurred between 25.5–22.5 ka by McArthur and Shepherd (1990).

The location and extent of major ice-marginal flows on Ruapehu, and the thickness of ice required to impound each flow are plotted in Figure 2.14. Approximate glacier thicknesses were estimated by calculating the vertical distance from the top of the flows to the bottom of the adjacent valleys. These are approximate estimates given that valley floor elevations may have subsequently been raised via deposition, or lowered via erosion since the glaciers were present. Upper extents of lava-ice margins are minimum values because younger deposits have covered these flows on upper flank slopes.

Figure 2.14. Elevation of major ice-marginal lava flow extent versus location on Ruapehu. Each bar represents an ice-marginal flow and, therefore, the past position of the glacier against which the flow was emplaced. Thicknesses of glaciers that bounded and dammed lava flows are represented by bar widths (see scale in key for thickness values in metres). $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages are written next to bars for lava flows that have been dated.

Overall, the data indicate that a substantial ice mass consisting of flank glaciers ≥ 100 m-thick that descended to ~ 1300 m a.s.l. existed on Ruapehu during MIS 3 and 2. There is no discernible difference in ice extent between ~ 51 – 41 ka and ~ 27 – 15 ka inferred from the distribution of dated ice-marginal lava flows, however, the thickness of ice required to impound the younger flows was apparently less than that for older flows (Fig. 2.14). The results corroborate glacial evidence from South Island, New Zealand that there was only minor variation in the maximum extent of glaciers between MIS 3 and 2 (Putnam et al., 2013b).

Widespread glacial retreat occurred from ~ 18 ka in South Island, New Zealand (Putnam et al., 2013a), and contemporaneous climate amelioration is preserved in terrestrial records from North Island (Newnham et al., 2003). Post-glacial eruption ages for some lava flows at Ruapehu have been inferred from their valley-floor setting, on the basis that glaciers had largely retreated by ~ 14 ka. The $^{40}\text{Ar}/^{39}\text{Ar}$ eruption age of 9 ± 3 ka for a valley-floor lava flow reported here indicates that valleys dissecting the lower flanks of the Ruapehu cone were largely ice-free by the time of its emplacement.

Valley-floor distributions of lava flows are therefore useful and reliable indicators of post-glacial ages for Ruapehu lava flows. Minor interaction between post-glacial flows and ice or snow occurred, however, as reflected by the presence of column-forming joints and pseudopillow fractures in some post-glacial lavas. This interaction is not surprising, given the presence and extent of glaciers on Ruapehu during historical times (Heine 1963). Post-glacial lava flows were bounded and deflected by summit glaciers on the upper flank, but volumes of ice and snow bodies were probably not great enough to impound lavas or generate overthickened flows (Fig. 2.14).

2.7. CONCLUSIONS

Field studies have been combined with preliminary $^{40}\text{Ar}/^{39}\text{Ar}$ eruption age data to provide evidence for large-scale interaction between andesite-dacite lava flows and glaciers during effusive eruptions at Ruapehu from ~ 51 – 15 ka. Key findings are as follows:

- Ice-bounded and ice-dammed lava flows display grossly overthickened margins adjacent to or within glaciated valleys, are intercalated with till, and have lateral

margins that are pervasively fractured by column-forming joints, pseudopillow fractures, crease structures and kubbaberg joints.

- These characteristics can be accounted for by impoundment and chilling of lava flows that were emplaced against large flank glaciers. Sinuous and valley-bottom flows were emplaced sub-glacially within channels at the margins and bases of glaciers where protracted melting of ice occurred.
- Fine-scale crease structures present on ice-marginal flows are described here as resulting from lava-ice interaction for the first time. They formed as a result of intermittent fracture propagation following cooling-induced contraction of lava against ice. This process was likely aided by marginal bulging of ice-bounded flows into void space created by thermal erosion of glaciers, and high pressures within fractures due to ingress of steam produced by heating of meltwater.
- New and existing $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages of ice-marginal lava flows indicate that a substantial ice mass consisting of large flank glaciers existed on Ruapehu from ~51–41 ka and ~27–15 ka. Glaciers with thicknesses of ~200–100 m descended to 1300 m a.s.l. during MIS 3 and 2.
- The $^{40}\text{Ar}/^{39}\text{Ar}$ eruption age of 9 ± 3 ka determined for a valley-floor flow on northern Ruapehu indicates that flank glaciers had retreated to near-historical extents by the time of emplacement for this lava flow.

CHAPTER 3

3. ERUPTIVE HISTORY AND EDIFICE EVOLUTION OF RUAPEHU VOLCANO, NEW ZEALAND

ABSTRACT

Ruapehu is an active ~150 km³ andesite-dacite composite volcano located at the southern end of the Taupo Volcanic Zone, New Zealand. The growth of the edifice has occurred throughout coeval eruptive and glacial histories since ~200 ka. High-precision ⁴⁰Ar/³⁹Ar eruption ages and whole-rock major element geochemical data for lava flows are presented in this chapter. The data are interpreted in the context of geomorphologic and geologic mapping, volcano-ice interaction processes and glacier reconstructions in order to present a new chronostratigraphic and edifice evolution model for Ruapehu.

Sub-glacial to ice-marginal effusive eruption of medium-K basaltic-andesites and andesites constructed the northern portion of the exposed edifice between ~200 and 150 ka, and the wide southeast planèze as well as parts of the northern, eastern and western flanks between ~160 and 80 ka. No eruption ages were returned for lava flows during the period from 80–50 ka, which may reflect an eruptive hiatus or alternatively is the result of erosion and burial of lavas and syn-eruptive glacial conveyance of lava flows to the ring-plain due to glacial advance at 70–60 ka. Edifice growth from ~50–15 ka occurred via effusive eruptions onto the glaciated flanks of the volcano, resulting in construction of ice-bounded planèzes and ridges. The distribution of dated ice-marginal lavas indicates a general decrease in glacier thicknesses over this time, excepting a short-lived period centred on ~31 ka when peak ice cover was reached. The compositional ranges of medium- to high-K andesite and dacite lava flows within 50–36 ka eruptive packages define broadly bimodal high- and low-MgO trends. Lavas erupted at ~35–22 ka have compositions that fill a transitional geochemical field between older dacites and younger andesites.

Large-scale retreat of flank glaciers since ~15 ka have resulted in intra-valley lava flow emplacement at elevations below ~1500 m on the edifice. Between 15 and 10 ka unstable

cones were constructed through effusive activity in the presence of remnant summit and upper flank glaciers and the emplacement of eruptive deposits on top of hydrothermally altered and fragmental sub-glacial and ice-marginal deposits. Debuitressing of two northern summit cones and a southern summit cone as ice underwent continued post-glacial retreat pre-conditioned two major sector collapses and deposition of debris avalanche deposits on the northern and south-eastern flanks, respectively. Ultimate triggering of the collapse events may have been the result of tectonic or volcanic activity. The northern collapse scar is infilled by a new cone comprising <10 ka lava flows that form the upper northern and eastern flanks of the edifice. Late Holocene-recent eruptive activity has occurred through Crater Lake, which occupies the site of the collapsed southern cone.

Deglaciation did not induce enhanced magma flux rates at Ruapehu as indicated by calculated eruptive volumes and their chronologies. However, volcano-ice interactions have had a fundamental influence on eruptive styles, sector collapse events, and the shape of the edifice by modifying the distribution, morphology and preservation of eruptive deposits for at least 200 kyr.

3.1. INTRODUCTION

Continental composite volcanoes are the typical surficial features of convergent margin magmatism where volcanic products are erupted, often in proximity to human populations. Sequences of lavas generally provide the best preserved record of volcanic edifice growth and allow investigation of the tempo of eruptive activity in such settings. High-resolution eruptive records constrained by precise temporal frameworks are required in order to document the stratigraphies of such volcanoes. These records underpin hazard assessment and enhance the value of geochemical and petrological datasets that inform evolutionary models of arc magma systems (e.g. Hildreth and Lanphere, 1994; Dungan et al., 2001). The $^{40}\text{Ar}/^{39}\text{Ar}$ radioisotopic system is a widely used geochronometer for measuring the eruption ages of Quaternary volcanic rocks with intermediate compositions (e.g. Gamble et al., 2003; Hildreth et al., 2003; Fierstein et al., 2011). Despite its general suitability, application of this technique has generally been restricted to Pleistocene volcanic rocks with sufficient K_2O concentrations (>1 wt. %) and non-glassy groundmass textures. High-precision instrumentation (Coble et al., 2011),

improved understanding of the behaviour of argon in volcanic glass (Clay et al., 2015), and development of methods to counter argon recoil processes that affect fine-grained rocks (Fleck et al., 2014) have increased the potential for this technique to be applied to Holocene age lavas. Despite these advances, incomplete exposure of volcanic edifices remains a hindrance to establishing comprehensive and cohesive eruptive chronologies. Glaciation and sector collapse are the principal agents of erosion and edifice destruction that generate stratigraphic unconformities and inhibit accurate reconstructions of eruptive events and volumes for composite volcanoes (e.g. Singer et al., 1997). The recognition and integration of volcano-ice interactions within eruptive stratigraphies of glaciated volcanoes is crucial to unravelling their evolution (Schmidt and Grunder, 2009). Moreover, deposits resulting from volcano-ice interactions can provide powerful paleoclimate proxies when paired with precise geochronology (e.g. Lescinsky and Fink, 2000; Mee et al., 2009). In this contribution, new high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ ages and whole-rock major element geochemistry for lava flows are integrated with geological mapping, glacier reconstructions and existing chronostratigraphic studies to interrogate the mid-Pleistocene to Holocene evolution of Ruapehu as a case study of typical arc volcanism. The foremost purpose of this study is to present a detailed ~200 kyr-long eruptive chronology and edifice evolution model for New Zealand's largest active composite volcano.

3.2. GEOLOGICAL SETTING

3.2.1. Regional geology

Volcanism in central North Island, New Zealand is associated with westward subduction of oceanic crust of the Pacific Plate at $\sim 45 \text{ mm yr}^{-1}$ beneath the Australian Plate along the Hikurangi Trench system (Fig. 3.1; Cole and Lewis, 1981; Reyners et al., 2006; De Mets et al., 2010). Most volcanic activity is manifested in the Taupo Volcanic Zone (TVZ), which is an extending arc that comprises northern and southern segments dominated by andesite-dacite composite cones and a central segment of highly productive silicic volcanism (Wilson et al., 1995). The southern TVZ segment comprises the prominent Tongariro and Ruapehu composite volcanoes as well as several smaller volcanic edifices (Cole, 1978). Extension in the southern TVZ occurs at a direction of $\sim 115^\circ$ and a rate of $2.3 \pm 1.2 \text{ mm yr}^{-1}$ (Villamor and Berryman, 2006a). This motion is manifested by the 40

km-wide Mount Ruapehu Graben, which is bounded by the Rangipo and Raurimu faults to the east and west, respectively, and by the NE-striking Karioi and the ENE-trending Ohakune fault sets to the south (Fig. 3.1; Villamor and Berryman, 2006a). Ruapehu volcano sits upon late Tertiary sediments and Mesozoic basement rocks. The latter is generally inferred to be the Kaweka terrane, a Jurassic greywacke-argillite sequence of felsic composition that outcrops in the ranges east of the Rangipo fault (Adams et al., 2009; Price et al., 2015). An index map of Ruapehu with geographical features referred to throughout the text is provided in Figure 3.2.

Figure 3.1. Digital elevation model (DEM) map of the Tongariro Volcanic Centre (red box on inset figure) at the southern end of the Taupo Volcanic Zone (TVZ) in North Island, New Zealand. The maps use the New Zealand Transverse Mercator 2000 projection (NZTM2000). Inset also shows the position of glaciated Southern Alps in South Island (grey shaded area). Key townships at Waiouru, Ohakune, National Park and Whakapapa Village are labelled. The major volcanic edifices in the map area are Hauhangatahi, Ruapehu and Tongariro. Main <15 ka vents are labelled with black stars. Note also the peripheral vents at Pukeonake cone and Ohakune Craters.

3.2.2. Volcanological overview

Ruapehu is New Zealand's largest active andesite volcano, with a $\sim 150 \text{ km}^3$ edifice surrounded by a volcaniclastic ring plain of similar volume (Hackett and Houghton, 1989; Gamble et al., 2003). The flanks of the edifice are composed of lava flows and autobreccias intercalated with glacial and pyroclastic deposits (Cole, 1978). Cone-forming lavas and autobreccias were grouped by Hackett (1985) into formations that represent the eruptive products of four main phases of edifice growth. These formations are the Te Herenga (250–180 ka), Wahianoa (160–115 ka), Mangawhero (60–15 ka) and Whakapapa (<15 ka). Ages and durations of the phases were subsequently constrained by $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages for lava flows from the Te Herenga (3 samples), Wahianoa (11 samples) and Mangawhero (7 samples) formations (Table 3.1; Gamble et al., 2003).

Table 3.1. Existing chronostratigraphic formations for Ruapehu volcano.

Formation	Eruptive period	Sample	WMPA $\pm 2\sigma$ (ka)
Whakapapa	<15 ka	n/a	n/a
Mangawhero	60 - 15 ka	X1-6 X1-16 R99/1 R97/39 T5-11 R-S44-10	21 ± 6 22 ± 7 23 ± 4 23 ± 8 45 ± 6 47 ± 4
Wahianoa	160 - 115 ka	R95/22 R96/5 R95/26 R96/16 R95/28 R96/17 R95/27 X1-10 R97-50 R96/9 R96/20	119 ± 12 129 ± 15 130 ± 23 131 ± 27 133 ± 11 134 ± 12 135 ± 14 138 ± 14 147 ± 10 147 ± 12 154 ± 12
Te Herenga	250 - 180 ka	T6-8 T6-24 T6-27	183 ± 13 197 ± 12 205 ± 27

$^{40}\text{Ar}/^{39}\text{Ar}$ WMPA (weighted mean plateau age) and 2σ uncertainty for lava flows measured by Gamble et al. (2003). Sample locations are displayed in Figures 3.4, 3. 9 and 3.10.

Gamble et al. (2003) concentrated on the clear stratigraphic sequencing of lava flows within the Wahianoa Formation exposed in the deeply glaciated Wahianoa and

Whangaehu valleys on the southeast flank of Ruapehu. Lavas of the Mangawhero Formation were inferred to have been erupted during discrete pulses of effusive activity centred on ~45 ka and ~22 ka whereas no eruption ages were determined for lavas of the Whakapapa Formation (Gamble et al., 2003). Complex stratigraphic relationships between lavas of the same and subsequent formations have been interpreted as the result of rapid transitions between construction and degradation of the edifice (Hackett and Houghton, 1989).

The ring plain comprises a thick apron of stacked pyroclastic and volcaniclastic material consisting of debris flow, debris avalanche and hyperconcentrated stream flow deposits interbedded with locally andesitic and distally derived rhyolitic tephra (Cronin and Neall, 1997; Donoghue and Neall, 2001; Tost et al., 2014). Aggradation has likely been rapid following eruptive phases (Hackett and Houghton, 1989) and during glacial periods (Cronin and Neall, 1997), while large-scale sector collapse events may have occurred following the transition from glacial to interglacial periods (Tost et al., 2015).

Explosive activity at Ruapehu since ~27 ka is recorded within tephra sequences on the eastern flank and ring plain (Donoghue et al., 1995a). During the period from ~22–10 ka, the largest known Plinian eruptions occurred at Ruapehu (Pardo et al., 2012), while apparently coeval but volumetrically minor pyroclastic flow deposits are also preserved on the eastern flank of the edifice (Donoghue et al., 1995a). The past 2 kyr of volcanic activity at Ruapehu have been characterised by low-volume ($<0.05 \text{ km}^3$) but frequent (25–30 yr periodicity) phreatomagmatic eruptions through Crater Lake (Donoghue et al., 1997) with additional phreatic eruptions occurring as often as annually (Houghton et al., 1987).

Past glaciation of Ruapehu is evident from the deep U-shaped valleys that indent the flanks of the edifice (Figure 3.2) as well as the presence of large lateral moraines and striated lava flow surfaces (McArthur and Shepherd, 1990; Waight et al., 1999). The most recent period of major glaciation of the edifice occurred between ~31 and 17 ka (Eaves, 2015), which overlaps with the ~20 ka global Last Glacial Maximum (LGM; Clark et al., 2009), when the termini of valley glaciers reached ~1200 m a.s.l. The impact of pre-historic glaciation of Ruapehu between phases of eruptive activity has been recognised as having generated major stratigraphic unconformities (Hackett and Houghton, 1989). The coincidence of emplacement of Mangawhero Formation lavas (60–15 ka) and glaciation

during the last glacial cycle (71–15 ka; Lisiecki and Raymo, 2005) suggests that syn-eruptive interaction between lava and ice was also an important aspect of the edifice growth history (Spörli and Rowland, 2006). Widespread evidence for lava-ice interaction during emplacement of flows of the Mangawhero Formation has now been documented (Conway et al., 2015). Glaciers have retreated rapidly in historical times (Heine, 1963), and only sparse accumulations of permanent ice are now present around the uppermost western, southern and eastern flanks, and over the broad ice-filled northern portion of the summit.

Figure 3.2. Index map for Ruapehu volcano, displaying major roads, river valleys and summit features referred to in the text. The major peaks of Tahurangi (Ta, 2797 m), Paretaitonga (Pa, 2662 m), Tukino (Tk), Te Heuheu (Th), Girdlestone (G), Pyramid Peak (Py) and Ringatoto (Ri) are marked with x symbols. Modern glaciers are numbered: Whakapapa (1); Mangaturuturu (2); Mangaehuehu (3); Wahianoa (4); Whangaehu (5); Mangatoetoenui (6). The summit also comprises the ice-filled Summit Plateau (SP) and active vent beneath Crater Lake (CL). Arrows indicate view directions for Figures 3.5, 3.7, 3.11, 3.12 and 3.21.

3.3. METHODS

3.3.1. Field studies and mapping

Field campaigns were conducted on foot with occasional helicopter assistance throughout the months of January–May from 2012 to 2015 as part of a wider mapping project (Townsend et al., 2016). The edifice is largely snow-free during these months, and the lack of vegetation above 1500 m above sea-level (a.s.l.) is advantageous for exposure on the mid- to upper elevation flanks of the volcano. Access is aided by ski fields on the eastern, northern and southern flanks, and the numerous recreational tracks. Stratigraphic and lithological boundaries for eruptive packages were drawn, largely on geomorphologic characteristics and later refined by petrological, geochemical and geochronological analyses. Lava flow volumes were calculated from observed extents and thicknesses of lava flows.

3.3.2. Whole-rock analyses by X-ray fluorescence

Lava flow samples were cleaned by using a diamond saw to cut away any weathered material. Samples were then crushed using a jaw crusher, and powdered using an agate or tungsten-carbide ring mill. Powders were made into fused lithium metaborate glass discs and analysed for major oxide concentrations by x-ray fluorescence spectroscopy (XRF) following the methods of Ramsey et al. (1995). Disc-making and analyses were carried out at the Open University, Milton Keynes, U.K. Internal standards WS-E (Whin Sill dolerite) and OU-3 (Nanhoron microgranite) were analysed once for every 20 sample analyses to monitor precision and accuracy of the results. Major oxide analyses were accurate to within 2 % of the recommended values for the internal standards. Analytical precision (2σ) was better than 2 % for all elements with concentrations >0.3 wt. %. Duplicate disks were made for three different Ruapehu lava sample powders and analysed as unknowns: duplicate analyses were accurate to within 5 % of each other for all major elements. Standard data are presented in Appendix A5.

3.3.3. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology

Radiometric $^{40}\text{Ar}/^{39}\text{Ar}$ dating was undertaken using crystalline groundmasses from interior zones of lava flows to produce reliable results (e.g. Gamble et al., 2003; Fierstein et al., 2011). Analysis required minimum groundmass plagioclase widths of 10 μm (to avoid reactor recoil) and groundmass glass abundances of < 5% (to minimise any erroneous contribution from glass-derived argon). Samples selected for radiometric dating were crushed and sieved, and the 250–350 μm fraction used. An LB-1 Barrier type Frantz magnetic separator was used to remove phenocrysts and xenoliths from the pure groundmass fraction. To remove altered and adhered material, groundmass separates were washed in water in an ultrasonic bath and repeatedly decanted for up to 20 hours, then washed in acetone to remove any hydrocarbons from grain surfaces, and finally rinsed in deionized water. Any remaining grains with adhering phenocrysts, xenoliths or areas of glass were removed by hand-picking. Encapsulated packets of ~200 mg of groundmass were irradiated for 1h in the central thimble of the USGS-TRIGA reactor in Denver, Colorado (Dalrymple et al., 1981). Samples were shielded from thermal neutrons and neutron flux was measured using Taylor Creek Rhyolite sanidine (TCR-2) fluence monitors with an assigned age of 27.87 Ma (M.A. Lanphere, written communication), equivalent to the widely used Fish Canyon sanidine at 27.63 Ma ($R = 1.00881 \pm 0.00046$). The reactor vessel was rotated continuously during irradiation to minimise any lateral neutron flux gradients. Fluence monitors were analyzed using a continuous laser system and a MAP 216 mass spectrometer described by Dalrymple (1989). Argon was extracted from feldspar separates using a Mo crucible in a Staudacher-type custom resistance furnace attached to the MAP 216 mass spectrometer following analytical procedures outlined in Calvert et al. (2005). Heating temperatures were monitored with an optical fiber thermometer and controlled with a LabView PID controller. Gas was purified continuously during extraction using two SAES ST-172 getters operated at 4 A and 0 A.

3.4. ERUPTIVE HISTORY

New and existing geochronological and geochemical data are used here to describe edifice-forming eruptive products at Ruapehu. This section is divided into the four chronostratigraphic formations defined by Hackett (1985), however, new data are used

here to refine the temporal ranges and compositional characteristics of these formations. The Mangawhero and Whakapapa formations are further broken down into eruptive packages that are defined based on the age, location, morphology, petrography and major element composition of lava flows. These packages will be formally classified as stratigraphic members by Townsend et al. (2016) where appropriate definition of type localities and characteristics will be presented. The temporal and spatial distribution of the packages is summarised in Figure 3.3, and shown in detailed maps in Figures 3.4, 3.9, 3.10 and 3.14.

Figure 3.3. Summary of the spatial and temporal distribution of effusive volcanic products at Ruapehu volcano that are mapped in Figures 3.4, 3.9, 3.10 and 3.14. Key for eruptive packages of the Mangawhero and Whakapapa formations is displayed at right. Temporal ranges for packages and formations take into account 2σ uncertainties of $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages for the relevant flows.

Table 3.2. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data for Ruapehu volcano lava flows.

Sample	Fmtn-Package	Plateau age				Total gas age	Isochron age
		N	^{39}Ar %	MSWD	(ka, $\pm 2\sigma$)	(ka, $\pm 2\sigma$)	(ka, $\pm 2\sigma$)
GL1983	WH-Crater Lake	6	79.8	1.06	0.2 ± 2.2	-1.8 ± 2.2	1.4 ± 8.8
CC564	WH-Iwikau	7	86.0	0.67	0.8 ± 5.6	-0.8 ± 5.6	4 ± 13.4
GL1030	WH-Iwikau	11	100.0	1.10	6.0 ± 2.4	6.5 ± 2.4	1.4 ± 7.4
CC279	WH-Iwikau	6	63.9	0.79	8.8 ± 2.8	8.6 ± 3.0	10.5 ± 17.2
CC569	WH-Iwikau	4	60.8	0.13	9.2 ± 8.0	-0.3 ± 8.6	22.2 ± 47.8
CC236	WH-Turoa	5	62.7	0.61	11.9 ± 2.2	9.3 ± 2.2	15.4 ± 15.2
CC393	WH-Tureiti	10	100.0	0.65	11.9 ± 2.8	12.3 ± 2.8	11.9 ± 8.8
CC397	WH-Tureiti	7	83.9	0.90	12.5 ± 2.6	10.2 ± 2.6	14.4 ± 5.0
CC335	WH-Paretetaitonga	7	79.8	0.80	14.8 ± 3.0	22.1 ± 3.0	10.8 ± 12.4
CC130	WH-Turoa	11	100.0	0.46	15.1 ± 2.4	15.2 ± 2.4	13.9 ± 6.0
CC226	MA-Makotuku	10	100.0	0.34	17.8 ± 2.2	18.1 ± 2.6	16.8 ± 4.2
CC408	MA-Makotuku	8	94.7	0.39	20.9 ± 2.8	19.6 ± 3.0	22.7 ± 7.4
CC143	MA-Waitonga	10	99.5	0.80	23.0 ± 1.6	23.0 ± 1.8	22.2 ± 4.6
CC513	MA-Whakapapaiti	3	67.9	0.50	25.7 ± 3.8	6.7 ± 4.4	39.4 ± 28.6
CC441	MA-Manganuioteao	6	86.6	1.34	25.7 ± 2.6	20.3 ± 2.8	34.1 ± 8.2
CC553	MA-Manganuioteao	10	100.0	0.40	27.2 ± 4.8	25.8 ± 5.8	29.0 ± 7.2
CC547	MA-Manganuioteao	6	72.6	0.77	30.7 ± 5.2	43.9 ± 4.6	28.6 ± 10.4
CC462	MA-Manganuioteao	9	94.6	0.54	30.9 ± 2.2	30.4 ± 2.6	30.8 ± 5.4
CC508	MA-Te Kohatu	3	57.4	1.11	37.6 ± 1.4	46.2 ± 1.4	37.8 ± 21.8
CC556	MA-Ngahuinga	7	90.8	0.53	38.3 ± 3.4	30.0 ± 4.0	37.9 ± 8.4
CC414	MA-Te Kohatu	11	100.0	1.78	39.1 ± 1.4	40.7 ± 1.4	36.5 ± 2.0
CC511	MA-Te Kohatu	9	97.7	0.44	39.2 ± 2.0	40.2 ± 2.4	38.4 ± 3.6
CC424	MA-Ngahuinga	10	100.0	0.96	39.6 ± 2.8	40.3 ± 3.2	38.6 ± 5.2
CC570	MA-Mananui	8	91.7	0.28	40.3 ± 2.2	37.7 ± 2.6	41.7 ± 3.6
CC545	MA-Mangaturuturu	8	91.6	1.33	38.4 ± 2.4	35.9 ± 2.6	40.7 ± 4.6
CC470	MA-Mangaturuturu	9	99.4	0.96	41.3 ± 1.8	41.2 ± 2.0	42.9 ± 4.2
CC140	MA-Mangaehuehu	11	100.0	0.52	41.8 ± 1.8	41.2 ± 2.0	44.6 ± 4.0
CC313	MA-Te Kohatu	4	70.5	1.73	42.6 ± 1.8	39.5 ± 1.4	49.6 ± 7.0
CC127	MA-Mangaehuehu	8	84.4	0.66	42.8 ± 1.0	43.9 ± 1.0	42.9 ± 2.2
CC216	MA-Mangaehuehu	12	100.0	1.32	43.1 ± 1.4	43.8 ± 1.4	41.5 ± 2.6
CC119	MA-Mangaehuehu	11	100.0	1.46	43.3 ± 1.6	42.6 ± 1.6	45.3 ± 2.4
CC552	MA-Mangaturuturu	6	91.8	0.68	43.4 ± 2.4	45.1 ± 3.0	41.9 ± 6.0
CC081	MA-Mangaehuehu	8	86.7	1.17	44.2 ± 1.8	46.8 ± 1.8	41.9 ± 6.2
CC453	MA-Ngahuinga	8	96.7	1.43	44.8 ± 3.0	45.4 ± 2.8	45.8 ± 5.8
CC089	MA-Mangaehuehu	9	96.9	1.72	45.4 ± 2.0	46.0 ± 1.6	47.2 ± 8.0
CC562	WA	6	83.7	0.51	88.1 ± 6.4	85.2 ± 9.0	85.0 ± 19.4
CC350	WA	10	100.0	recoil	95.9 ± 7.0	95.5 ± 4.2	98.6 ± 16.8
CC209	WA	9	98.9	0.75	120.7 ± 4.0	119.5 ± 5.0	123.6 ± 5.4
CC213	WA	4	54.2	1.25	121.4 ± 2.8	122.2 ± 2.4	123.7 ± 16.0
CC375	WA	7	89.2	1.64	121.7 ± 4.2	119.6 ± 3.4	125.8 ± 9.8
CC197	WA	9	97.2	0.72	133.6 ± 6.4	136.0 ± 6.8	138.1 ± 13.6
CC518	TH	10	100.0	0.36	158.8 ± 8.2	157.6 ± 9.6	158.9 ± 13.4
CC322	TH	9	99.1	2.02	169.4 ± 7.8	171.0 ± 6.0	176.4 ± 17.2
CC276	TH	10	94.5	0.86	174.6 ± 3.4	171.0 ± 5.8	169.2 ± 7.2
CC348	TH	7	81.5	1.00	186.2 ± 6.8	173.1 ± 7.2	203.3 ± 22.4
CC306	TH	10	100.0	recoil	187.9 ± 34.4	146.6 ± 11.4	207.5 ± 22.2

Formation abbreviations are: WH (Whakapapa); MA (Mangawhero); WA (Wahianoa); TH (Te Herenga). N is number of heating steps, % ^{39}Ar is the proportion of released radiogenic gas, and MSWD is the mean standard weighted deviation of each age plateau calculation. Bold numbers are the preferred ages for each sample, which are all mean weighted plateau ages, except for CC545 where the isochron age was preferred.

Table 3.3. Summary of the compositional ranges for eruptive packages.

Formation	Eruptive package	SiO ₂	K ₂ O	Mg#
Whakapapa	Crater Lake [^]	61	2.2	55
	Iwikau	57 - 59	1.2 - 1.6	50 - 60
	Saddle Cone*	56 - 59	1.2 - 1.7	53 - 56
	Tureiti	60	1.7 - 1.8	48
	Paretetaitonga	57 - 59	1.5 - 1.7	51 - 56
	Rangataua	59 - 60	1.7 - 1.8	48
	Turoa	59 - 60	1.5 - 2.0	50 - 60
Mangawhero	Makotuku	60 - 62	1.8 - 2.1	44 - 50
	Waitonga	61 - 63	1.8 - 2.0	51 - 58
	Te Piripiri	58 - 60	1.4 - 1.9	56 - 60
	Horonuku [#]	60 - 62	1.8 - 1.9	54 - 60
	Whakapapaiti	65	2.1	57
	Manganuioteao	60 - 63	1.9 - 2.6	45 - 52
	Mananui	64	2.8	50
	Te Kohatu	64 - 65	2.9 - 3.3	54 - 57
	Mangaturuturu	63 - 64	2.7 - 3.0	42 - 45
	Mangaehuehu	57 - 62	1.4 - 2.3	60 - 69
	Ngahuinga	57 - 61	1.6 - 2.1	48 - 58
Wahianoa	undifferentiated	56 - 60	0.9 - 1.7	42 - 62
Te Herenga	undifferentiated	54 - 57	0.7 - 0.9	51 - 62

Range of SiO₂ and K₂O contents and Mg# [100Mg/(Mg + Fe)] shown. Composition for Crater Lake[^] is based off the dated lava flow (GL1983). Compositional ranges for Saddle Cone* and Horonuku[#] packages are constrained by data from Price et al. (2012).

⁴⁰Ar/³⁹Ar geochronology data are presented here for 46 lava samples (Table 3.2), including three ages that were reported in Conway et al. (2015). Total gas, isochron and weighted mean plateau ages (WMPA) were calculated for each sample experiment. Total gas ages were calculated from the sums of radiogenic ⁴⁰Ar and potassium-derived ³⁹Ar in all step-heating increments of the analysis. Isochron ages were calculated from ⁴⁰Ar/³⁶Ar versus ³⁹Ar/³⁶Ar correlation using the algorithm of York (1969). Plateau ages are the inverse-variance weighted means calculated for the steps of an age spectrum comprising contiguous gas fractions that represent >50 % of the total ³⁹Ar released from the sample. Total gas ages are similar to plateau ages (within 2σ uncertainty) for nearly all samples. There are 2 exceptions for post-glacial lavas and 4 exceptions for syn-glacial samples: the difference between plateau and total gas ages in these cases can be explained by the low numbers of heating steps (n = 3–7) included in plateau age calculation for these samples. The isochron age was preferred as the most suitable eruption age estimate for sample CC545 because the ⁴⁰Ar/³⁶Ar intercept was not within 2σ error of the atmospheric value. Two experiments resulted in recoil spectra patterns indicative ³⁹Ar loss during irradiation. To preclude an underestimation of the eruption age due to reduced ⁴⁰Ar/³⁹Ar values at high temperature increments, recoil model ages were calculated from the entire spectra

(100% fraction of ^{39}Ar released) of the two affected samples using the method outlined in Fleck et al. (2014). Major element compositions for eruptive packages are summarised in Table 3.3 and full data are available in Appendix 5.

3.4.1. Te Herenga Formation (200–150 ka)

The oldest exposed volcanic products on Ruapehu are medium-K basaltic-andesite dikes, lava flows and volcanoclastic breccias of the Te Herenga Formation that form the eroded remnants of an edifice on the northern flank of Ruapehu (Figs. 3.4, 3.5).

Figure 3.4. Distribution of Te Herenga Formation and Wahianoa Formation eruptive products. Locations for dated samples (open circles with sample numbers in *italics*) and relevant figures (cross or arrow, with bold numbers) are displayed. Sample locations for lavas dated by Gamble et al. (2003) that are referred to in this study are also displayed (open squares with numbers with a ‘R’ prefix).

The timing of this volcanism is constrained by three existing and five new $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Tables 3.1, 3.2). The oldest exposed volcanic product dated in this study yielded an imprecise eruption age of 187.9 ± 34.4 ka (age $\pm 2\sigma$ error), which is comparable to the existing value of 205 ± 27 ka for the oldest exposed products measured by Gamble et al. (2003). An older limit of 200 ka is used for the Te Herenga Formation here in order to reflect the most precise eruption ages measured for early lavas (Tables 3.1, 3.2). Ruapehu volcano has a lifetime inferred to extend back to at least ~ 340 ka (Gamble et al., 2003).

Figure 3.5. View of the eroded Te Herenga Formation edifice and post-glacial Whakapapa Formation lavas on the northern flank of Ruapehu. Distinct geographical features and elevations are marked in the top panel. Mapped extents of eruptive deposits are drawn in the bottom panel. Locations and eruption ages (weighted mean plateau ages: $\text{WMPA} \pm 2\sigma$) of dated samples from this study are displayed. The location of the most mafic lava flow sampled on Ruapehu ('Ruapehu Basalt'; Price et al., 2012) is noted. Abbreviations are: WA (Wahianoa Formation); MN (Mananui package), and SC (Saddle Cone package); PR (Pinnacle Ridge fall deposit); and the Iwikau (IW) and Taranaki Falls (TF) flow groups within the Iwikau package.

An age of 186.2 ± 6.2 ka was measured for the most mafic lava flow sampled from Ruapehu (53.8 wt. % SiO_2 ; ‘Ruapehu basalt’ in Price et al., 2012), which had previously been assigned to the Mangawhero Formation. This flow is one within a series of flows forming the nose of a ridge elevated ~ 150 m above younger deposits (Fig. 3.5). Three eruption ages and their uncertainties ($\text{WMPA} \pm 2\sigma$) bridge the previously interpreted hiatus between 180–160 ka (Gamble et al., 2003) and, thus, the younger limit of Te Herenga Formation is adjusted here to 150 ka. The oldest deposits of the northern edifice form much of Pinnacle Ridge and are a ~ 100 m-thick unit of monomict volcanoclastic breccias intruded by dikes and quenched lobes of lava exposed at elevations up to 2000 m a.s.l. (Figs. 3.5, 3.6a). Breccia clasts display radial fractures indicative of quench-contraction cooling and are hosted in a palagonitised ash matrix (Fig. 3.6a). These deposits are interpreted here to represent hyaloclastite breccias that were erupted under ice/meltwater. From the core of the northern edifice at Pinnacle Ridge, lava flows and breccias flowed north and are now exposed in deep valleys and along prominent ridges, where they were depositionally impounded by large glaciers (Fig. 3.5).

Figure 3.6. Examples of eruptive products of the Te Herenga Formation. Locations of images are labelled in Figure 3.4. a) Hyaloclastite breccia unit exposed beneath Pinnacle Ridge is composed of dense, fresh lava within an orange palagonite matrix. b) Breccia and laminated ash unit exposed on the northeast flank of the edifice. c) Thick lavas located north of Pinnacle Ridge. Person circled for scale. d) Characteristic pyroxene glomerocryst within a lava sample.

Breccia units are monomict, encompassed in steep lensoidal packets, range from poorly- to moderately-sorted with maximum clast sizes of 80 cm, and occasionally display weak bedding and rare lenses of finely laminated ash (Fig. 3.6b). The distribution of lavas and characteristics of breccias indicate that ice- and meltwater-marginal fragmentation, transportation and emplacement/deposition occurred during this time. Te Herenga Formation volcanics are petrographically distinguished from younger lavas by their devitrified groundmass textures and prominent pyroxene glomerocrysts that range in diameter from 4–12 mm (Fig. 3.6d). Lavas range from 54–57 wt. % SiO₂ and 0.7–0.9 wt. % K₂O, making them the least evolved products exposed on Ruapehu (Table 3.3).

3.4.2. Wahianoa Formation (166–80 ka)

Lava flows of the Wahianoa Formation (Hackett, 1985) flowed primarily to the southeast from a vent focus located south of the exposed Te Herenga Formation eruptives.

Wahianoa Formation lava flows are medium-K basaltic-andesites and andesites (56–60 wt. % SiO₂) that exhibit slightly elevated K₂O contents compared to Te Herenga Formation lavas (Table 3.3). The lower boundary (154 ± 12 ka; Gamble et al., 2003) for the Wahianoa Formation is constrained by an age for the stratigraphically lowest lava flow within the Whangaehu valley. The lava is at the base of a planze comprised of a ~300 m-thick sequence of alternating lava flows, pyroclastic flows and debris flows between the deeply incised Wahianoa and Whangaehu valleys (Figs. 3.4, 3.7, 3.8a). Individual flows within the sequence generally exhibit planar thicknesses of 1–2 m, but occasionally swell into 15 m-thick knuckles indicative of ponding in paleo-topographic depressions, and/or against ice (Fig. 3.8c). Lavas are intercalated with autobreccias and debris avalanche deposits on metre scales (Fig. 3.8c). Wahianoa Formation lava flows are also exposed within the Ohinepango River valley to the northeast and the Mangaturuturu River valley to the west, and beneath younger syn-glacial lavas on the northwest and northern flanks of the volcano (Fig. 3.4). At the core of the southeastern planze, a voluminous mound of breccia, intruded by dykes and lava lobes, is inferred to have a subglacial or subaqueous origin. The unit comprises monomict, sub-angular to sub-rounded clasts displaying radial fractures and quenched rinds that are cemented in an orange-pink palagonitized ash matrix, interpreted to be a hyaloclastite breccia (Figs. 3.8a, b).

Figure 3.7. View of the eastern side of Ruapehu volcano. Distinct geographical features are marked in the top panel. Mapped extents of eruptive products are drawn in the bottom panel. Locations and eruption ages (WMPA $\pm 2\sigma$) of dated samples from this study are displayed. Abbreviations are: MK (Makotuku package) and CL (Crater Lake package).

A minimum age constraint of 154 ± 12 ka for this breccia is provided by overlying dated lava flows (Gamble et al., 2003). However, an unconformity separates these lavas of the southeast planèze from the breccia and may indicate that the latter is significantly older than ~ 160 ka. Comparison of existing and new geochronology data presented for Te Herenga Formation above indicates that coeval effusion may have occurred from northern (Te Herenga) and southern (Wahianoa) vents at ~ 160 – 150 ka.

Figure 3.8. Characteristic features of breccias and lava flows of the Wahianoa Formation. a) Unconformity between voluminous mound of hyaloclastite breccia (hy) and lava flows, autobreccias and debris flows of the Wahianoa Formation (WA). Red circle shows position of Whangaehu Alpine Club hut. b) Intrusion of lava within hyaloclastite breccia. c) Overthickened knuckle of lava (*) within sequence of alternating planar lava flows, autobreccias and debris flows on the true right bank of the Whangaehu River valley. d) Planar and platy jointed Wahianoa Formation andesite lava flow (WA; 88.2 ± 6.4 ka) overlying debris flow deposits (df) in the Whangaehu River valley.

New ages of 120.7 ± 4.0 and 121.4 ± 2.8 ka were determined for flows located at 1400 and 1500 m a.s.l. on the southeast flank of Ruapehu that correspond to the upper sequence of the Wahianoa Formation as defined by Gamble et al. (2003). A similar sequence is exposed on the northeast flank, with an age of 121.7 ± 4.2 ka measured for a flow sampled on the upper true right bank of the Ohinepango Stream valley. The existing age range for the Wahianoa Formation is extended here to account for lavas that are exposed on the lower northern (95.9 ± 7.0 ka) and eastern (88.1 ± 6.4 ka) flanks (Fig. 3.4). These

lavas have very low slope angles, are covered by till, and are located at low elevations within glacially eroded valleys (Fig. 3.8d). The characteristics indicate that the flows were emplaced onto an edifice that was relatively ice-free during this period, which coincides with part of a previously inferred eruptive hiatus at Ruapehu (Gamble et al., 2003). Despite the disparate distribution of interglacial andesites on southwest, west and northwest flanks, the lavas are interpreted to have been sourced from one central magma system contiguous to that which sourced older lavas of the Wahianoa Formation.

3.4.3. Mangawhero Formation (50–15 ka)

The Mangawhero Formation was interpreted to encompass volcanic products erupted during effusive episodes centred at ~45 ka (based on two lava flow ages) and ~22 ka (based on five lava flow ages; Gamble et al., 2003). Twenty-five lava flow ages measured for this study span a near-continuous range from ~48–15 ka, and are used to redefine the chronological and areal extent of lava flows that comprise the Mangawhero Formation. The majority of WMPA ($n = 17$) fall within a period from ~45–38 ka.

No eruption ages were returned between 37 and 31 ka, although this period is bridged by 2σ uncertainties of the plateau ages for three new samples and one sample from Gamble et al. (2003). The majority of Mangawhero Formation flows display strong evidence for interaction with ice and were emplaced on moraine ridges along the lateral margins of glaciers or dammed behind large volumes of valley-filling ice (Conway et al., 2015).

As a result of excellent exposure and optimal groundmass textures for dating Mangawhero Formation lava flows were sampled extensively, which has allowed for the detailed discrimination between eruptive packages presented below and in Figure 3.9 (~50–36 ka) and Figure 3.10 (~35–15 ka). New Zealand indigenous Māori names have been adopted for these eruptive packages that relate to local geographical features and places. These names will be classified as formal Members by Townsend et al. (2016). Time brackets for the eruptive packages are defined by taking into account individual $^{40}\text{Ar}/^{39}\text{Ar}$ WMPA and 2σ uncertainties for all relevant flows in the package.

Figure 3.9. Distribution of earlier Mangawhero Formation eruptive packages (50–35 ka). Locations for dated samples and relevant figures are displayed, as in Fig. 3.4. Girdlestone Peak is marked ‘G’.

3.4.3.1. Ngahuinga package (48–35 ka)

This sequence of andesite flows border the Whakapapaiti Stream valley and are exposed on the western and northwestern flanks. The timing of this effusive activity is bounded by an eruption age of 44.8 ± 3.0 ka for the deepest exposed flow. The true left ridge of the Whakapapaiti Stream valley includes a series of at least four individual ≤ 5 m-thick ice-bounded flows (Fig. 3.11), the second-oldest of which yielded an eruption age of 39.6 ± 2.8 ka. On western Ruapehu, an ice-bounded Ngahuinga package andesite flow was emplaced at 38.3 ± 3.4 ka.

3.4.3.2. *Mangaehuehu package (47–40 ka)*

The Mangaehuehu package comprises voluminous andesitic lava flows that form the southern portion of the Ruapehu edifice between the Wahianoa and Mangaturuturu river valleys, as well as western parts of the edifice (Fig. 3.7). Eruption of Mangaehuehu package lavas is tightly constrained between 47 and 40 ka when taking into account all 6 new individual $^{40}\text{Ar}/^{39}\text{Ar}$ WMPA and 2σ uncertainties measured for these flows. The eruption age of 47 ± 4 ka (and duplicate age of 53 ± 4 ka) determined by Gamble et al. (2003, sample R-S44-10) was not used to define the eruptive package age range because of the low number of heating steps used in the analyses.

The flows are defined by distinctly high MgO contents (and Mg-values; Table 3.3) compared to other Ruapehu lavas at equal SiO_2 contents, which enables undated distal flows to be unambiguously assigned to this package. Lava samples collected from Girdlestone Peak by Hackett (1985) display identical compositional characteristics to Mangaehuehu package lavas and the glacially sculpted peak, which exposes dikes (Hackett, 1985), is interpreted to represent an eroded vent-proximal region. Mangaehuehu package lavas cover an area of $\sim 100 \text{ km}^2$, with distal flows exposed up to 18 km from Girdlestone Peak on the western flank of Ruapehu (Fig. 3.9).

Mangaehuehu package lavas were bounded by glaciers between elevations of 2600 and 1500 m a.s.l. and have been partly eroded and buried by subsequent glacial activity such that much of the surface of the southern flank is composed of glacial till and outwash. Exposures of stacked flows (Fig. 3.13a) and the distinct MgO and K_2O contents of each sample within the total $\sim 57\text{--}62$ wt. % SiO_2 continuum indicate that the samples represent a package of flows that were erupted from a common magma source that was tapped throughout the ~ 7 kyr eruptive period. The remote southern flank of the Ruapehu volcanic edifice had previously been sparsely sampled and was mapped predominantly as Wahianoa Formation (Hackett and Houghton, 1989; Price et al., 2012), meaning that this substantial cone-building episode had not previously been recognised. As their age range indicates, Mangaehuehu and Ngahuinga package lavas were emplaced contemporaneously, and no clear stratigraphic ordering between them can be ascertained due to their disparate spatial distributions. However, Mangaehuehu package is inferred to underlie some Mangaturuturu and Ngahuinga lavas on western flank (Fig. 3.11).

3.4.3.3. *Mangaturuturu package (46–36 ka)*

This eruptive package is represented by ice-bounded dacite lava flows erupted between ~46 and 36 ka that form a planèze on the western flank between the Mangaturuturu and Manganuioteao river valleys (Fig. 3.12). The flows overlie Wahianoa Formation lavas and breccias in the deeply incised upper catchment of the Mangaturuturu River (Fig. 3.12) and cap Whakapapaiti andesites along the northern part of the once ice-bounded planèze (Fig. 3.13b). In addition to their distinct spatial location (Fig. 3.9), Mangaturuturu package lavas are differentiated from other dacite flows erupted during this time by their lower MgO contents at equivalent SiO₂ and K₂O contents (Table 3.3).

3.4.3.4. *Te Kohatu package (44–36 ka)*

Te Kohatu package dacite lavas were emplaced adjacent to large valley glaciers on the northwest flank between ~44 and 36 ka to form prominent ice-bounded and ice-dammed flows between 1500 and 2100 m a.s.l. (cf. Conway et al., 2015; Figs. 3.11, 3.13c). The eruption age of 46 ± 5 ka determined for dacite sample T5-11 by Gamble et al. (2003) was not used to define the age range of the Te Kohatu package because it conflicts with the stratigraphic order of several dated flows on the northwest flank as constrained by new data. Te Kohatu dacites are observed to overlie remnants of the Te Herenga and Wahianoa formations, and Mangaehuehu and Ngahuinga eruptive packages. A Te Kohatu package ice-bounded flow emplaced at 39.1 ± 1.4 ka caps Ngahuinga package andesites exposed on the true left of the Whakapapaiti Valley (Fig. 3.11). The dacites also comprise two >100 m-thick ice-dammed flows emplaced at 39.2 ± 2.0 ka and 37.6 ± 1.4 ka at ~1500 m a.s.l. on the western flank; the distinct WMPA are consistent with the flows' stratigraphic positions. Another large ice-dammed flow within this package was emplaced within the broad, glaciated Whakapapaiti Stream valley at 42.6 ± 1.8 ka. Based on their spatial distribution and ice-contact margins, Te Kohatu package lavas were erupted from a central summit vent. Compared to other Ruapehu dacites, Te Kohatu package flows have higher MgO contents.

Figure 3.10. Distribution of later Mangawhero Formation eruptive packages (35–15 ka). Locations for dated samples and relevant figures are displayed, as in Fig. 3.4. Sample locations for lavas dated by Gamble et al. (2003) that are referred to in this study are also shown (numbers with a ‘X’ prefix).

3.4.3.5. *Mananui package (42–38 ka)*

This package comprises a single ice-dammed dacite flow that was emplaced against a glacier on the lower northern flank at 40.3 ± 2.2 ka (Fig. 3.5). The flow is isolated stratigraphically and spatially from other dacite flows higher on the edifice but is compositionally identical to flows of unknown age exposed at the Lower Tama Lake crater (Hackett, 1985). The Mananui dacite flow is characterised by MgO contents (2.8 wt. %) midway between that of the Mangaturuturu (2.2 wt. %) and Te Kohatu (3.3 wt. %) package flows at equivalent SiO₂ (~64 wt. %) and K₂O (~2.8 wt. %) contents. These geochemical characteristics are shared by a dacite clast sampled by Hackett (1985) from

the ~10.5 ka Murimotu Formation debris avalanche deposit, the source area of which coincides with a central vent location inferred for the Mananui dacite lava. Dacite exposed at the Tama Lakes also shares a similar composition, and is here grouped within the eruptive package (Fig. 3.9).

Figure 3.11. View of the Whakapapa River valley on the northwest flank of Ruapehu volcano. Distinct geographical features are marked in the top panel. Mapped extents of eruptive units are drawn in the bottom panel. Locations and eruption ages (WMPA $\pm 2\sigma$) of dated samples from this study are displayed. NG and TK are abbreviated labels for Ngahuinga and Te Kohatu packages, respectively.

Figure 3.12. (opposite). View of the Mangaturuturu Valley on the western flank of Ruapehu. Elevations are marked in the top panel and mapped extents of eruptive units are drawn in the bottom panel. Locations and eruption ages (WMPA $\pm 2\sigma$) of dated samples from this study are displayed. ME and MT are abbreviated labels for Mangaehuehu and Mangaturuturu packages, respectively.

3.4.3.6. Manganuioteao package (36–22 ka)

Manganuioteao package andesite lavas were emplaced as ice-bounded flows on the western flank of Ruapehu at 30.9 ± 2.2 ka and on the true right ridge that bounds the glaciated Mangaturuturu River valley at 30.7 ± 5.2 ka (Fig. 3.12). These flows cap older Te Kohatu and Mangaturuturu package dacites, however, a younger Manganuioteao andesite dated at 27.2 ± 4.8 ka forms an ice-bounded flow that is inset within the Mangaturuturu valley relative to the older, morphologically higher ~41 ka ice-bounded dacites and ~31 ka andesites (Fig. 3.12). The youngest dated lava within the Manganuioteao package is an ice-bounded flow emplaced at 25.7 ± 2.6 ka, which is exposed at 1600 m a.s.l. on the southwestern flank. These andesites are significant because they bridge the period between previously interpreted pulses of effusion at ~45 and ~22 ka (Gamble et al., 2003), thus revealing the continuity of effusive activity at this time. Moreover, the compositions of the flows (60–63 wt. %) fill a transitional geochemical field between older dacites and younger andesites.

3.4.3.7. Whakapapaiti package (30–22 ka)

Whakapapaiti package dacite flows are exposed at the base of the now-dissected Paretaitonga Peak as an ice-bounded flow on the outboard eastern side of the formerly more extensive Whakapapaiti Glacier, and on the upper western and southwestern flanks of Ruapehu (Fig. 3.10). Only one lava has been dated, at 25.7 ± 3.8 ka. The lavas are distinguished by their low K₂O contents relative to dacite flows erupted from 46–35ka.

3.4.3.8. Horonuku package (29–15 ka)

Horonuku package andesite lavas form major ice-bounded flows on eastern Ruapehu between elevations of 1600 and 1300 m a.s.l. (Fig. 3.10). Thicknesses of the flows and their heights above valley floors indicates that these flows were emplaced against ~100 m-thick glaciers. Two of these flows were dated by Gamble et al. (2003) at 23 ± 4 ka and 22 ± 7 ka (Table 3.1), and have not been further dated in this study. The flows are overlain by till and, at higher elevations on the edifice, by younger lava flows and pyroclastic deposits related to growth of the present summit cones.

3.4.3.9. *Te Piripiri package (27–15 ka)*

Te Piripiri package lavas form the lower northeast flank of the Ruapehu edifice and have later been blanketed by thick tephra on the predominantly downwind side of the edifice. The flows exhibit evidence of lava-ice interaction (Conway et al., 2015) and were emplaced at 21 ± 6 ka, as constrained by Gamble et al. (2003). Andesite lavas of this package range from 58–60 wt. % SiO_2 and have average MgO contents of ~5 wt. % (Table 3.3).

Figure 3.13. Features of Mangawhero Formation lavas. a) Northward view toward Girdlestone Peak (G) showing multiple flows within the Mangaehuehu eruptive package (ME). b) An ice-bounded Mangaturuturu eruptive package (MT) dacite lava overlies Ngahuinga eruptive package (NG) andesite lava and is capped by younger moraine (m) on the western flank of Ruapehu. A lava flow of the Te Herenga Formation (TH) is exposed on the valley floor at the base of the ridge. c) Column-forming joints on the margin of a Te Kohatu eruptive package ice-bounded dacite lava flow on northwest Ruapehu. Red circles are drawn around people separated by a distance of ~15 m. d) Northeast-looking view toward Girdlestone (G) and Tahurangi (Ta) of lava flows and moraines. An ice-bounded lava of the Makotuku eruptive package (MK) with an age of 20.9 ± 2.2 ka (sample CC408) is overlain by moraines with ~15–11 ka ^3He exposure ages (Eaves, 2015). The locations of post-glacial Turoa eruptive package (TR) and Rangataua eruptive package (RT) lava flows are also displayed.

3.4.3.10. Waitonga package (25–21 ka)

This eruptive package is exposed on the southwest flank of Ruapehu and is constrained by eruption ages of 23.0 ± 1.6 ka (Table 3.2) and 23 ± 8 ka (Gamble et al., 2003). Despite covering a wide spatial extent and with exposure from 2200–1200 m a.s.l., the flows exhibit a tight compositional range with ~62.1 wt. % SiO₂, ~3.6 wt. % MgO and 2.0 wt. % K₂O. Flows display evidence for interaction with glaciers, particularly at higher elevations (e.g. Fig. 3.6c in Conway et al., 2015), and are overlain by moraines at lower elevations, which have been dated by ³He surface exposure geochronology at ~15–11 ka (Eaves, 2015).

3.4.3.11. Makotuku package (24–16 ka)

Makotuku package lavas are located as ice-bounded and sub-glacial flows at mid-elevations on the southwestern flank and an extensive break-out flow, which overlies the Waitonga package lavas on the southwest flank of Ruapehu at ~1300 m a.s.l. (Figs. 3.10, 3.13d; Conway et al., 2015). This stratigraphic ordering is supported by an age of 20.9 ± 2.8 ka measured from an ice-bounded flow at 1720 m a.s.l. Lavas of this unit were also emplaced on southeast Ruapehu as ice-bounded or possibly sub-glacial flows (Conway et al., 2015). An eruption age of 17.8 ± 2.2 ka was measured for one flow, which is overlain by till, interpreted to have been deposited at ~15–11 ka (Eaves, 2015). Despite the interaction with glacial ice, the fine-scale columns (~10 cm-wide) are remarkably well-preserved, suggesting that only minor glaciation occurred in the valley after emplacement of the flow and/or that the glacier was already retreating. Additionally, Makotuku andesites unconformably overlie the core of the Wahianoa planèze beneath Mitre Peak on southeastern Ruapehu (Fig. 3.7), and the flows may have run onto and spilled over the edges of the former glacier to be sporadically preserved high above the valley on its northern and southern sides. Makotuku package flows are characterised by relatively low SiO₂ and MgO contents compared to Waitonga package lavas.

3.4.4. Whakapapa Formation (<15 ka)

The Whakapapa Formation comprises post-glacial lava flows erupted at <15 ka at Ruapehu (Hackett, 1985). Some lava flows assigned to this formation by Hackett (1985) and Price et al. (2012) are now re-mapped to older formations, while conversely some flows previously assigned to the Mangawhero Formation are now assigned to the Whakapapa Formation here. New $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data presented here provide the first absolute ages for these flows (Table 3.2). Whakapapa Formation lavas are categorised into eruptive packages that form the mid-upper flanks of the edifice (Fig. 3.14). Of the post-glacial flows, two samples yielded positive eruption ages within 2σ uncertainty of 0 ka (Table 3.2). While the dating method precludes more precise chronological control, these are nevertheless valuable data that indicate late Holocene (<5 ka) eruption ages for these lavas, consistent with their geomorphological characteristics. A further 8 samples yielded WMPA of ≤ 15 ka (Table 3.2). Time brackets for the eruptive packages are defined by taking into account individual $^{40}\text{Ar}/^{39}\text{Ar}$ WMPA and 2σ uncertainties for all relevant flows in the package, or are given an approximate central age for packages with one dated flow. For flows without $^{40}\text{Ar}/^{39}\text{Ar}$ data, ages are inferred from stratigraphic and geomorphic relationships.

3.4.4.1. Paretaitonga package (~15 ka)

A sequence of 1–2 m-thick lava flows, breccias and pyroclastic material caps the peak of Paretaitonga (2751 m a.s.l.; Fig. 3.15c) and the upper northwest flank (Fig. 3.11). Lavas flowed into the Whakapapaiti Stream valley down to ~1300 m a.s.l. Interaction of lava with snow and ice at upper levels (>2200 m a.s.l.) is evident in the form of deflected and impounded flow morphologies and the presence of fine-scale column-forming joints and pseudopillow fractures on flow margins (Conway et al., 2015). However, evidence for wholesale damming of these flows is absent, suggesting that ice volumes were of lesser extent than during eruption of Mangawhero Formation lavas. Similarly the summit geometry of a partial cone of successive lavas suggests a relatively ice-free vent area was established. The timing of flow emplacement is constrained by an age of 14.8 ± 3.0 ka, measured for a mid-sequence lava flow within the Paretaitonga package. Further age constraints come from the flows' emplacement above Whakapapaiti dacite (25.7 ± 3.8 ka) and the switch to northern flank construction following sector collapse and emplacement

of the Murimotu Formation debris avalanche deposit at 10.5 ka (see Iwikau package below). Individual flows were emplaced relatively rapidly, as they are stacked in a similar manner within the Whakapapa valley and share similar compositions (58.5 wt. % SiO₂; 4.5 wt. % MgO; 1.6 wt. % K₂O).

Figure 3.14. Distribution of Whakapapa Formation eruptive products and debris avalanche deposits. Locations for dated samples and relevant figures are displayed, as in Fig. 3.4.

3.4.4.2. Turoa package (17–10 ka)

Andesite lavas within the Turoa package were emplaced above and adjacent to older ice-marginal flows over much of the upper southwest flank at 1500–2800 m a.s.l. of the Ruapehu edifice between the Mangaturuturu and Mangaehuehu valleys. Timing of effusion is constrained by an age of 15.1 ± 2.4 ka for a lava flow that was bounded to the

south by a glacier that had a greater volume than the current Mangaehuehu Glacier. The youngest lavas of the Turoa package are a group of at least three andesite flows erupted in quick succession that exhibit complex stratigraphic relationships with older ice-marginal flows on the flank west of Tahurangi. The middle of the three observed flows yielded an eruption age of 11.9 ± 2.2 ka (Table 3.2). The flows exhibit fracture textures indicative of interaction between lava and ice/snow at ~ 1600 m a.s.l., however, evidence of wholesale impoundment by ice is absent. The remnant southwest Turoa cone exhibits a relatively intact sequence of lavas to the west-southwest, indicating that a relatively ice-free vent area was established. The northern and eastern portions of the cone are absent (Fig. 3.15c), however, and are inferred to have collapsed to form the Mangaio Formation debris avalanche deposit, which was emplaced down the eastern flank at ~ 4.6 ka (Donoghue and Neall, 2001).

Figure 3.15. Features of Whakapapa Formation package lavas. a) Contact (dotted line) between ~ 26 ka Whakapapaiti eruptive package dacite lavas (WH; orange) and overlying ~ 15 ka Paretaitonga package andesite lavas (PT; dark). Star marks ice-bounded knuckle. b) Exposure of the chilled base of an Iwikau package andesite lava flow with column-forming joints, which grades into baked till on the eastern Summit Plateau. c) View of the western side of the summit reveals the collapse scars (dotted lines) inward of summit cones comprised of Turoa (TR) and Paretaitonga (PT) package lava flows. The collapsed southern cone has been infilled by eruptive products of the Crater Lake package (CL). d) Fine-scale column-forming joints at the base of a glassy Turoa package andesite lava on southwest Ruapehu. Sledgehammer is ~ 1 m-long.

3.4.4.3. Rangataua package (~15 ka)

Rangataua package consists of a ~15 km-long series of overlapping flow lobes and pyroclastic deposits on Ruapehu's southern flank (Hackett, 1985; Price et al., 2012). The source of the flow is uncertain: the topographically highest outcrop is at 1980 m, where welded spatter and pyroclastic material was interpreted by Hackett (1985) to represent a collapsed vent. Alternatively, the vent may have been higher on the volcano and the lava flowed initially down the Mangaehuehu Glacier before it was diverted off the glacier through a low saddle to be emplaced on the relatively ice-free southern flank. Whichever hypothesis is correct, the Rangataua eruptive package was excluded from the Mangaehuehu valley to the west, likely due to the presence of valley-filling ice at the time of eruption. At lower elevations (~1600–1400 m a.s.l.) the flow laps onto ~15–11 ka moraines (Eaves, 2015). Rangataua package andesites are uniformly glassy, and no samples suitable for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology could be obtained. The ~15 ka age is therefore inferred from contact relationship with the moraines and their exclusion from the Mangaehuehu Valley by then present ice.

3.4.4.4. Tureiti package (15–9 ka)

This package consists of glassy, flow-banded, slope-mantling lavas and pyroclastic material on the upper northeast flank of Ruapehu. The lavas, two of which are dated at 12.5 ± 2.6 ka and 11.9 ± 2.8 ka, overlie Te Piripiri package andesite lavas of the Mangawhero Formation and exhibit evidence (ice-contact fracture networks and flow morphologies) for interaction with ~20 m-thick accumulations of ice/snow at 1400–1800 m a.s.l. The remnant Tureiti cone is well-formed and appears to have established a relatively ice-free vent area, however, its uppermost portion is not preserved. Distinct vent foci and magma systems are inferred for Tureiti and Paretaitonga cones based on the compositional characteristics of their respective lava flows (Fig. 3.14; Table 3.3).

3.4.4.5. Iwikau package (<10 ka)

This package comprises andesite lava flows erupted from a cone that is concealed beneath the present-day Summit Plateau ice field (Fig. 3.14). The north-western and eastern rims

of the cone sit at a lower elevation (<2700 m) than upper outcrops of lavas of the Paretaitonga (2751 m) and Tureiti (2732 m) packages, indicating that the summit height had been reduced prior to eruption of Iwikau package lavas. Changes to the summit morphology coincide with: (1) cessation of construction of the west-northwest Paretaitonga package-forming cone (~15 ka) and northeast Tureiti package-forming cone (~12 ka), and (2) emplacement of the 10.5 ka Murimotu Formation debris avalanche deposits at <1100 m a.s.l. on north-eastern Ruapehu from a sector collapse event (Palmer and Neall, 1989; Eaves et al., 2015). Iwikau eruptive package lavas were emplaced atop the Murimotu Formation on the north-western flank of Ruapehu and are therefore inferred to be younger than 10.5 ka. Three distinct flow groups within the Iwikau eruptive package are defined on the basis of spatial distribution and geochemistry and are temporally constrained by the first radiometric ages for these Holocene lava flows:

1. The Taranaki Falls lava flow (8.8 ± 2.8 ka) is rootless from the summit vent perhaps due to emplacement over, or erosion by, a now-retreated glacier. Below 1700 m a.s.l. the flow is confined to the floor of the Wairere Stream valley and displays levees perched up to 80 m above the adjacent valley sides at the narrowest point in the valley (Fig. 3.5), suggesting that the lava was emplaced as a single flow that filled the valley before being drained. The flow terminates at 1120 m a.s.l. with a ~40 m-high bluff, which likely formed as the flow attenuated on nearly flat ground rather than due to glacial impoundment.

2. The Iwikau group of flows is a voluminous sequence of lavas that forms the northern flank of the edifice from west of Pinnacle Ridge to the easternmost part of the upper Whakapapaiti Stream catchment, (Fig. 3.5). They unconformably overlie Tureiti package flows and form the prominent Te Heuheu and Tukino peaks on northern Ruapehu (Figs. 3.2, 3.14). Evidence for lava-ice interaction above 1800 m a.s.l. is present in the form of overthickened flow margins with fine-scale fracture networks indicative of chilling against ice (Conway et al., 2015). The timing of flow emplacement is constrained by a new $^{40}\text{Ar}/^{39}\text{Ar}$ eruption age of 6.0 ± 2.4 ka (Table 3.2), which was collected from a mid-sequence flow within the group.

3. The Mangatoetoenui group of flows lies unconformably above Wahianoa Formation and Mangawhero Formation Tukino package flows on the eastern flank of Ruapehu volcano (Fig. 3.7). Interaction of flows with ice and till occurred on the summit

(Fig. 3.15b) and upper flanks. Eruption of these flows is constrained by an age of 9.2 ± 8.0 ka for a flow at the Tukino ski field, which is ice-bounded and shows evidence for impoundment against a ~60 m-thick glacier, consistent with an early Holocene eruption age. An age of 0.8 ± 5.6 ka was measured for a flow on the eastern flank at 1300 m a.s.l. that appears to have not been affected by lower flank ice (consistent with a late Holocene eruption age) and laps onto the lateral margin of an ice-bounded Tukino package andesite flow within the Mangawhero Formation. Mangatoetoenui lavas were previously recognised as having encountered ice by Spörli and Rowland (2006), and were assigned to the Mangawhero Formation on the assumption that ice of sufficient volume to bound the flow must have been present at or before 20 ka. The new age data presented here instead indicate that ice thicknesses sufficient to impound 20–80 m-thick lava flows were present on the upper eastern flank at 1500–2200 m a.s.l. during the early Holocene. Glacial striae observed on the top of Mangatoetoenui lavas further indicate they were overrun, but not substantially eroded, by Holocene glaciers after their emplacement.

3.4.4.6. Saddle Cone package (<10 ka)

The Saddle Cone package comprises the Holocene northern flank-vent-sourced Saddle Cone lavas and an isolated glassy lava flow on the northern flank at ~1850 m a.s.l. (Figs. 3.5, 3.14). Previously inferred to have been erupted from a flank vent at 1990 m a.s.l. (Hackett, 1985), the upper isolated flow may instead have originated from a summit vent eruption that delivered the lava down an ice- or snow-covered flank to its current termination. Saddle Cone andesites (~58.5 wt. % SiO₂) were erupted from the Saddle Cone vent at 1500 m a.s.l. The freshness of Saddle Cone package lavas and minimal tephra cover is consistent with their proposed ~10 ka eruption ages based on tephra cover sequences (Nairn et al., 1998).

3.4.4.7. Pinnacle Ridge fall deposit (~10 ka)

The Pinnacle Ridge fall deposit is an isolated unit of the post-glacial Whakapapa Formation (Figs. 3.5, 3.14; Hackett and Houghton, 1989). It is a welded pyroclastic fall deposit that has a distinctly higher SiO₂ content (~61 wt. %) when compared to Iwikau

eruptive package lavas (Hackett, 1985). It was vented from a source close to its outcrop location on lower Pinnacle Ridge (Hackett and Houghton, 1989).

3.4.4.8. Crater Lake package (<5 ka)

This eruptive package comprises volcanic products erupted from Crater Lake, which consists of the unconsolidated mound of tephra and lava that forms Pyramid Peak (Figs. 3.2, 3.14) and a glassy andesite lava flow located within the Whangaehu valley (Fig. 3.12). The Whangaehu andesite lava flow can be traced from its termination at ~1300 m a.s.l. to a vent source at Crater Lake, and yielded a WMPA within error of present day (0.2 ± 2.2 ka). In contrast to all other post-glacial flows, this lava has a relatively high SiO₂ content of ~61.5 wt. %, but lies within the wide compositional spectrum for historical products erupted through the Crater Lake (~58–64 wt. % SiO₂; Gamble et al., 1999; Nakagawa et al., 2002; Kilgour et al., 2013).

3.5. DISCUSSION

3.5.1. Review of ⁴⁰Ar/³⁹Ar geochronology data

Sequential sampling of stacked lava flows at composite volcanoes permits testing of the stratigraphic integrity of radioisotopic eruption age data and robust investigation of time-composition relationships. Excepting flows of the Wahianoa Formation, thick sequences of lavas are rarely exposed at Ruapehu, however, due to the relationship between volcano growth and glacier fluctuations, resulting in complex stratigraphic contacts and lava flows with disparate, non-overlapping distributions (Conway et al., 2015). New and existing ⁴⁰Ar/³⁹Ar eruption ages now form a high-fidelity ~200 kyr-long chronostratigraphic framework (Fig. 3.16), which constrains eruptive events and episodes in detail and allows interpretation of time-composition-volume relationships at Ruapehu. The timing of eruption history is compared to a global paleoclimate record from Lisiecki and Raymo (2005) for purposes of comparing the timing of volcanism to general periods of cool and warm climate as represented by the marine isotope stages (MIS) that are labelled in Figure 3.16.

Previous workers have postulated that Ruapehu has an eruptive history that began >100 kyr prior to the age of its oldest ~200 ka lavas (Tanaka et al., 1997; Gamble et al., 2003), although no eruptive products of such age have been described from the edifice. Age constraints from marine terraces, cover bed stratigraphy and $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages for lava clasts (geochemically associated with Ruapehu) within distal debris avalanche deposits indicate that initial edifice growth began at ~340 ka (Tost and Cronin, 2015).

Figure 3.16. Effusive history of Ruapehu volcano compared to the global $\delta^{18}\text{O}$ record and marine isotope stages (MIS; Lisiecki and Raymo, 2005). $^{40}\text{Ar}/^{39}\text{Ar}$ ages are displayed for samples from this study (black diamonds) and Gamble et al. (2003; grey diamonds) with 2σ uncertainties (bars).

At the opposite extreme, a key objective of this study was to test the limitations of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer for young flows. WMPA eruption ages of <5 ka determined for this study (Table 3.2) are consistent with late Holocene ages from field evidence for the relevant flows. Three experiments on Holocene lavas produced 2σ uncertainties of 2.2–2.8 ka, which are comparable to those for older Mangawhero Formation lava flows and permitted the discrimination of lava flows into early (10–5 ka) or late Holocene (<5 ka) timeframes. This level of precision has previously not been achieved in any other studies of such young andesite lavas (e.g. Jicha et al., 2012). The results of this study support the application of $^{40}\text{Ar}/^{39}\text{Ar}$ dating to determine eruption ages for Holocene andesite lavas

with optimal 2σ uncertainties of ~2 kyr. Several Holocene flows were unable to be dated because emplacement and erosion of the lava had not exposed slowly cooled holocrystalline interior zones. These include andesite lava flows of the Rangataua and Saddle Cone eruptive packages.

3.5.2. Volcanic evidence for glacial history

Recognising and incorporating volcano-ice interactions into geological mapping of glaciated composite volcanoes is important for understanding their eruptive histories and morphologies, and can also provide valuable paleoclimate information (Stevenson et al., 2006). The crystalline or well-lithified nature of glaciovolcanic deposits (i.e. lava flows and volcanic breccias that have interacted with ice; Edwards et al., 2015) makes them resistant to erosion and, therefore, useful for extracting geochronological information that is pertinent to former ice extents (Russell et al., 2014). This gives them an advantage over glacial deposits and landforms such as till and moraines, which are susceptible to erosion between and during subsequent glaciations. Ruapehu has coeval eruptive and glacial histories and the past presence of ice on the edifice has strongly influenced emplacement of effusive products (Conway et al., 2015). Defining the temporal distributions of effusive glaciovolcanic products using $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology enables former glacier extents at Ruapehu volcano to be constrained. Glacial impoundment and the associated overthickening and slow cooling of the interior zones of thick flows of the Mangawhero Formation have produced favourable groundmass textures for $^{40}\text{Ar}/^{39}\text{Ar}$ dating. These zones have been exposed via erosion of the steep and finely fractured quenched lava flow margins. Fortuitously, Mangawhero Formation lava flows also contain relatively high K_2O contents that further aid $^{40}\text{Ar}/^{39}\text{Ar}$ measurement. The precision of the age measurements here permit ice extent reconstructions that are resolvable on timescales of 2-3 kyr during the period 50–15 ka.

3.5.2.1. Sub-glacial volcanism

Edifice-forming units of volcanoclastic breccia that underlie sequences of lava flows emplaced from ~200 ka (Te Herenga Formation) and ~166 ka (Wahianoa Formation) were originally interpreted as hydrothermally altered vent-association breccias (Hackett

and Houghton, 1989; Smith et al., 1999). Their volcanic origins are re-interpreted here as hyaloclastite breccia formed via magma-water/ice interaction. Basaltic and rhyolitic hyaloclastites have been described from Iceland and Antarctica (e.g. McGarvie, 2009; Skilling, 2009; Smellie et al., 2011), however, intermediate composition subglacial hyaloclastite breccias have only been observed or documented very rarely (e.g. Kerlingarfjöll, Iceland; Stevenson et al., 2009). Emplacement of the hyaloclastite mounds was also associated with ice-marginal effusion of basaltic-andesite lava flows. Once eruptive vents breached the surface of the confining glaciers and meltwater, lavas flowed downslope between glaciers and were sequentially emplaced marginal to glaciers at lower elevations. The northern ridges (Te Herenga Formation) and southeast planèze (Wahianoa Formation) are interpreted to have formed in this way. These older edifices resemble tindar ridges or complex tuyas, however, without the wide coherent lava caps typical of basaltic tuyas (Russell et al., 2014). Exposed thicknesses of basal hyaloclastite breccias of the Te Herenga and Wahianoa formations are ≥ 100 m, indicating that glaciers of at least equivalent ice thicknesses were present.

The most precise eruption ages measured for Te Herenga Formation lavas are between ~190 and 170 ka (Fig. 3.16). Emplacement of Te Herenga Formation hyaloclastite breccias are therefore inferred to have occurred during this time, which coincides with the glacial MIS 6 (Fig. 3.16; Lisiecki and Raymo, 2005). Hyaloclastite breccias beneath the Wahianoa Formation on the southeastern flank of Ruapehu are also assigned a MIS 6 emplacement age based on their position beneath lavas with eruption ages of <160 ka. This reconstruction implies that the large ice caps and glaciers were sustained on Ruapehu at elevations of ~2200–1500 m a.s.l. throughout MIS 6. An earlier edifice, reflecting volcanism at Ruapehu at ~340 ka (Gamble et al., 2003; Tost et al., 2015), provided sufficient elevation to host the ice mass. The elevation information taken from the distribution of the Te Herenga and Wahianoa formation breccias should be considered in the context of subsidence associated with a tectonic overprint of down-faulting and extension, however, suitably precise slip rates are not available to quantify this issue (Villamor and Berryman, 2006a).

3.5.2.2. Preservation and exposure of MIS 5 volcanic products at Ruapehu

It has been proposed that the deflection of lava flows by valley glaciers toward emergent ridges occurs during glacial periods in contrast to emplacement of lavas within valleys during interglacial periods (Lescinsky and Sisson, 1998). While the relationship between an interglacial climate and consequent valley-floor lava emplacement is evident for Holocene flows at Ruapehu volcano (Conway et al., 2015), it is harder to ascertain the same link for older interglacial lavas that may have been subsequently eroded and/or buried.

The hypothesis of valley-floor lava emplacement was tested for MIS 5, a relatively warm period and a previously inferred period of eruptive inactivity in Ruapehu's history (Fig. 3.16; Gamble et al., 2003), by measuring eruption ages for lava flows with characteristics of interglacial flows (i.e. intra-valley locations, low slope angles, long-run-out distances, covered by till). Eruption ages of 95.9 ± 3.5 and 88.1 ± 3.2 ka were measured for two such lava flows, which fall within MIS 5 (Lisiecki and Raymo, 2005). The lava flows have comparable compositions to older planze-forming lava flows of the Wahianoa Formation, and are therefore inferred to represent products from a continued magma system rather than being sourced from a new system that commenced at ~100 ka. The previously interpreted eruptive hiatus at ~115–80 ka (Gamble et al., 2003) reflected a sampling gap for poorly preserved lavas erupted during middle-late MIS 5 (Fig. 3.16). This is likely to be a common feature at glaciated composite volcanoes globally (e.g. Volcn Parinacota; Hora et al., 2007).

3.5.2.3. Glacier reconstructions using ice-marginal lava flows

In a compilation of paleoclimate records from speleothems, Williams et al. (2015) identified that during the last glaciation (i.e. MIS 4-2; Lisiecki and Raymo, 2005), maximum ice extents in New Zealand occurred at ~66–61 ka, an advance of mountain glaciers occurred at ~42–38 ka, and the timing of the New Zealand equivalent of the global LGM (i.e. ~26–19 ka; Clark et al., 2009) occurred at ~32–28 ka. Exposure age dating of moraines in the South Island of New Zealand has led to the identification of moraine-building events under full glacial conditions at ~42 ka, ~28–25 ka, 21 ka and 18 ka (Putnam et al., 2013a, 2013b; Kelley et al., 2014). Two discrete glacial advances are

recorded by moraine formation at >57 ka and ~30–18 ka at nearby Tongariro volcano (Eaves et al., 2016a). The distribution of ice-marginal lava flows erupted since ~50 ka at Ruapehu provides a valuable independent record of glaciation at this location in New Zealand.

Former ice extents at Ruapehu through time are constrained by a compilation of the elevations, extents, distances above glaciated valleys, and ages for lava flows that were emplaced against major valley-filling glaciers (Fig. 3.17). The vertical offset of ice-marginal flows above glaciated valley floors is used to estimate former glacier thicknesses (values rounded to nearest 10 m). The data indicate that former glaciers were 100–160 m-thick at elevations of ~1500 m a.s.l. between ~48 and 35 ka. Moraines and lower extents of ice-marginal flows indicate that glaciers descended to elevations of ~1200 m a.s.l., which is consistent with full glacial conditions at this time (McArthur and Shepherd, 1990; Eaves et al., 2016a). Synchronous cooling between Antarctica and New Zealand at ~42 ka has been proposed from moraine evidence in the Pukaki glacier region in South Island, New Zealand (Kelley et al., 2014). The age data for ice-marginal dacite lava flows on northwest Ruapehu serve to indicate the period of cooling may have lasted until at least 38 ka.

A sequence of ice-bounded flows that form the true right side of the deeply glaciated Mangaturuturu River valley allows a detailed interpretation of glacier volume fluctuation during MIS 3–2. With increasing height above the glaciated valley floor, lava flows yielded ages of 27.2 ± 4.8 ka, 43.4 ± 2.4 ka, 40.7 ± 4.6 ka, and 30.7 ± 5.2 ka (Fig. 3.12). A separate but proximal lava flow within the Manganuioteao package dated at 30.9 ± 2.2 ka is also elevated above its adjacent glacial valley by ~180 m. The distribution of dated lava flows indicates that the glacier volume within the Mangaturuturu valley was greater at ~31 ka than at ~44–35 ka.

The glacier is inferred to have retreated rapidly after ~31 ka to account for the ice-marginal emplacement of the flow closest to the valley floor at ~27 ka. Emplacement of eruptive products and/or edifice collapse may have changed the summit and flank morphology of Ruapehu and, in doing so, altered ice pathways to restrict or enhance glacier flow into different catchments. This may have resulted in glacier dynamics unrelated to climate over the time period of emplacement of these lava flows. Notably, the ~31 ka timing of maximum glacier thicknesses on western Ruapehu is broadly

consistent with full glacial conditions in the New Zealand Southern Alps at Pukaki at ~28 ka (Kelley et al., 2014) and Waimakariri prior to ~26 ka (Rother et al., 2015) and the incidence of New Zealand's global LGM equivalent at 32–28 ka inferred by Williams et al. (2015). The distribution of ice-bounded flows erupted between ~28 and 18 ka on southwest Ruapehu indicate former glacier thicknesses during this period were <100 m at elevations of 1500–1700 m a.s.l. The data imply that glacial conditions at Ruapehu volcano during the global LGM at ~20 ka were not as fully developed as during former periods of cooling centred at ~42 and ~31 ka.

Figure 3.17. Ice extent at Ruapehu over the last 50 kyrs. Glacier thicknesses are inferred from the height of dated ice-marginal lava flows above glaciated valley-floors and rounded to the nearest 10 m. Age data are presented in Table 3.2. Samples are coloured according to their elevation on the edifice. Shaded areas represent periods of glacial advance in New Zealand. The timing of cooling periods (a) and (b) is inferred from Southern Alps glacial moraines (Putnam et al., 2013a; Kelley et al., 2014) and speleothem records (Williams et al., 2015). The timing of period (c) correspond to the global Last Glacial Maximum (Clark et al., 2009). The timing of period (d) is inferred from moraines on Ruapehu and Tongariro volcanoes (Eaves, 2015).

Lava flows emplaced at <20 ka provide key clues to the rate of deglaciation at Ruapehu. The 17.8 ± 2.2 ka age of an ice-bounded andesite flow that was emplaced against a >50 m-thick ice-wall within the Wahianoa River valley indicates that glacial retreat was underway by this time. Although the flow interacted with ice, it is ~200 m lower than moraine crests bounding a valley that was fully glaciated at ~43 ka as indicated by eruption ages for ice-bounded lavas on its western side (Fig. 3.7). Any post-LGM glacial

advances within the valley were not sufficient to have significantly eroded the fine columns that characterise this ice-bounded lava flow. Changes in the distribution and morphology of lava flows erupted since ~15 ka are linked to the post-LGM history of Ruapehu. On the upper flanks (>2200 m a.s.l.) of the edifice <15 ka lava flows display evidence (i.e. localised ice-contact fracture networks, metre-scale overthickening, superficial glacial striae) for minor interaction with glaciers similar in extent to those present in historic times (Heine, 1963). At <1700 m a.s.l., <15 ka lava flows were emplaced on the floors of the previously glaciated valleys. Eruption ages for these flows constrain wholesale glacier retreat at Ruapehu between 18 and 15 ka. However, glacial fluctuations in response to short-term climate variability since ~18 ka on Ruapehu are complex (Eaves, 2015) and beyond the resolution of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology dataset. The geomorphic distinction between ice-bounded lava of the syn-glacial Mangawhero Formation and intra-valley lavas of the post-glacial Whakapapa Formation is underpinned by the new geochronology data reported in this study.

3.5.3. Compositional evolution of Ruapehu lava flows

Whole-rock geochemical analyses of Ruapehu lavas show archetypical continental crust-like major and trace element characteristics of global orogenic andesites and dacites (Cole, 1978; Gill, 1981). On closer inspection, they comprise diverse crystal cargoes hosted within dacitic to rhyolitic melts and are interpreted to represent the products of a complex interplay of assimilation, crystal fractionation, crustal anatexis and magma mixing processes within the lithosphere (Hildreth and Moorbath, 1988; Gamble et al., 1999; Price et al., 2012). The extent of magma differentiation generated by the combination of these processes has been inferred to have generally increased with time as reflected by increasing SiO_2 contents and $^{87}\text{Sr}/^{86}\text{Sr}$ values in progressively younger eruptive products (Graham and Hackett, 1987; Price et al., 2012). However, a lack of age data for post-50 ka lava flows has precluded a detailed investigation of this trend. A principal goal when studying composite volcanoes is to assess the variation in magma compositions over time-scales of tens to hundreds of kyr. The time-sequenced compositional variation of Ruapehu lava flows represents the ~200 kyr-long development of the overall magmatic system. While this idea has been explored for Ruapehu in previous work using a combination of petrology, major and trace element geochemistry,

and radiogenic isotope characteristics (Graham and Hackett, 1987; Gamble et al., 1999; 2003; Price et al., 2005; 2012), the improved chronological control and sampling resolution achieved in this study permits further interrogation.

Figure 3.18. Compositional evolution of lava flows versus eruption ages determined in this study (black diamonds) and by Gamble et al. (2003; grey diamonds). Error bars are 2σ uncertainties of the eruption age measurements.

Ruapehu lava flows display a gradual increase in SiO_2 and K_2O from ~200 to 80 ka (Fig. 3.18). The 186.2 ± 6.8 ka eruption age determined for the most mafic lava exposed on Ruapehu (CC348; ‘Ruapehu basalt’ of Price et al., 2012) amends its previous assignment to the Mangawhero Formation by Hackett (1985). Following a gap in effusive activity between 80 and 50 ka, compositional diversity was greatest during the period from ~48–35 ka and, despite a lack of lavas with SiO_2 contents between ~62 and 63 wt. %, effusion of dacite was prevalent during this time. Based on their MgO contents, lavas that were erupted between ~48 and 35 ka define a broad bimodal diversity (Fig. 3.19).

Mangaehuehu package andesites and Te Kohatu package dacites form a high-MgO trend when plotted against SiO_2 , whereas Ngahuinga package andesites and Mangaturuturu package dacites align with a lower-MgO compositional array, which is also representative of all other Ruapehu lavas (Fig. 3.19). The only other lavas from Ruapehu that plot on the high-MgO trend are ~26 ka Whakapapaiti package dacite flows, however, these have distinctly lower K_2O concentrations (Table 3.3). The coeval eruption of compositionally

distinct andesite and dacite packages, some of which have wide-ranging linear trends, implies the presence of a complex magma system for Ruapehu volcano at this stage of edifice growth. A gap in lava flow ages at ~80–50 ka precedes this phase (Fig. 3.16) and may represent a period during which magma bodies were stalled and differentiated by a range of processes, including mixing, crystal fractionation and crustal assimilation.

Lava flows erupted at ~30 ka have a relatively narrow range of compositions that are intermediate within the range defined by the 48–35 ka lavas and fall within the 62–63 wt. % SiO_2 compositional gap mentioned above. Post-25 ka lava flows display a trend to progressively less silicic and less potassic compositions with time, following eruption of Whakapapaiti package dacites (Fig. 3.18). The one exception to this trend is the late Holocene Whangaehu lava flow within the Crater Lake eruptive package (61.5 wt. % SiO_2). The strength of this trend contrasts with prior studies that surmised that Ruapehu eruptive products have generally become more evolved and compositionally variable with time (Graham and Hackett, 1987; Gamble et al., 1999; Price et al., 2012). This inference was influenced by inaccurate age control and incomplete sampling and has been refined with the improved chronostratigraphy provided here.

Figure 3.19. SiO_2 versus MgO (wt. %) diagram for 50–36 ka lava flows and ~26 ka Whakapapaiti package dacite. Open blue diamond is the dacite clast sample from the Murimotu Formation (Hackett, 1985). Lines are drawn for high- and low-MgO trends. Dotted lines correspond to the compositional gap for 50–36 ka lavas. Shaded fields indicate compositional ranges for pre-80 ka (i) and post-25 ka lavas (ii).

A model of random tapping of small batches of magma that have followed distinct lithospheric pathways of mixing and contamination has been inferred to explain the

generation of magmas and the complex and non-systematic geochemical changes over timescales of tens of years to tens of kyr observed in erupted products at Ruapehu (Gamble et al., 1999, 2003; Price et al., 2005, 2012) as well as globally (e.g. Dungan et al., 2001; Frey et al., 2004). In contrast, the enlarged dataset and careful sequencing of lavas presented here reveals a systematic and coherent long-term compositional evolution of effusive products. These trends are explored in detail in Chapter 4.

3.5.4. Integrating explosive and effusive records at Ruapehu

Effusive and explosive records are only rarely integrated in the study of complex volcanoes or volcanic fields (e.g. Hildreth and Fierstein, 2012) due to the different distributions and preservation potentials of lava flows and pyroclastic deposits. Amalgamating the two is important for understanding the hazards and periodicity of eruptive behaviour at arc volcanoes and requires high-resolution geochemical and geochronological control for both lava flows and pyroclastic deposits. Pyroclastic deposits on Ruapehu volcano are documented for the period from ~27–10 ka (Donoghue et al., 1995a; Cronin and Neall, 1997; Pardo et al., 2012). This period coincides in time with frequent effusive activity (Fig. 3.16), which allows for the investigation of compositional, spatial and temporal relationships between effusive and explosive andesitic volcanism at Ruapehu. Lava flows with different compositions and spatial distributions were erupted at this time (Figs. 3.9, 3.10, 3.14), indicating that vents plumbed multiple different magma reservoirs during this period.

The composition, age and spatial distribution of Mangawhero Formation lavas and Whakapapa Formation lavas that formed post-glacial cones (northwest cone comprising ~15 ka Paretaitonga package lavas; southwest cone comprising ~17–10 ka Turoa package lavas; and northeast cone comprising Tureiti package lavas at ~15–9 ka) are compared with tephras to test whether these cones were the sources for both effusive and explosive eruptions (Fig. 3.20). Te Piripiri package lavas (21 ± 6 ka) and Mangatoetoenui eruptive unit tephras (~22 ka) on northeast Ruapehu display distinctly lower SiO₂ and K₂O contents than other eruptive products of this age, however, they do not overlap (Fig. 3.20). Tephras of the Shawcroft (~13 ka), Oruamatua (13–12 ka), and Okupata-Pourahu (11.6 ka) eruptive units (terms from Donoghue et al., 1995a) define a compositional range that also overlaps with lava flows of the same age (Fig. 3.20).

Pardo et al. (2012, 2014) suggested that the vent focus changed from north to south on Ruapehu's summit plateau for the ~ 11.6 ka eruptive phase based on isopach maps for tephra deposits. New results presented here indicate that voluminous effusive activity was occurring from both northern and southern vents during this period giving rise to emplacement of Tureiti and Turoa package lavas, respectively. Effusive activity later continued from a northern vent that erupted the Taranaki Falls flow (8.8 ± 2.8 ka), Iwikau flows (6.0 ± 2.4 ka) and Mangatoetoenui flows (0.8 ± 5.6 ka). These lava flow extents and ages preclude a complete switch to a southern eruptive vent at 11.6 ka as inferred by Pardo et al. (2012, 2014).

Figure 3.20. SiO_2 (wt. %) versus eruption age for Mangawhero and Whakapapa formation lava flows and pyroclastic deposits. Boxes represent SiO_2 and age ranges for each eruptive package (colour key and abbreviations in Fig. 3.3). Numbered bars represent whole-rock compositional ranges (data from Pardo et al., 2012) for pyroclasts from Plinian eruptions forming the: Mangatoetoenui Tephra (1); Shawcroft Tephra (2); Oruamata Tephra (3); Okupata-Pourahu Tephra (4). Whole-rock compositional range for pyroclasts from historical eruptions (grey bar) uses data from Gamble et al. (1999), Nakagawa et al. (2002) and Kilgour et al. (2013).

The systematic long-term variation of lava flow compositions outlined in the preceding section (Compositional evolution) contrasts with the wide compositional array of historic pyroclastic deposits, which encompasses the SiO_2 content of most post-glacial Whakapapa Formation lavas (Gamble et al., 1999; Nakagawa et al., 2002; Kilgour et al., 2013; Fig. 3.20). This distinction likely reflects a difference in the sizes of the magma bodies involved in the respective eruptive styles: lavas were sourced from larger and

more homogenized magma bodies whereas historical pyroclastic eruptions have tapped small, ephemeral and isolated magma bodies. Both effusive and explosive activity have occurred in parallel through to the late Holocene, however, only volumetrically minor lava eruptions have occurred historically (Houghton et al., 1987). Conversely, pyroclastic eruptions with volumes similar to historic events have not been well-preserved in the prehistoric geological record.

3.5.5. Edifice-ring plain relationships

Composite volcanoes are inherently unstable due to the deposition of complexly intercalated lavas and pyroclastic deposits at high elevations on steep slopes. Glaciated volcanoes are additionally prone to sector collapse due to the prevalence of glacial erosion and ice-marginal lava emplacement processes in addition to hydrothermal alteration, all of which act to destabilise volcanic material. The recognition of glacial debuttressing as a key factor in the generation of landslides in alpine settings (e.g. Cossart et al., 2008) also applies to glaciated volcanoes (e.g. Capra et al., 2013). The volume of Ruapehu's edifice is matched by its surrounding ring plain (Hackett and Houghton, 1989), reflecting a high flux of volcanoclastic material. Previous workers have suggested that erosion during glacial periods MIS 4 and 2 resulted in accelerated lahar deposition on northeast Ruapehu (Cronin and Neall, 1997). In contrast, Tost et al. (2014) inferred that large volume sector collapse events from Ruapehu occurred at the transition from glacial to interglacial periods during the period of ~340–200 ka. Links between Ruapehu's edifice and ringplain are evaluated here through consideration of the processes that governed edifice instability throughout its growth history.

3.5.5.1. Links between syn-glacial volcanism and ring plain deposits

The recognition of volcano-ice interaction processes at Ruapehu has significant implications for understanding the generation of pre-historic debris avalanches and lahars. First, widespread evidence for lava-ice interaction for flows of the Mangawhero Formation (50–15 ka) indicates that large flank glaciers were then extant on Ruapehu. Modelling indicates that glaciers of such volume were likely fed by a large summit ice mass (Eaves, 2015). Lavas could only be emplaced on glaciated flanks of the edifice if

eruptive vents were able to penetrate the summit ice field and feed material to emergent planèze flanks between valley glaciers (Lescinsky and Sisson, 1998). In doing so magma-ice interaction must have generated (1) large quantities of meltwater as the ice was thermally eroded (Wilson and Head, 2007), and (2) volcaniclastic deposits that were subject to intense hydrothermal alteration as lava was fragmented and fluxed by meltwater and steam (e.g. Tuffen et al., 2001).

Mixtures of lava, ash and meltwater would have produced syn-eruptive lahars, and the presence of hydrothermally altered deposits especially in the summit vent area may have had a longer-lasting impact by forming an unsteady base upon which subsequent summit lavas were emplaced. Such deposits are exposed between Tahurangi and Girdlestone Peak. Second, widespread ice-marginal emplacement of lavas at Ruapehu during MIS 3-2 produced steep flows perched above or on the side of valleys. Steep, thick, and pervasively fractured lava flows are liable to collapse and produce debris avalanches (e.g. Hickson, 2000). The collapse of steep ice-marginal lava flows onto glaciers during glacial periods (when ice extent fluctuated) or into valleys during interglacial periods are likely to have generated debris avalanches at Ruapehu. Third, a proportion of lava flows was likely emplaced onto glaciers during eruption and eventually conveyed to the ring-plain as clastic material fragmented by quench-contraction and glacier motion. The revised chemostratigraphy of Ruapehu volcano will enable dated ice-marginal lavas on the edifice to be matched with corresponding ring plain debris avalanche and laharcic deposits using geochemical correlation in future studies.

3.5.5.2. Causes of Holocene sector collapse events at Ruapehu

Recognition and dating of major stratigraphic unconformities can provide understanding of the factors that promote sector collapses at composite volcanoes (e.g. Ownby et al., 2007). The cause of two major Holocene sector collapse events that resulted in the emplacement of debris avalanche deposits on the northern and southeastern flanks of Ruapehu are explored in this section. The Murimotu Formation comprises a hummocky debris field on northern Ruapehu that was emplaced at ~10.5 ka (Palmer and Neall, 1989; Eaves et al., 2015). The Mangaio Formation comprises debris flow diamictons emplaced on the southeastern flank of Ruapehu at ~4.6 ka (Donoghue and Neall, 2001). The 10.5 ka timing of emplacement of the Murimotu Formation follows the emplacement of lava

flows of the Paretaitonga (14.8 ± 3.0 ka) and Tureiti (12.5 ± 2.6 ka; 11.9 ± 2.8 ka) eruptive packages on the upper northwest and northeast flanks respectively. These lavas form now-truncated summit cone structures that correspond to the inferred source position of the collapse (Figs. 3.14, 3.21). The cones are inferred to have been ice-bounded at the summit due to evidence for ongoing lava-ice interaction for upper flank lava flows of this age (Fig. 3.15a) and the deposition of ~ 15 – 11 ka moraines at elevations of ~ 1800 m a.s.l. (Eaves, 2015). The presence of a summit ice cap during cone construction likely resulted in the production of clastic deposits during interaction with ice and/or water and extensive hydrothermal alteration of deposits (Fig. 3.15b). Due to the preceding ~ 30 kyrs of volcano-ice interaction during MIS 3-2, the summit region was likely composed of steep topography, hydrothermally altered and fragmental deposits, which also provided an inherently unstable base beneath the younger cones (Fig. 3.15a).

Previous hypotheses for the generation of the northern sector collapse have invoked destabilisation of the northwest flank due to emplacement of a dacite cryptodome (McClelland and Erwin, 2003) or intrusion of dykes (Hackett and Houghton, 1989; Palmer and Neall, 1989). Emplacement of a dacite lava dome was proposed based on the measurement of $\sim 350^\circ\text{C}$ emplacement temperatures for clasts within the deposit (McClelland and Erwin, 2003). Geochemical analyses were not undertaken for the clasts from which geomagnetic data and emplacement temperatures were acquired, however, and only one analysis has reported a dacitic composition for a clast within the Murimotu Formation (Hackett, 1985). Substantial dacite effusion occurred between 46 and 36 ka (Figs. 3.9, 3.18), with a later episode at ~ 26 ka, that produced lava flows on the northern and western flanks. There is no precedent for dome-forming activity during these periods of dacite effusion at Ruapehu recorded on the exposed edifice. Contrary to the conclusion from Hackett and Houghton (1989), dacite flows have now been mapped on the upper northwest flank of the Ruapehu edifice (Figs. 3.9, 3.10) and are exposed within the sector collapse scar region at 2600 m a.s.l. (Fig. 3.15a). Furthermore, effusion of dacite at ~ 10.5 ka is contradictory to the coherent trend towards basaltic-andesite compositions seen in eruptive products since ~ 25 ka (Fig. 3.18).

The occurrence of dacite clasts within the deposit can be accounted for by incorporation of older Mangawhero Formation dacite flows from the source area, as proposed by Palmer and Neall (1989). The characterisation of distinct compositions for dacite within the Mangawhero Formation allows correlation of the clast analysed from the Murimotu

Formation by Hackett (1985) with the Mananui package flow (Fig. 3.19). This dacite flow on northern Ruapehu is inferred to have been erupted from a central or northern vent that coincides with the area of edifice collapse (Figs. 3.9, 3.21).

Figure 3.21. View of the northern flank of Ruapehu. The 10.5 ka Murimotu Formation debris avalanche deposit is inferred to have originated from collapse of pre-Holocene cones comprised of Tureiti and Paretetaitonga eruptive packages. The sector collapse source area and pathway has been infilled and covered by Iwikau package andesite lava flows. Timing of emplacement of the lava flows is constrained by a measured eruption age of 6.0 ± 2.4 ka.

Deglaciation is here considered a primary factor for the 10.5 ka sector collapse of northern Ruapehu, however, an earthquake or eruption may have provided the immediate

trigger for failure of the edifice. Post-LGM warming is inferred to have been a global trigger for sector collapses at glaciated volcanoes, due to the debuttreasing of volcanic material emplaced against ice or undercut by glacial erosion, lithospheric unloading and associated faulting, increased fluid circulation, and initiation of a more humid climate (Capra, 2006). Wholesale deglaciation of the Ruapehu edifice is inferred to have occurred from 18–15 ka, as discussed above (see Glacier reconstructions using ice-marginal lava flows), although a summit ice cap and upper flank glaciers are likely to have remained for several kyrs after the initial onset of deglaciation at 18 ka. Rapid climate amelioration from ~11 ka is indicated by regional records (e.g. Newnham et al., 2003). The retreat of glaciers and summit ice would have debutressed the Paretaitonga and Tureiti cones and resulted in destabilisation of the steep, hydrothermally altered edifice underlying the cones.

The collapse coincides with a period of regional extension and elevated volcanic activity around the northern flank of Ruapehu (Nairn et al., 1998). Disruption via seismic or volcanic activity may have provided the eventual trigger for the collapse of the cones. A similar process is invoked for emplacement of the Mangaio Formation debris avalanche deposit on southeast Ruapehu at ~4.6 ka. The northeastern portion of the southern cone that is composed of Turoa package lava flows has collapsed. Destabilisation of the cone during Holocene glacial retreat is here proposed to have caused its collapse into the Whangaehu River valley following emplacement of the cone's uppermost lavas at 11.9 ± 2.2 ka. The inferred link between deglaciation and sector collapse at Ruapehu volcano serves as a warning for future potential hazards during the current period of rapid warming and deterioration of ice masses on glaciated composite volcanoes in mid-latitudinal regions (e.g. Rivera et al., 2006).

3.5.6. Eruptive volumes and rates

The long-term eruptive rate for Ruapehu of $0.6 \text{ km}^3 \text{ kyr}^{-1}$ since ~250 ka using a total edifice volume of 150 km^3 was previously determined by Hackett and Houghton (1989) and Gamble et al. (2003). The rate is $1.2 \text{ km}^3 \text{ kyr}^{-1}$ when the equivalent volume of ring plain deposits is included. These rates are broadly comparable to those calculated for Mt. Katmai ($0.79 \text{ km}^3 \text{ kyr}^{-1}$; Hildreth et al., 2003) and El Misti ($0.63 \text{ km}^3 \text{ kyr}^{-1}$; Thouret et al., 2001), but are substantially greater than those for most other well-dated composite

volcanoes, which are $<0.35 \text{ km}^3 \text{ kyr}^{-1}$ (Table 3.4). Conservative volumes for eruptive products of Ruapehu were calculated here using the revised mapping results of this study (Table 3.4).

Table 3.4. Volumes and eruptive rates for global examples of arc composite volcanoes.

Volcano	Volume (km^3)	Duration (kyr)	Avg rate ($\text{km}^3 \text{ ka}^{-1}$)	Reference
Mt Baker (stratocone)	15	43	0.35	Hildreth and Lanphere, 2003
Parinacota	46	160	0.28	Hora et al., 2007
Tatara-San Pedro	55	930	0.06	Singer et al., 1997
El Misti	70	112	0.63	Thouret et al., 2001
Katmai	70	89	0.79	Hildreth et al., 2003
Puyehue	80	320	0.25	Singer et al., 2008
Seguam	80	320	0.25	Jicha and Singer, 2006
Ceboruco-San Pedro	81	810	0.1	Frey et al., 2004
Tanaga	90	300	0.3	Jicha et al., 2012
Mt Adams (stratocone)	200	520	0.38	Hildreth and Lanphere, 1994
Ruapehu				
Te Herenga Formation	28	50	0.56	
Wahianoa Formation	74	60	1.23	
Mangawhero Formation	28	35	0.8	
Whakapapa Formation	12	15	0.8	

References for global examples indicated in table. Revised volumes, durations and eruptive rates for Ruapehu formations in this thesis are defined here.

A large volume of the modern edifice is composed of till that within any one glacial catchment can represent a diverse assemblage of clasts of variable age and composition. It is therefore impossible to reconstruct the volumes of lava from individual formations and eruptive packages that comprise moraines and outwash fans on the Ruapehu edifice. However, estimated volumes of glacially eroded eruptive products from the Te Herenga, Wahianoa and Mangawhero formations are incorporated into the measurements made in this section. Half-volumes of right-angle circular cones were calculated to approximate pre-eroded volumes of 28 km^3 and 74 km^3 for the Te Herenga and Wahianoa formations, respectively (Table 3.4). These calculations oversimplify the geometry of the volcanic edifices formed during these periods of volcanism but are intended to account for the substantial amount of material that has been eroded and transported to the ring plain.

A total eruptive volume of 28 km^3 for the Mangawhero Formation was calculated by applying average lava flow thicknesses based on field observations to the measured areal extent of syn-glacial lava flows. The estimate also incorporates the inferred volume of lava flows emplaced onto glaciers and eroded by glacial and fluvial activity. The volume

of lava transported to the ring plain by glaciers both during (via supra-glacial emplacement of lava) and following effusive eruptions is difficult to quantify. Furthermore, a low degree of certainty is assigned to this calculation to reflect the generalised thickness estimates that are biased by outcrops at flow margins where lavas were impounded and overthickened against ice. Conversely, the recognition of ice-marginal flow emplacement improves the accuracy of the estimate by discounting the back-calculation of eruptive volumes inferred to have been lost via valley incision. Post-glacial lava flows of the Whakapapa Formation were calculated to total 12 km³ in volume. This value has a higher degree of confidence than that given to volumes for pre-15 ka eruptive products due to the minimal post-emplacement erosion and burial of Whakapapa Formation lavas. The abnormally shallow and consistent slope gradient observed for the northern flank of Ruapehu is considered to be the result of infilling of a deeper glaciated valley by debris avalanche deposits of the Murimotu Formation, upon which Iwikau package lavas were subsequently emplaced (Fig. 3.21).

The volume of Te Herenga Formation eruptive products is likely underestimated due to burial and limited exposure of the edifice constructed at ~200–150 ka. The value of ~28 km³ is significantly lower than previously determined (65 km³; Hackett and Houghton, 1989), which likely assumed a much greater mass beneath the current composite volcano. Much of this buried volume may be able to be accounted for by earlier volcanic products (i.e. erupted between 340 and 200 ka). The revised volume estimate of 74 km³ for Wahianoa Formation eruptive products reported here is greater here than in previous studies because it incorporates lavas erupted during MIS 5 that are interpreted to be poorly preserved.

No lava flow eruption ages have yet been returned that lie during or in the 10 kyr either side of MIS 4 (Fig. 3.16). Two hypotheses are presented to explain this absence: 1) there was an eruptive hiatus, perhaps forced by loading of the edifice due to voluminous edifice growth over the previous >100 kyr and compounded by particularly voluminous ice cover centred on 60 ka; or 2) effusive activity continued but, due to extensive glaciation of the edifice, lava flows were not emplaced on flanks and were instead transported supra-glacially to the ring plain. Full glacial conditions in alpine regions during MIS 4 have been inferred from speleothem records (Williams et al., 2015), and extensive glaciation of Ruapehu is implied by exposure age dating of moraines on nearby Tongariro at ~60 ka (Eaves, 2015). If lavas were either unable to break through a thick ice cap that covered

eruptive vents or were erupted onto fully glaciated flanks with no emergent topography resulting in conveyance to the ring plain, they would not be recognised in the lava record on the Ruapehu edifice. Alternatively, compositional characteristics of lavas erupted during the following period of ~48–35 ka indicate that their source magmas underwent an extended period of differentiation, which may implicate a preceding eruptive hiatus and indicates that the former hypothesis is probable.

Voluminous effusion occurred during glacial MIS 3 and 2, and continued into the current interglacial MIS 1 (Fig. 3.16). A central question to glaciovolcanic studies is whether glacial retreat after ~20 ka and the associated reduction of confining pressures on magma chambers led to increased rates of eruption in post-glacial times (Tuffen, 2010).

Qualitative arguments for accelerated volcanic activity following deglaciation have been presented for Mazama in western USA (Bacon and Lanphere, 2006) and three Chilean volcanoes (Gardeweg et al., 1998; Singer et al., 2008; Mee et al., 2009). Approximately equal eruption rates have been calculated here for the syn- and post-glacial effusive periods, indicating that deglaciation did not lead to elevated volcanic activity at Ruapehu.

3.6. EVOLUTIONARY MODEL FOR RUAPEHU

Geomorphological, geological, glaciological, geochronological and geochemical datasets acquired from this study have been combined with pre-existing data to reveal the evolution of Ruapehu. This is summarised in a 10-stage development model outlined below:

1. Sub-glacial eruption and emplacement of Te Herenga Formation breccias and lavas occurred onto a pre-existing ice-capped edifice that had been active for a previous ~140 kyr. The vent-proximal section of this complex edifice is exposed at Pinnacle Ridge. Breccias were deposited in meltwater corridors and ice-marginal lava flows were emplaced on ice-free flanks and ridges extending north from the vent area from ~200–150 ka.
2. Sub-glacial eruption of Wahianoa Formation breccias and dykes occurred prior to 166 ka. Ice-marginal emplacement of a voluminous lava flow and breccia sequence constructed the southeast planèze flank from 166–110 ka.

3. Eruptions of andesite lavas from a central vent onto an edifice with reduced ice mass continued from ~100–80 ka. These lava flows were emplaced within glacially eroded valleys due to the absence of flank glaciers during MIS 5.
4. An eruptive hiatus and period of magma accumulation, storage and fractionation occurred from ~80–50 ka. The Ruapehu edifice was covered in ice during this time, corresponding to the advance of glaciers during MIS 4.
5. Eruption of andesite-dacite lava flows onto a glaciated edifice from ~48–36 ka resulted in ice-marginal emplacement of lava flows and construction of high planèzes and ridges on the mid-lower southern and western flanks of the edifice. Ice-dammed and ice-bounded flows were overthickened by 100–160 m at elevations of 1500 m a.s.l. Wide compositional ranges within individual eruptive packages and substantial effusion of dacite indicate that this eruptive period was preceded by magma storage and fractionation, as inferred above.
6. Effusive activity continued from ~35–25 ka, with ice-marginal emplacement of lavas onto the glaciated edifice. The positions of ice-bounded flows indicate that ice cover during the last glacial period (MIS 4-2) was most extensive at ~31 ka.
7. Eruption of lavas onto the glaciated Ruapehu edifice continued from ~25–15 ka, with coeval explosive activity. Impoundment of flows occurred at lower elevations than the preceding ~20 kyrs and ice-bounded lava flows were thickened by up to 100 m.
8. Construction of glacially-bound summit cones and emplacement of upper flank lavas occurred between ~15–10 ka. Turoa, Paretaitonga, and Tureiti cones were built adjacent to summit glaciers prior to 10 ka, atop steep, altered underlying vent-proximal eruptives.
9. Deglaciation during rapid warming resulted in destabilisation of the perched, ice-buttressed summit cones and led to a sector collapse event at 10.5 ka, resulting in emplacement of the Murimotu Formation debris avalanche deposit on the northern flank of Ruapehu. Iwikau package lava flows (<10 ka) were emplaced on top of the Murimotu Formation to the north and on the upper-mid eastern flank. The lavas form a cone that sits within the 10.5 ka collapse scar and is now filled by ice within the Summit Plateau.
10. Destabilisation and collapse of the southern summit cone, composed of Turoa package lavas resulted in another sector collapse event and deposition of the Mangaio

Formation on eastern Ruapehu at ~4.6 ka. Activity over at least the last ~2 ka has been focussed through Crater Lake within the scar of the collapsed southern cone. This activity has included the effusive eruption of Ruapehu's youngest andesite lava flow into the Whangaehu valley, the formation of the small-volume scoria cone surrounding the lake, and historic phreatomagmatic and lahar events.

CHAPTER 4

4. NEW PETROLOGICAL, GEOCHEMICAL AND GEOCHRONOLOGICAL CONSTRAINTS ON ANDESITE-DACITE MAGMA GENESIS AT RUAPEHU

ABSTRACT

The geochemical variation of lavas erupted at Ruapehu provides information on the development and evolution of a magma system feeding a large composite volcano in a continental volcanic arc setting. New petrological, geochemical and microanalytical data are integrated here with existing published data, and placed within the high-resolution stratigraphic framework from Chapter 3 to document the evolution of the exposed portions of the Ruapehu edifice.

A general increase in SiO₂, K₂O and incompatible trace element contents (e.g. Rb, Zr) and ratios (La/Yb) in basaltic-andesite and andesite lavas erupted from ~200 to 80 ka is matched by increasing values of ⁸⁷Sr/⁸⁶Sr, as constrained by existing isotopic data. Following an apparent ~30 kyr eruptive hiatus, magma compositional diversity was relatively large for the eruptive period from 50–35 ka. Over a ~8 wt. % SiO₂ range, the basaltic-andesite to dacite lavas erupted during this period define a high-K/Ca trend and elevated incompatible trace element contents compared to all other documented eruptive products from Ruapehu. Melt inclusion, interstitial glass and melt pockets in partially fused feldspathic xenoliths contained within dacite lavas from this period contain high K₂O (5–6 wt. %) and Rb contents (250–280 ppm). The whole-rock characteristics are interpreted to reflect the generation and assimilation of partial melts of the greywacke-argillite basement within the magma system beneath Ruapehu following >150 kyr of progressive heating of the lithosphere. The glass compositions can be explained by selective partial melting and assimilation of a K- and Rb-rich mineral phase (e.g. biotite) within the meta-sedimentary mineral assemblage.

Lavas erupted at 50–35 ka are also unique within the lifetime of Ruapehu in that they contain a lineage of highly-magnesian andesites and dacites. The mineral assemblage of the lavas, which also display strong evidence for crustal assimilation (e.g. isotopic data, abundant xenoliths), is characterised by abundant reverse-zoned pyroxene crystals with resorbed and rounded cores overgrown by rims with $\sim\text{Mg}\#_{90}$. The pyroxene crystal population records a mixing event between recharging mafic magmas and stalled felsic magmas in the crust. This process has been described elsewhere for several examples of highly-magnesian andesites and dacites but is in contrast to other types of Mg-rich andesites that are arguably derived from mantle melting processes.

Whole-rock compositions of lavas erupted at ~ 35 –26 ka are intermediate between those of the andesites and dacites erupted at 50–35 ka, whereas from 26 ka onwards the lavas display a strong reversion to more mafic and less potassic compositions with time. Furthermore, these lavas have lower whole-rock incompatible trace element contents and ratios, and contain less potassic melt inclusions when compared to the 50–35 ka lavas. Post-26 ka lavas are interpreted to have assimilated less enriched melts due to the exhaustion of fertile phases in the crustal column from prior melting and/or higher degrees of melting of continental crust associated with ongoing magma and heat flux through the volcanic plumbing system beneath the Ruapehu edifice.

The expanded and revised geochronology for Ruapehu has permitted the detailed geochemical sequencing of lava flow compositions in this chapter and consequently revealed systematic changes in the degrees of magma differentiation by fractionation and crustal assimilation processes throughout the ~ 200 kyr lifetime of the exposed edifice. The results highlight the value of well calibrated chronostratigraphic frameworks for investigating time-composition relationships at composite volcanoes.

4.1. INTRODUCTION

The compositional ranges of eruptive products generated over the lifetime of continental arc volcanoes often display linear compositional spectra that extend from basalt to dacite and, occasionally, rhyolite (e.g. Hildreth et al., 2003; Hora et al., 2007; Singer et al., 2008; Hildreth and Fierstein, 2012). The time-sequenced geochemical variations of eruptive products are typically non-systematic, however, and do not necessarily reflect the long-term evolution of a common magma source by simple progressive fractionation

and assimilation (cf. Eichelberger et al., 2006). The timescales of compositional heterogeneity specified by the products of short-lived eruptive episodes ($<1\text{--}20$ yr; e.g. Clynne, 1999; Coombs et al., 2000, 2013) or preserved in lava flow sequences ($1\text{--}10$ kyr; Gamble et al., 1999, 2003; Frey et al., 2004), indicate that magmas with diverse parentage are generated and erupted relatively frequently. At an extreme, for the geochemical differences within consecutively erupted samples to be attributed to variations within the initial mantle source region of arc magmas (i.e. different degrees of melting or contribution of fluid or melt from the subducted slab and sediment), eruptive products would need to represent individual aliquots of magma that retained their signature from a mantle source (e.g. Davidson et al., 2005). In most cases, however, compositional sequences are instead likely to reflect the eruption of discrete batches of magma that have followed unique pathways of differentiation in the crust (e.g. Hobden et al., 1999; Gamble et al., 2003; Frey et al., 2004; Eichelberger et al., 2006; Sisson et al., 2013).

The processes of crustal anatexis, magma mixing and crystal fractionation and separation are the primary agents of magma differentiation within the middle to upper crust beneath arc volcanoes (e.g. Price et al., 2012; Kent, 2013; Lee and Bachmann, 2014). Two commonly documented signatures of intermediate arc magmas that arise from these processes are: (a) the generation and entrapment of melts that are substantially more silicic than their host whole-rock compositions (see compilations by Reubi and Blundy, 2009; Kent, 2013), and (b) disequilibrium petrographic textures that reflect mixing between silicic components with mafic magmas and their crystal material and/or evolving intensive parameter such as pressure, temperature and degassing (e.g. Clynne, 1999; Dungan and Davidson, 2004; Kent et al., 2010; Koleszar et al., 2012). Because the felsic and mafic end-members seldom erupt independently at composite volcanoes, their cryptic existence within crustal magma systems is recorded within mineral-hosted melt inclusions or interstitial glass (e.g. Reubi and Blundy, 2008) and the crystal cargo of the derivative intermediate composition magmas (e.g. Streck et al., 2007). Thus, the nature and origin of felsic and mafic sources, and the processes by which they interact, may be elucidated by microanalytical investigations (Davidson et al., 2007). Constraining these magma sources and the subsequent mixing parameters and processes is critical to understanding the assembly of arc magmas and the recycling of elements throughout Earth's subduction zones.

The longevity of subduction zones results in the repetitive transfer of heat to the lithosphere (e.g. Dufek and Bergantz, 2005) as primary magmas are generated in, and ascend from, the mantle wedge. The composition of eruptive products from composite volcanoes therefore record the cumulative effect of progressive heating and conditioning of the lower, middle, and upper crust because their source magmas have passed through these regions. How magmatic sources and processes vary throughout time and what controls those variations are fundamental questions for understanding both the eruption potential of arc volcanoes and the development of continental crust. Critical to addressing these questions is the collection of high-resolution eruptive histories for arc volcanoes that are constrained by field studies and radiometric age data so that eruptive products can be accurately sequenced (e.g. Dungan et al., 2001; Frey et al., 2004). In this regard, Ruapehu represents an ideal case study to investigate the compositional development of a magma system throughout the lifetime of a composite volcano as represented by exposed rocks. The geochronological framework for the effusive history of Ruapehu outlined in Chapter 3 is used here to sequence whole-rock and microanalytical mineral and melt compositions in order to investigate the genesis of andesite-dacite magmas in a continental arc setting.

4.2. BACKGROUND AND PREVIOUS WORK

The mountain that has been named Ruapehu is a 150 km³ composite volcanic edifice primarily composed of stacked sequences of lava flows and associated breccias intercalated with till and subsidiary volumes of proximal pyroclastic flow and fall deposits. The greatest volume of lava flows are porphyritic andesites that comprise mineral assemblages dominated by plagioclase and pyroxene. However, basaltic-andesites and dacites have also been erupted over the time period studied here, and a range of complex crystal and lithic cargoes are found throughout the eruptive products. The crystals are typically not in equilibrium with the host whole-rock compositions (Price et al., 2012). Furthermore, melt inclusion and matrix glass compositions from lava flows of the Wahianoa and Whakapapa formations (Price et al., 2005, 2012) and from pyroclasts in historical tephra deposits (Donoghue et al., 1995b; Gamble et al., 1999; Kilgour et al., 2013) range from dacite to rhyolite and are significantly more silicic than the host whole-rock compositions.

Detailed petrographic descriptions were first undertaken by Clark (1960) and later advanced by Cole (1978). Graham and Hackett (1987) described six petrographic types with corresponding models of magma formation, additionally constrained by geochemical and isotopic data. Significantly, these models accounted for the crust-like geochemical and isotopic composition of Ruapehu lavas by invoking partial melting and assimilation of mid-upper crustal greywacke-argillite basement during magma genesis (see also Graham, 1987).

The overall development of the magma system beneath Ruapehu was later explored within stratigraphic contexts by Waight et al. (1999), Gamble et al. (1999, 2003) and Price et al. (2005). A model for the polybaric generation of derivative magmas by multiple episodes of melting, mixing, assimilation and fractionation within an open magmatic system was generated from these studies (see Price et al., 2012 for summary). This model allows for the non-systematic geochemical and isotopic variations observed over timescales ranging from short-lived explosive episodes and cycles (1–50 yr; Gamble et al., 1999; Kilgour et al., 2013) to successive lava flow emplacement phases (1–10 kyr; Waight et al., 1999; Gamble et al., 2003).

Over the >200 kyr lifetime of Ruapehu, however, a general progression towards more evolved compositions with time was proposed based on whole-rock geochemical variations using the available stratigraphic constraints (Graham and Hackett, 1987; Price et al., 2012). The oldest lavas exposed on the edifice (Te Herenga Formation) have distinct $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ characteristics that set them apart from all subsequent lavas (Price et al., 2005). On this basis, Graham et al. (1990) and Price et al. (2005, 2012) argued that Te Herenga Formation lavas were contaminated by Phanerozoic oceanic crust whereas younger lavas assimilated partial melts of shallower meta-sedimentary source rocks in the mid-upper crust.

Within the context of prior datasets from Ruapehu there are three key areas that warrant further investigation on the basis of the new data obtained for this thesis:

1. Time-composition relationships. Incomplete sampling of the edifice and a lack of chronological controls have hampered a comprehensive definition of the geochemical evolution of the Ruapehu magma system. Complex stratigraphic relationships as a result of lava-ice interaction and sparse radiometric eruption age constraints (see Chapters 2 and 3) have prohibited accurate definition of the relative and absolute eruption ages for lava

flows of the Mangawhero and Whakapapa Formations that form much of the modern-day edifice. A new high-resolution, high-precision geochemical stratigraphy for lava flows (Chapter 3) allows investigation of the broad evolution and distinct periods and modes of magmatism during the lifetime of Ruapehu.

2. Nature and origin of silicic melts. Melt inclusion and matrix glass data have previously been acquired for lavas of the Wahianoa and Whakapapa formations (Price et al., 2005), but there is a lack of data for Te Herenga Formation eruptive products as well as newly defined packages identified within Mangawhero Formation. Outstanding questions in this regard include: (a) are the rhyolitic melts contained within Ruapehu lavas comparable to the products of silicic volcanism elsewhere in New Zealand's continental volcanic arc, and (b) are the distinct whole-rock compositions of Te Herenga Formation lavas reflected in their melt inclusion compositions?

3. Felsic-mafic interactions. In light of the dominance of silicic melt compositions, is there evidence for mafic recharge in the generation of intermediate (andesite-dacite) magmas, as postulated from local (Nakagawa et al., 2002) and global (Kent et al., 2010) studies? Is this a common process involved in the generation of magnesian andesites and continental crust at volcanic arcs globally?

4.3. METHODS

An extensive sample suite of lava flows was acquired during fieldwork from 2012–2015. The distribution of samples collected for this study is compared to previous sample locations in Figure 4.1. A full sample list is available in Appendix A3. The analytical techniques employed to determine whole-rock, mineral and glass compositions are outlined in this section.

4.3.1. XRF: whole-rock major elements

Fresh interiors of samples were acquired by using a diamond saw to cut away any remaining weathered surfaces not already removed in the field. Samples were crushed and then milled using an agate or tungsten-carbide ring mill to form a whole-rock powder.

Figure 4.1. Location of previously sampled material (black triangles) and new samples (red triangles) of edifice-forming eruptive products. Previous samples are from Hackett (1985) and Price et al. (2012). A full list of new sample locations is given in Appendix A3. The map projection is New Zealand Transverse Mercator (NZTM 2000) and values next to ticks are accordingly in metres.

Major element compositions for 238 whole-rock powder samples were determined using an ARL® 8420+ dual goniometer wavelength dispersive X-ray fluorescence (XRF) spectrometer at the Open University, United Kingdom. Fused lithium metaborate glass discs were prepared for each powder and analysed following the methods of Ramsey et al. (1995). Glass disks were formed by mixing 1 part by weight (0.70 g) of rock powder

(dried at 110 °C) with 5 parts by weight of dried lithium metaborate flux and fusing in a muffle furnace for 15 minutes at 1100 °C in 95% Pt - 5% Au crucibles. Loss-on-ignition (LOI) measurements were undertaken on dried rock powders by heating in a pre-ignited aluminium crucible to 1000 °C for 1 hr and recording percentage weight loss. Internal standards WS-E (Whin Sill Dolerite) and OU-3 were analysed repeatedly throughout analysis sessions. Approximate 2 standard deviation (2sd) analytical precisions are <2 relative % for all elements, excepting those with concentrations <0.5 wt. %, for the 22 replicate analyses of each standard. High accuracy is indicated by the close agreement (generally within ~1 % offset) between average values for the standard analyses and recommended values for each element. Similar values (within ~2 % offset) were calculated from the difference between duplicate analyses of samples. XRF standard data are presented in Appendix A5.

4.3.2. Solution ICP-MS: whole-rock trace elements

A subset of 73 whole-rock powders was selected for trace element analysis. Samples were prepared for analysis at Victoria University of Wellington (VUW), New Zealand. Aliquots of whole-rock powders prepared for XRF major element analysis were prepared for trace element analysis using methods of acid digestion outlined in Appendix A6. Whole-rock trace element analysis was carried out by solution inductively coupled plasma mass spectrometry (ICP-MS), using a Thermo-Fisher Element2 sector-field ICP-MS equipped with an ESCI auto sampler at VUW using methods similar to those of Eggins et al. (1997). The ICP-MS was tuned using a 10 ppb multi-element standard diluted to 1 ppb, where instrumental conditions such as torch position and carrier/make-up gas flow were adjusted to achieve the lowest relative standard deviation (RSD), typically <1-2%, and to optimise sensitivity.

Concentrations were calculated by sample-standard bracketing, thus the analysis sequence followed an order starting with the primary standard (BHVO-2), followed by 3 samples, the secondary standard (USGS standard BCR-2), and finishing back on the primary standard. Total procedural blanks for solution ICP-MS were within background count levels on all measured elements. In this study ⁴³Ca was used for an internal correction, as CaO concentrations of sample powders had previously been determined by XRF. This

method allows correction for any major changes or inconsistencies, which may be caused by sample loss during sample preparation.

Trace element abundances in samples were calculated relative to the bracketing standard (BHVO-2) according to equations 1 and 2:

$$1. \text{ Sample } C_i = (\text{Sample }_{CPS} / \text{BHVO }_{CPS}) \times (\text{Sample }_{Dil} / \text{BHVO }_{Dil}) \times C_{ref}$$

$$2. \text{ Sample } C_i (\text{Ca corrected}) = eq. 1. \times (C_{Ca \text{ XRF}} / C_{Ca \text{ ICP-MS}})$$

Where C_i , C_{ref} and C_{Ca} are the concentrations of the measured isotope, the reference value for the bracketing standard and Ca, respectively, the latter of which was determined by XRF and ICP-MS. Reference values for BHVO-2 were acquired from Georem preferred values (<http://georem.mpch-mainz.gwdg.de/>). X_{Dil} is the concentration of material in the aliquot dilution.

International standard BCR-2 was analysed throughout analysis sessions in order to monitor the precision and accuracy of data acquired by solution ICP-MS. Approximate 2sd analytical precisions calculated from 18 replicate analyses of BCR-2 are <13 relative % for all elements (most are ~8–10 %) except Nb (~24 %). Analyses of BCR-2 are accurate to within 5 % of preferred values for all elements (most are within 1–2 %), except Cr, U (~6 %), Cu (~18 %) and Ni (~30 %). The bulk powder (TPI) of a single large clast from Taupo ignimbrite was used as an additional secondary standard throughout analysis sessions. From replicate analyses of TPI, most trace element analyses are precise to ± 5 –10 %. Separate dilutions of the same sample powder were also analysed to monitor accuracy of the analyses as well as the reliability of the sample preparation procedure and homogeneity of powders. Values of 5–10 % offset for all elements from analyses of duplicate digestions further indicate high levels of reproducibility for the solution ICP-MS technique used in this study. Full standard data are presented in Appendix A6.

4.3.3. EPMA: mineral and glass major elements

Major element compositions for minerals and glass in 15 lava samples were analysed by electron probe microanalysis (EPMA) using the JEOL JXA 8230 instrument at VUW. This instrument is equipped with 5 wavelength dispersive X-ray spectrometers (WDS), an

energy dispersive X-ray spectrometer (EDS) and highly sensitive detectors for acquisition of back-scattered electron (BSE) images. Thin sections were prepared from lava samples and coated with a ~25 nm film of carbon before analysis.

For quantitative measurements of pyroxene, plagioclase and glass the instrument was calibrated using international mineral (Kakanui augite and labradorite plagioclase) and glass (VG-568) standards of similar composition to the material being analysed for most elements and synthetic oxides for elements in low abundance (<1 wt. %). For each element, calibration was undertaken during a 30 seconds peak-search and a 15 seconds background measurement. Analysis of crystal phases were performed using a focussed electron beam (~1 µm-wide) at a current of 12 nA and accelerating voltage of 15 kV. The beam was defocussed to a width of 5 µm during analysis of melt inclusion and groundmass glass. Due to the commonly small sizes of melt inclusions and interstitial glass patches, a 5 µm-diameter beam was used (rather than 10 µm). The current was reduced to 8 nA and counting times for Na were reduced to 15 seconds on the peak and 10 seconds for the background to minimise potential devolatilisation. Na and K were measured first during glass analysis sequences also to minimise alkali loss. Element concentrations were calculated using the ZAF correction method (where Z is atomic number, A is absorption and F is fluorescence; Carpenter, 2008 and references therein).

Calibration and secondary standards were analysed as unknowns to monitor instrumental drift and precision and accuracy of the measurements throughout analytical sessions. All standard data are presented in Appendices A7 (glass analyses) and A8 (mineral analyses). Values of approximate 2sd precisions measured from repeated analysis of glass standard VG-568 are within 1–5 relative % for major element oxides SiO₂, Al₂O₃ and K₂O, and ~14 % for Na₂O. Analyses are accurate to ≤2 % for SiO₂, Al₂O₃ and K₂O, and to 4 % for Na₂O of the preferred values of the standard. The level of analytical precision and accuracy is comparable to that obtained using a 10 µm-wide beam (Barker, 2014) and indicates that using a beam width of 5 µm does not result in significant alkali loss under the analytical conditions used. Values for precision and accuracy are high for other (minor) element oxides with concentrations <1 wt. %. Approximate 2sd analytical precision from repeated analysis of mineral standards are generally 1–7 relative % for major element oxides with concentrations >0.5 wt. %. Analyses of the standards are accurate to within 5 % of the preferred values for those major element oxides.

4.3.4. Laser ablation ICP-MS: glass trace elements

Laser ablation ICP-MS analyses of interstitial glass and xenolith-hosted glass in dacite lava sample CC415 were carried out at VUW using a Resonetics RESolutionS155-SE laser ablation system equipped with an ATL ArF Excimer laser (wavelength 193 μm), coupled to an Agilent 7500CS ICP-MS. Tuning and optimisation of the ICP-MS was undertaken by rasterising a 50 μm -diameter circular laser beam across standard specimen NIST 612 at a scan rate of 5 $\mu\text{m s}^{-1}$ and using a 10 Hz pulse frequency. Instrument conditions were adjusted to achieve optimal sensitivity throughout the tuning stage. US Geological Survey analytical standard GSD-1G was used as a calibration standard for these analyses. The laser diameter was set to 30 or 20 μm -diameter, and pulsed at a frequency of 10 or 5 Hz during analysis; the latter parameter options were used for smaller patches of glass in samples. Samples and standards were ablated for 60 seconds followed by a 60 second dwell period prior to the next analysis.

Data was processed using LaserTRAM software developed at Oregon State University (Loewen, 2013). The software was used to select a 20 second background interval and a ~20 second ablation interval for each analysis. The software corrected for the background and normalised the count rates for each element over the ablation interval to the concentration of ^{29}Si as determined by EPMA for the sample. The selected ablation interval was divided into 5 subintervals of equal duration using the software and background-corrected counts recorded in each of these were binned before calculating normalised ratios for each subinterval. Final normalised ratios for each sample are the median value of the normalised ratios calculated for each subinterval.

Trace element abundances were then calculated using known concentrations in the bracketing standard (GSD-1G). BHVO-2G and BCR-2G were analysed as secondary standards. Because the analysis session was intended as a preliminary exercise for collecting trace element data for Ruapehu glasses, only 2 spots on each standard, and 11 spots on samples were analysed. Analyses of standards were generally accurate to within 15 % of reference values, and mostly <5 % for the light rare earth elements and elements of interest for the purposes of this study (Rb, Sr, Zr, Ba). Exceptions to these values were calculated for Tm and Hf in BCR-2G and Cs, Eu and Lu in BHVO-2G. The standards data are given in Appendix A9.

4.4. RESULTS

4.4.1. Petrography

Petrographic descriptions for Ruapehu lava flows have been presented in numerous previous studies (e.g. Cole, 1978; Graham, 1987; Graham and Hackett, 1987; Graham et al., 1990; Price et al., 2012). Brief descriptions are provided for the sample suite used here for completeness and because new portions of the edifice have been sampled.

Compositional features of the mineral phases are summarised in section 4.5.6. Ruapehu lava flows are moderately to highly porphyritic, with only rare examples of crystal-poor types (<10 % phenocrysts). Plagioclase phenocrysts (>100 μm across) occur in all samples examined and most commonly have sieved cores with complexly zoned rims. Shapes range from anhedral to euhedral and maximum lengths reach 12 mm.

Orthopyroxene, clinopyroxene and olivine phenocrysts are present throughout Ruapehu lavas in varying proportions. For the more basaltic-andesite lavas of the Te Herenga and Whakapapa formations, clinopyroxene and orthopyroxene are equally abundant.

Orthopyroxene is the major ferromagnesian phase in lavas of the Mangawhero Formation. Amphibole occurs within Mangawhero dacite lavas studied here only as rare pseudomorphs that are replaced by symplectite assemblages of plagioclase, pyroxene, oxides and glass. The groundmasses of Ruapehu lavas typically consist of felted aggregates of microcrystalline plagioclase and orthopyroxene with volumetrically minor but ubiquitous oxide phases and small patches of glass. Magnetite is the dominant oxide phase present throughout the groundmass of Ruapehu lavas, although rare ilmenite and spinel are also present. Patches of glass in microcrystalline-free areas ~5–10 μm -wide are only rarely present in samples acquired from the margins of ice-bounded Mangawhero Formation flows and fluidal Whakapapa Formation flows that cooled rapidly.

Cristobalite is a significant and, until now, unrecognised constituent of effusive eruptive products at Ruapehu volcano. It is present as prismatic crystals on vesicle walls in moderately glassy samples and felted throughout the groundmass of holocrystalline portions of lava flows (Fig. 4.2). Both vesicle and groundmass types exhibit the typical fish-scale crack textures (cf. Horwell et al., 2013; Fig. 4.2). Tabular or amorphous cristobalite is often intergrown with fibrous biotite in areas of devitrified groundmass (Fig. 4.2e). Biotite is not observed as a phenocryst elsewhere in Ruapehu lavas and so is interpreted in these circumstances to be related to deposition of the cristobalite. The only

samples in which cristobalite was not observed were from glassy ice-bounded dacite lava flows.

Meta-sedimentary and meta-igneous xenoliths are present in most samples and are particularly common in lavas of the Mangawhero and Whakapapa formations. The former types are typically fine-grained assemblages of plagioclase, orthopyroxene and magnetite, which are likely to be metamorphic equivalents (or refractory residua) of the greywacke crust beneath Ruapehu (Price et al., 2005). Some crustal fragments contain glass and biotite (e.g. Graham, 1987). Meta-igneous granulite xenoliths are composed of plagioclase, orthopyroxene and ilmenite with minor clinopyroxene and olivine and display relic igneous or cumulate textures.

Figure 4.2. Back-scattered electron (BSE) images of cristobalite in Ruapehu lava flows. (a) Cristobalite within the holocrystalline groundmass of Te Herenga basaltic-andesite sample CC348. (b) Prismatic cristobalite crystals within a vesicle in Mangawhero andesite sample CC079. (c) Cristobalite felted through the groundmass of Mangawhero dacite sample CC313. See text for explanation. (e) Tabular cristobalite and patches of biotite within zone of devitrified groundmass in Mangawhero andesite sample CC154. (f) Large tabular cristobalite grain filling a vesicle in Whakapapa andesite sample CC335. Abbreviations are c (cristobalite), px (pyroxene), pl (plagioclase), ol (olivine), ox (oxide), bt (biotite). White scale bars are 100 μ m.

4.4.2. Whole-rock major and trace element compositions

A summary of whole-rock compositions for Ruapehu volcano lava flows was presented by Price et al. (2012), however, the major and trace element variations between and within edifice-forming formations are re-evaluated here in light of the extended sampling coverage and improved geochronological control from work in this thesis. Representative major and trace element data are presented for Ruapehu lavas in Table 4.1. Full whole-rock major and trace element data are presented in Appendix A5 and A6.

Te Herenga Formation lavas are basaltic-andesites with Mg# [$100\text{Mg}/(\text{Mg} + \text{Fe})$] of 51–62. The most mafic lava flow sampled on Ruapehu volcano (53.8 wt. % SiO_2) was erupted at 186.2 ± 6.8 ka, which now places it within the Te Herenga Formation (Hackett, 1985; Price et al., 2012; see Chapter 3). Te Herenga lavas exhibit a relatively narrow compositional range for all major and trace elements that is generally distinct from younger lavas, excepting some overlap with the Wahianoa Formation (Figs. 4.3, 4.4).

Figure 4.3. Bivariate plots of whole-rock K/Ca, Al_2O_3 , MgO and Ni versus SiO_2 . Abbreviations for and-member samples referred to in the text are TK (Te Kohatu package, high-K dacite), WH (Whakapapa package, low-K dacite) and ME (Mangaehuehu package high-MgO andesite). Grey dots are data from Price et al. (2012). Type 2 plagioclase-phyric andesites of the Wahianoa Formation (Graham and Hackett, 1987) are labelled (T2).

A notable characteristic of Te Herenga lavas is their low K/Ca values (~ 0.11 ; Fig. 4.3) when compared to younger lavas. Incompatible trace element contents are essentially constant over their ~ 3 wt. % SiO_2 range (Fig. 4.4). Wahianoa Formation lavas are basaltic-andesites and andesites with $\text{Mg\#}_{42-62}$ that exhibit slightly elevated SiO_2 , and incompatible trace element contents when compared with Te Herenga Formation lavas (Figs. 4.3, 4.4). Previously un-sampled lavas erupted from ~ 100 – 80 ka have major element compositions that match ~ 166 – 100 ka lavas of the Wahianoa Formation. Values of K/Ca range from 0.12 – 0.31 and define a steeper positive trend than that of Te Herenga lavas (Fig. 4.3). Within the Wahianoa Formation, a distinct group of flows is identified by low-MgO, high- Al_2O_3 contents indicative of higher modal abundances of plagioclase relative to pyroxene (Graham and Hackett, 1987). Mangawhero Formation lavas are divided on the basis of the age data in Chapter 3 into early (50 – 35 ka), middle (35 – 26 ka) and late (26 – 15 ka) age brackets in this chapter. Lavas of the ~ 50 – 35 ka suite are compositionally diverse, covering an 8.2 wt. % range in SiO_2 from basaltic-andesite to dacite. These flows also show strong positive trends for incompatible trace element abundances and a distinct trend defined by high K/Ca values over the range in SiO_2 compared to older and younger lavas (Figs. 3.4, 4.4). The high-K dacites contain up to 550 ppm Ba, 200 ppm Zr and 150 ppm Rb (Fig. 4.4). Despite the broadly linear relationship between SiO_2 and incompatible trace elements, lavas of this age can be categorised into high- and low-MgO types. The high-MgO trend is defined by lavas of the Mangaehuehu and Te Kohatu eruptive packages, and low-MgO andesites and dacites are grouped within the Ngahuinga and Mangaturuturu eruptive packages (Chapter 3; Fig. 4.3). Mananui dacite package, which forms a spatially isolated flow on the northern flank of Ruapehu (Chapter 3), has an intermediate MgO content. The two main trends exhibit an apparent compositional gap at ~ 62 – 63 wt. % SiO_2 . The high-MgO andesites of the Mangaehuehu package ($\text{Mg\#}_{60-69}$) and dacites of the Te Kohatu package ($\text{Mg\#}_{54-57}$) also exhibit relatively high Cr and Ni contents and low Al_2O_3 at equivalent SiO_2 contents compared to all other eruptive products from Ruapehu volcano (Fig. 4.3). The eruptive phase linked to emplacement of Mangaehuehu package andesite flows, which define a 5.2 wt. % range in SiO_2 contents, is constrained by maximum and minimum ages of 45.4 ± 2.0 ka and 41.8 ± 1.8 ka (Chapter 3). This is a remarkable feature of the Mangaehuehu package when considering that a comparable range of ~ 4.8 wt. % SiO_2 was defined by the ~ 300 m-thick sequence of Wahianoa Formation lavas exposed on southeast Ruapehu that was emplaced between ~ 166 and 115 ka (Gamble et al., 2003).

Table 4.1. Representative whole-rock major and trace element data for Ruapehu lavas.

Sample	GL1983	GL1030	CC335	CC130	CC226	CC364	CC408	CC143	CC513	CC462	CC547
Package	CL	IW	PT	TR	MK	TP	MK	WT	WH	MG	MG
Age (ka)	<2	6	15	15	18	21	21	23	26	30	30
SiO ₂	61.45	57.30	58.51	60.08	61.37	58.29	60.87	62.26	65.61	60.73	62.46
TiO ₂	0.72	0.68	0.73	0.70	0.89	0.70	0.78	0.67	0.62	0.86	0.81
Al ₂ O ₃	15.71	16.71	17.09	15.91	17.25	16.08	17.28	16.20	14.88	16.87	17.00
Fe ₂ O ₃	6.41	7.57	7.51	6.59	6.03	7.57	6.42	5.84	5.02	6.49	5.74
MnO	0.10	0.12	0.12	0.10	0.09	0.12	0.10	0.10	0.08	0.10	0.09
MgO	3.94	5.20	3.96	4.95	2.52	5.22	2.64	3.58	3.43	3.23	2.44
CaO	6.03	7.67	7.16	6.51	5.91	7.34	6.02	5.59	4.50	6.10	5.15
Na ₂ O	3.25	3.21	3.22	3.25	3.68	3.00	3.75	3.56	3.69	3.41	3.56
K ₂ O	2.23	1.39	1.57	1.76	2.07	1.54	1.97	2.03	2.06	2.03	2.56
P ₂ O ₅	0.16	0.14	0.14	0.14	0.18	0.14	0.17	0.17	0.11	0.19	0.19
LOI	-0.13	0.12	-0.15	0.01	-0.17	-0.07	-0.10	0.05	0.36	-0.16	0.24
Total	99.19	100.41	99.63	99.44	99.95	98.92	99.08	99.89	100.25	100.00	99.49
⁷ Li	22.1	19.9	15.9	20.7	22.2	13.6	25.7	26.7	27.0	21.6	31.3
⁴⁵ Sc	19.7	25.2	24.4	22.1	17.2	27.2	17.9	17.7	15.4	19.6	15.8
⁵¹ V	159	194	199	161	195	205	172	128	120	172	144
⁶⁰ Ni	34.7	65.2	18.2	66.8	13.4	41.0	7.7	52.4	49.9	19.0	14.5
⁶³ Cu	21.6	34.6	26.3	33.3	14.6	50.8	32.7	29.9	18.4	28.9	23.5
⁶⁶ Zn	61.5	66.3	77.5	59.3	58.8	68.4	66.7	59.9	73.1	68.2	60.6
⁶⁹ Ga	17.0	18.3	19.2	17.6	18.8	16.9	19.4	18.1	17.4	18.5	18.6
⁸⁵ Rb	86.3	46.8	59.2	62.7	78.4	57.4	69.0	75.5	84.7	72.6	110.2
⁸⁸ Sr	251	299	257	264	304	225	305	266	229	305	258
⁸⁹ Y	19.7	17.9	21.2	16.8	20.8	19.8	19.6	20.0	13.7	21.9	23.2
⁹¹ Zr	151	96	119	123	153	113	136	133	149	153	172
⁹³ Nb	5.86	4.03	4.81	5.31	6.17	4.54	5.13	6.23	6.77	6.53	7.18
¹³³ Cs	3.68	1.79	2.02	2.70	2.62	2.07	2.13	2.80	3.45	2.66	2.96
¹³⁷ Ba	408	337	338	355	452	311	417	409	410	425	454
¹³⁹ La	15.0	10.0	13.7	12.5	16.0	12.2	14.9	15.6	8.7	17.9	19.9
¹⁴⁰ Ce	32.9	22.2	29.4	26.7	35.1	26.7	32.9	34.7	17.7	38.7	41.6
¹⁴¹ Pr	4.03	2.77	3.64	3.29	4.35	3.35	3.95	4.26	2.21	4.74	5.27
¹⁴⁶ Nd	15.8	11.9	14.7	13.1	17.1	13.6	16.1	17.1	9.1	19.0	21.0
¹⁴⁷ Sm	3.52	2.97	3.38	3.02	3.77	3.12	3.58	3.69	2.21	4.22	4.48
¹⁵¹ Eu	0.90	0.87	0.92	0.86	1.01	0.85	0.97	0.90	0.71	1.08	1.05
¹⁵⁷ Gd	3.78	2.94	3.62	3.05	3.82	3.51	3.72	3.71	2.31	4.33	4.68
¹⁵⁹ Tb	0.55	0.49	0.57	0.47	0.57	0.53	0.54	0.58	0.37	0.63	0.66
¹⁶³ Dy	3.39	2.99	3.59	2.97	3.46	3.38	3.44	3.42	2.34	3.82	4.07
¹⁶⁵ Ho	0.69	0.61	0.74	0.59	0.73	0.71	0.70	0.68	0.50	0.77	0.81
¹⁶⁶ Er	2.04	1.77	2.14	1.76	2.10	2.07	1.99	2.02	1.48	2.23	2.38
¹⁶⁹ Tm	0.30	0.27	0.32	0.27	0.30	0.30	0.30	0.30	0.22	0.32	0.33
¹⁷³ Yb	2.02	1.78	2.13	1.75	2.05	2.03	1.94	1.86	1.47	2.07	2.26
¹⁷⁵ Lu	0.29	0.27	0.33	0.26	0.30	0.30	0.29	0.27	0.22	0.31	0.33
¹⁷⁸ Hf	4.06	2.71	3.26	3.44	4.12	3.12	3.63	3.62	4.01	4.02	4.49
²⁰⁸ Pb	12.8	7.15	9.27	10.5	10.2	7.49	9.47	17.1	12.0	10.5	9.83
²³² Th	8.12	4.34	5.67	5.97	7.32	5.35	6.46	6.43	6.42	7.24	8.85
²³⁸ U	2.21	1.22	1.43	1.60	1.85	1.42	1.63	1.73	1.91	1.76	2.41

Major oxide values are in weight % and are normalised to anhydrous totals (100 wt. %) with LOI (loss on ignition) and original analytical totals displayed. Trace elements contents are in ppm. Package abbreviations are: CL (Crater Lake); PT (Paretaitonga); TR (Tureiti); MK (Makotuku); WT (Waitonga); WH (Whakapapaiti); MG (Manganuioteao).

Table 4.1. (cont.) Representative whole-rock major and trace element data for Ruapehu lavas.

Sample	CC508	CC570	CC125	CC216	CC424	CC470	CC562	CC209	CC213	CC326	CC348
Package	TK	MN	ME	ME	NG	MT	WA	WA	WA	TH	TH
Age (ka)	39	40	43	43	40	41	88	121	121	170	187
SiO ₂	65.03	63.57	56.80	60.19	59.34	63.49	57.55	58.36	58.40	55.24	53.79
TiO ₂	0.71	0.85	0.70	0.77	0.76	0.83	0.62	0.68	0.70	0.65	0.67
Al ₂ O ₃	15.27	15.84	14.25	15.00	16.81	16.74	16.51	19.70	17.25	17.21	16.62
Fe ₂ O ₃	4.74	5.51	7.44	6.55	6.52	5.27	7.38	6.06	7.40	9.16	9.20
MnO	0.07	0.08	0.12	0.10	0.10	0.08	0.12	0.09	0.12	0.15	0.15
MgO	2.86	2.80	8.61	5.53	4.22	2.21	5.60	2.34	4.36	5.30	6.75
CaO	4.45	4.87	7.67	6.36	6.81	4.87	7.82	7.49	6.89	8.42	9.17
Na ₂ O	3.42	3.50	2.85	3.28	3.48	3.64	3.37	3.92	3.31	3.12	2.82
K ₂ O	3.27	2.78	1.41	2.05	1.80	2.68	0.93	1.22	1.44	0.66	0.71
P ₂ O ₅	0.18	0.20	0.14	0.18	0.16	0.20	0.11	0.13	0.13	0.09	0.11
LOI	0.10	-0.02	-0.10	-0.02	-0.11	0.20	-0.09	0.06	0.11	0.01	-0.25
Total	100.28	99.44	99.89	100.20	99.07	99.62	99.54	100.16	99.90	99.27	99.39
⁷ Li	36.7	31.0	19.5	23.6	20.0	24.8	14.9	13.6	21.7	10.2	8.34
⁴⁵ Sc	14.3	15.8	27.1	21.6	19.9	16.0	27.0	16.8	23.9	32.0	34.5
⁵¹ V	121	143	191	164	170	146	196	175	188	233	249
⁶⁰ Ni	30.4	36.7	175.9	123.3	49.2	12.1	54.9	15.4	30.1	28.6	54.7
⁶³ Cu	27.9	39.1	39.2	88.5	37.4	12.3	47.6	93.8	43.1	74.0	38.3
⁶⁶ Zn	30.2	68.0	61.8	59.2	60.8	66.5	70.1	64.6	81.0	87.1	81.4
⁶⁹ Ga	17.8	18.6	15.5	17.3	18.4	19.0	17.8	20.9	18.8	17.9	17.5
⁸⁵ Rb	144	111	52.8	79.7	61.8	105	25.4	36.2	44.9	16.6	17.5
⁸⁸ Sr	203	232	227	241	252	243	289	327	250	211	226
⁸⁹ Y	23.2	23.5	17.5	21.8	18.5	21.3	14.6	19.1	19.2	18.9	18.7
⁹¹ Zr	215	199	114	150	130	186	69.3	92.8	101	59.4	58.5
⁹³ Nb	9.00	8.36	4.16	6.26	4.58	7.22	3.00	3.79	4.46	1.83	1.89
¹³³ Cs	5.15	3.83	2.32	2.38	2.00	3.30	0.61	1.07	1.56	0.42	0.37
¹³⁷ Ba	552	509	302	404	345	495	236	316	332	184	222
¹³⁹ La	20.9	20.2	10.6	16.7	12.8	16.6	6.23	11.0	11.4	5.44	6.01
¹⁴⁰ Ce	45.3	44.0	23.5	35.7	28.4	36.5	14.5	22.8	25.7	11.3	13.5
¹⁴¹ Pr	5.43	5.31	2.90	4.40	3.50	4.53	1.93	3.00	3.29	1.69	1.94
¹⁴⁶ Nd	21.0	21.5	12.0	18.1	14.6	18.0	8.43	12.7	13.5	7.67	8.97
¹⁴⁷ Sm	4.53	4.56	2.95	3.92	3.29	4.01	2.10	3.05	3.22	2.17	2.38
¹⁵¹ Eu	0.91	1.01	0.82	0.93	0.87	1.03	0.71	0.92	0.87	0.74	0.81
¹⁵⁷ Gd	4.59	4.60	3.08	4.09	3.40	4.18	2.29	3.12	3.27	2.55	2.81
¹⁵⁹ Tb	0.64	0.66	0.48	0.62	0.50	0.59	0.39	0.49	0.52	0.45	0.46
¹⁶³ Dy	3.88	4.11	2.92	3.75	3.22	3.67	2.58	3.11	3.29	3.09	3.08
¹⁶⁵ Ho	0.80	0.82	0.60	0.75	0.65	0.74	0.53	0.65	0.68	0.68	0.67
¹⁶⁶ Er	2.23	2.35	1.78	2.18	1.83	2.16	1.51	1.90	1.94	1.97	1.98
¹⁶⁹ Tm	0.32	0.34	0.26	0.33	0.27	0.32	0.23	0.28	0.30	0.30	0.29
¹⁷³ Yb	2.15	2.23	1.67	2.08	1.78	2.15	1.52	1.80	1.95	1.99	1.92
¹⁷⁵ Lu	0.32	0.33	0.25	0.31	0.26	0.32	0.24	0.28	0.29	0.31	0.30
¹⁷⁸ Hf	5.40	5.30	2.97	4.17	3.41	4.92	1.99	2.57	2.85	1.73	1.73
²⁰⁸ Pb	17.1	17.5	7.69	12.4	12.4	12.8	4.99	7.37	27.3	6.00	3.63
²³² Th	12.1	10.0	4.91	7.08	5.82	9.82	2.36	3.39	4.15	1.40	1.63
²³⁸ U	3.58	2.70	1.29	2.02	1.49	2.59	0.65	0.93	1.10	0.44	0.43

Major oxide values are in weight % and are normalised to anhydrous totals (100 wt. %) with LOI (loss on ignition) and original analytical totals displayed. Trace elements contents are in ppm. Package and Formation abbreviations are: TK (Te Kohatu); MN (Mananui); ME (Mangaehuehu); NG (Ngahuinga); MT (Mangaturuturu); WA (Wahianoa Formation); TH (Te Herenga Formation).

Table 4.2. Summary of SiO₂ ranges for eruptive packages of the Mangawhero Formation.

Age ka	Package		SiO ₂ (wt. %)						
	Andesite	Dacite	54	56	58	60	62	64	66
26-15	Makotuku	Whakapapaaiti							
	Waitonga								
	Te Piripiri								
	Horonuku								
35-26	Manganuioteao								
50-35	Ngahuinga	Mangaturuturu	(low-MgO)						
		Mananui	(med-MgO)						
	Mangaehuehu	Te Kohatu	(high-MgO)						

The time periods correspond to early (50–35 ka), middle (35–36 ka), and late (26–15 ka) Mangawhero Formation lavas, as referred to in the text. Early Mangawhero Formation are further subdivided into high-, medium- and low-MgO types.

The low-MgO group of lavas erupted between ~50 and 35 ka comprises Ngahuinga package andesites that have Mg#_{48–62} and major element compositions that overlap with middle (~35–26 ka) and late (~26–15 ka) Mangawhero Formation andesites as well as lavas of the older Wahianoa and younger Whakapapa formations. Mangaturuturu package dacites fit the low-MgO trend but are separated from the low-MgO andesites by a 2.6 wt. % gap in SiO₂ content.

Manganuioteao package lava flows emplaced on the western flank of Ruapehu volcano from ~35 to 26 ka exhibit SiO₂, K₂O and trace element contents that are intermediate between the low-MgO andesites and dacites erupted at 50–35 ka. Late Mangawhero Formation lava flows erupted at ~26–15 ka are andesites and rare dacites (Whakapapaaiti eruptive package lavas). These flows define distinctly lower trends for SiO₂ versus K/Ca and incompatible trace elements (e.g. Rb, Ba, Zr) when compared to middle (~35–26 ka) and early (~50–35 ka) Mangawhero Formation lavas (Figs. 4.3, 4.4).

The major and trace element compositions of ~26–15 ka andesites generally overlap with younger flows of the Whakapapa Formation (Fig. 4.3), which are andesites and basaltic-andesites with Mg#_{47–60}. Numerous eruptive packages within the Whakapapa Formation that were sourced from discrete vents and summit cones are defined and described in Chapter 3. Taken together, Whakapapa Formation lavas define a SiO₂–K/Ca trend contiguous with ~26–15 ka Mangawhero Formation lavas (Fig. 4.3).

Figure 4.4. Bivariate plots of whole-rock SiO_2 (wt. %) versus selected trace elements (ppm) and trace element ratios. End-member abbreviations are the same as in Figure 4.3.

4.4.3. Whole-rock multi-element diagrams

Whole-rock trace element contents for Ruapehu lavas have been normalised with respect to values for average continental crust from Rudnick and Gao (2003) and are plotted on multielement diagrams in Figure 4.5. Representative samples are displayed for the different periods of volcanism. A generalised crustal composition is used to normalise the lava trace element concentrations in order to indicate the effects of upper crustal contamination on Ruapehu magmas.

Normalised concentrations for all trace elements (except Ti) are ≤ 1 for Te Herenga Formation lavas. These flows display positive Ba, Sr and Sm anomalies. Trace element patterns for Wahianoa Formation lavas share general similarities to Te Herenga Formation lavas, however, a notable difference is the slightly higher Rb values, which causes an associated loss of a positive Ba anomaly.

Figure 4.5. Multielement diagrams for Ruapehu lavas. Whole-rock trace element concentrations are normalised to average values of continental crust from Rodnick and Gao (2003). Grey line repeated in all panels is Te Herenga basaltic-andesite sample CC348. Approximate eruption age (ka) is labelled for each sample.

Normalised trace element concentrations for Mangawhero Formation lavas display several distinct features when compared to older eruptive products: positive Rb, Pb and P anomalies, negative Ba, Sr, and Eu anomalies, and upward-concave Sm to Eu patterns.

These anomalies are most pronounced for dacites erupted between 50 and 35 ka. One notable difference for ~35–26 ka flows of the Manganuioteao eruptive package compared to older Mangawhero Formation lavas is the subdued positive and negative anomalies for Pb and Sr, respectively. Andesites erupted at ~26–15 ka display similar but subdued features compared to older Mangawhero Formation andesites. The ~26 ka Whakapapaite package dacite exhibits relatively low La, Ce, Y and Yb. Whakapapa Formation lavas display similar features to Te Herenga and Wahianoa Formation lavas in multielement diagrams, although they generally have higher trace element abundances.

4.4.4. Whole-rock isotopic compositions

Existing isotopic data for Ruapehu lavas (from compilation in Price et al., 2012) have been assigned approximate ages here based on new geochronological constraints presented in Chapter 3. Previous studies (Gamble et al., 1999, 2003; Price et al., 2005, 2012) have shown Te Herenga lavas to have distinctly higher $^{143}\text{Nd}/^{144}\text{Nd}$ and lower $^{87}\text{Sr}/^{86}\text{Sr}$ whole-rock isotopic compositions from all subsequent eruptive products (Fig. 4.6). $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions of Wahianoa Formation lavas overlap with the most radiogenic Te Herenga samples (~0.7050), however they have distinctly lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. Lavas erupted from ~50 to 35 ka display a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ values that extends to the most radiogenic measurements for Ruapehu volcanic rocks within ~40 ka Te Kohatu eruptive package dacites (Graham and Hackett, 1987). Lavas erupted at ~26–15 ka and <15 ka display comparably wide ranges but are generally defined by less radiogenic values.

Figure 4.6. Whole-rock $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions for Ruapehu lavas. Data are from Price et al. (2012). Approximate ages were assigned to samples to display general evolution pattern in the right panel.

4.4.5. Groundmass, melt inclusion and xenolith glass compositions

Acquisition of glass analyses from the groundmass of lava samples was hindered by the ubiquity of microcrystalline plagioclase and pyroxene in even the glassiest flows available, however, crystal-free glassy groundmass zones ~10 µm-wide were present in some samples (Fig. 4.7). Bearing in mind the above caveats, representative groundmass glass compositions were acquired by using a defocussed electron beam (5 µm-diameter) for analysis. A summary of the data is presented in Table 4.3 and a full list of analyses is present in Appendix A7.

Figure 4.7. EPMA back-scattered electron (BSE) images of glass in Ruapehu lavas. (a) Groundmass texture of glassy Mangawhero dacite sample CC415. Microcrystals of plagioclase (dark, tabular grains) and pyroxene (bright needle-shaped grains) are present throughout the groundmass. Equant pyroxene grain at right is bordered by a microcrystalline reaction corona. (b) Melt inclusions and their SiO₂ and K₂O contents (in weight %) in a pyroxene host from Te Herenga basaltic-andesite sample CC326. (c) Pocket of quenched glass hosted within a feldspathic xenolith fragment in Mangawhero dacite sample CC415. (d) Interstitial glass embayed within a pyroxene crystal cluster in Mangawhero dacite sample CC415. Rb content (in ppm) displayed for glass in (c) and (d). Scale bar in each panel is 100µm.

Te Kohatu package dacites of the early Mangawhero Formation (~50–35 ka) and Turoa package andesites of the Whakapapa Formation (<15 ka) have rhyolitic (73–75 wt. %

SiO₂) groundmass glass with K₂O contents of 5–6 wt. %. Mangaehuehu package andesite of the Mangawhero Formation (CC069) has distinctly lower SiO₂ (68–70 wt. %) and K₂O (2.5–3.5 wt. %) contents in groundmass glass than the Mangawhero dacites and Whakapapa andesite. Te Herenga Formation lavas have holocrystalline groundmass textures with felted areas of cristobalite due to devitrification and, thus, no groundmass glass compositions could be measured for these flows.

Table 4.3. Summary of melt inclusion and xenolith and groundmass glass compositions.

Group	Value	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	CaO	Na ₂ O	K ₂ O	Total
WH mi n=45	avg	74.0	0.5	14.9	1.1	1.9	3.6	3.8	99.6
	max	77.0	1.4	19.0	2.2	3.6	4.5	5.6	100.5
	min	70.3	0.2	13.0	0.5	1.0	0.8	1.8	98.4
	2sd	3.7	0.4	2.6	0.8	1.4	1.3	2.2	1.3
WH gms n=16	avg	73.8	1.2	12.2	3.1	1.0	3.4	5.0	99.7
	max	75.1	1.4	12.5	3.8	1.1	4.1	5.2	100.3
	min	73.3	1.0	11.7	2.5	0.7	3.2	4.1	98.1
	2sd	1.0	0.2	0.5	0.6	0.2	0.4	0.5	1.4
TK mi n=67	avg	73.0	0.7	13.7	2.1	1.3	3.3	5.4	99.9
	max	75.6	1.2	16.2	3.3	2.8	4.2	6.2	100.8
	min	70.0	0.2	12.1	1.0	0.7	1.0	4.0	98.5
	2sd	3.0	0.5	2.5	0.9	1.0	0.9	1.1	1.1
TK i/x n=17	avg	73.8	1.0	12.7	2.3	1.0	3.0	5.8	98.0
	max	75.2	1.3	15.5	2.8	1.4	3.7	6.3	99.0
	min	70.5	0.7	12.1	1.7	0.9	2.7	5.5	97.1
	2sd	2.7	0.4	1.9	0.6	0.2	0.4	0.4	1.1
TK gms n=13	avg	74.4	0.8	12.6	2.2	1.2	3.0	5.5	101.0
	max	75.4	0.8	15.1	2.7	2.3	3.8	5.9	101.8
	min	71.7	0.6	12.0	1.7	0.8	2.7	4.4	100.3
	2sd	2.1	0.1	1.7	0.4	0.9	0.6	0.8	0.8
ME mi n=30	avg	72.8	0.6	15.1	1.3	1.8	4.0	4.2	100.0
	max	67.6	0.1	13.0	0.4	0.6	3.0	3.2	99.0
	min	76.6	1.9	17.5	3.0	3.6	7.2	5.6	100.6
	2sd	4.9	1.0	2.0	1.4	1.6	1.4	1.1	0.8
ME gms n=13	avg	69.4	1.7	13.0	5.1	2.5	4.5	3.0	99.9
	max	70.1	1.8	13.8	5.8	2.9	5.0	3.4	100.4
	min	69.0	1.6	12.3	4.3	2.4	4.1	2.6	99.3
	2sd	0.7	0.1	0.8	0.8	0.3	0.5	0.5	0.5
TH mi n=24	avg	72.7	0.5	15.9	1.5	2.4	4.3	2.4	100.4
	max	78.7	1.1	17.8	2.1	3.4	5.9	3.5	101.8
	min	69.7	0.1	12.9	0.6	1.3	1.6	1.7	98.1
	2sd	5.6	0.8	3.0	0.8	1.1	1.6	0.8	2.0

Major oxide values are in weight % and are normalised to anhydrous totals (100 wt. %). Table is divided into groups of analyses from mi (melt inclusions), gms (groundmass glass) and i/x (interstitial and xenolith glass) from within different formations or packages: WH (Whakapapa Formation), TK (Te Kohatu package, Mangawhero Formation), ME (Mangaehuehu package, Mangawhero Formation), TH (Te Herenga Formation). From multiple analyses of glass within each group values are displayed for avg (average), max (maximum), minimum (minimum) contents for each element, as well as 2sd (2 standard deviation).

Melt inclusion data acquired in this study were measured for glass hosted within pyroxene phenocrysts. Plagioclase-hosted melt inclusions were commonly observed to have recrystallized and were therefore not analysed. In addition, evidence for partial (along the crystal rim) or complete replacement of melt inclusions by plagioclase, pyroxene and/or Fe-Ti oxides in pyroxene-hosted types was also observed and such inclusions were not analysed. Pristine (or near-pristine with minimal evidence for post-entrapment crystallisation of the host mineral) and sufficiently large inclusions ($\sim 5 \mu\text{m}$ in size; Fig. 4.7) were selected for analysis.

Melt inclusions within Te Herenga Formation basaltic-andesites are rhyolitic (70–79 wt. % SiO_2) with K_2O contents predominantly between 2–3 wt. % (Fig. 4.8). Pyroxenes in high-magnesian Mangaehuehu package andesites (CC069, CC077, CC154) contain dacitic to rhyolitic (~ 68 –75 wt. % SiO_2) melt inclusions with K_2O contents of 3–5 wt. %.

Figure 4.8. SiO_2 - K_2O compositions for glass in Ruapehu lavas. Different symbols are used for whole-rock (wr, coloured diamonds), melt inclusion (mi; open diamonds), groundmass glass (gm; coloured crosses) and xenolith glass (xg; open blue circles).

Melt inclusions within crystal clots in Te Kohatu package dacites (CC415, CC479) have distinctly high-K₂O contents (~4–6 wt. %) but similar SiO₂ contents (~70–75 wt. %) when compared to other lavas. Veins of quenched melt within feldspathic xenoliths (An_{65–68}) and pockets of interstitial glass in Te Kohatu package dacites (see Fig. 4.7) also have high K₂O contents (~5.4–6.2 wt. %) together with high Rb (~250 ppm), Zr (~400 ppm) and Ba (~780 ppm) and low Sr (~60 ppm) contents (Table 4.5). These glasses had low EPMA analytical totals (~97–98 wt. %) compared to groundmass glass and pyroxene hosted melt inclusions from the same sample (~100 wt. %) as well as analytical standards (~99–100 wt. %) that were analysed at the same time. Melt inclusion compositions in Whakapapa Formation lava samples are dacitic to rhyolitic (68–77 wt. % SiO₂) and display a wide compositional range from Te Herenga-like low-K types (~2 wt. % K₂O) through to high-K types with ~5.5 wt. % K₂O that overlap with groundmass glass compositions.

Table 4.4. LA-ICPMS trace element data for xenolith and interstitial glass.

Sample	X1-1	X2-1	X2-2	IG40-1	IG12 (n=7)
⁴⁵ Sc	11.6	11.1	9.9	10.6	12 ± 2
⁵¹ V	64.6	52.6	32.7	70.3	57 ± 28
⁶⁶ Zn	40.7	33.2	46.9	50.9	50 ± 7
⁸⁵ Rb	255.3	274.2	272.7	272.1	271 ± 12
⁸⁸ Sr	56.3	57.4	49.5	90.5	55 ± 6
⁸⁹ Y	35.5	36.1	31.9	31.4	39 ± 4
⁹¹ Zr	402.2	434.7	420.3	396.6	486 ± 22
⁹³ Nb	13.1	13.7	14.8	11.8	15 ± 2
¹³³ Cs	18.0	17.8	18.3	17.4	18 ± 2
¹³⁷ Ba	788.7	785.8	741.4	1410.6	834 ± 44
¹³⁹ La	33.9	35.5	30.8	35.2	41 ± 5
¹⁴⁰ Ce	73.2	74.5	69.4	77.6	86 ± 9
¹⁴¹ Pr	8.3	9.2	8.0	8.2	9 ± 1
¹⁴⁶ Nd	32.1	31.3	29.3	29.7	37 ± 4
¹⁴⁷ Sm	7.0	7.8	5.7	9.1	8 ± 2
¹⁵¹ Eu	0.5	0.6	0.7	1.0	1 ± 0.5
¹⁵⁷ Gd	7.5	7.6	3.7	8.5	8 ± 3
¹⁵⁹ Tb	0.9	0.7	0.6	1.2	1 ± 0.2
¹⁶³ Dy	6.6	4.9	5.8	5.3	6 ± 2
¹⁶⁵ Ho	1.4	1.0	0.6	1.0	1 ± 0.2
¹⁶⁶ Er	3.6	2.8	2.9	2.5	4 ± 1
¹⁶⁹ Tm	0.7	0.5	0.7	0.2	0.5 ± 0.3
¹⁷² Yb	2.6	2.9	2.2	4.2	4 ± 1.5
¹⁷⁵ Lu	0.4	0.5	0.3	0.3	0.5 ± 0.2
¹⁷⁸ Hf	12.2	12.4	11.9	11.8	14 ± 3

Values are in ppm. Sample prefix X indicates analysis of xenolith glass and IG for interstitial glass. X2-1 and X2-2 are analyses from the same xenolith. Average values ± 2 standard deviations are shown for 7 analyses from IG12.

4.4.6. Crystal chemistry and compositional zoning

A summary of compositional data for crystals in Ruapehu lavas is presented in Figure 4.9 and in Table 4.5. Typical zoning features of the major mineral phases are displayed in Figures 4.10–4.13.

Figure 4.9. Summary of the range of mineral compositions in Ruapehu lavas. Orthopyroxene and clinopyroxene compositions (En %) are shown in top panels; plagioclase anorthite compositions (An %) are displayed in the bottom panel. Coloured bars indicate the range of core compositions; open bars indicate the range of rim compositions. Ranges are compiled for samples from the Te Herenga Formation (TH), the Mangawhero Formation Mangaehuehu package (MA-ME), and Te Kohatu package (MA-TK), and the Whakapapa Formation (WH). Age ranges for eruption of the formations and packages are shown in ka.

Table 4.5. Summary of EPMA data for major mineral phases in Ruapehu lavas.

Number	Sample Information			Whole-rock		Phenocryst compositional range (rim)			
	Fmtn	Package	Age (ka)	SiO ₂ (wt.%)	Mg#	Opx (Mg #)	Cpx (Mg #)	Plg (An %)	OI (Mg #)
CC281	WH	SC	10	56.0	56	62-77 (68-80)	65-85 (59-81)	52-81 (67-80)	73-75
CC260	WH	TR	12	57.4	52	63-68 (68-78)	67-81 (71-75)	50-90 (56-73)	na
CC335	WH	PT	15	58.5	51	61-77 (65-70)	69-84 (71-73)	54-89 (58-88)	70-72
CC193	WH	RT	15	59.3	47	61-69 (65-71)	70-74 (71-73)	50-87 (53-79)	na
CC415	MA	TK	38	64.2	55	59-86 (58-90)	72-77 (67-86)	38-64 (45-62)	72-75
CC479	MA	TK	38	64.9	54	59-86 (58-73)	70-87 (67-88)	40-70 (42-63)	na
CC313	MA	TK	42	64.4	57	49-85 (54-74)	67-83 (66-88)	38-81 (33-65)	na
CC069	MA	ME	42	59.3	65	68-90 (68-85)	72-88 (72-85)	48-82 (40-70)	82-84
CC077	MA	ME	42	60.1	65	65-84 (69-90)	68-89 (72-87)	50-83 (52-60)	na
CC154	MA	ME	42	60.9	64	69-82 (61-89)	70-85 (74-80)	42-76 (46-61)	78-80
CC089	MA	ME	43	58.7	66	70-78 (77-89)	72-78 (69-87)	53-68 (51-70)	78-80
CC125	MA	ME	44	56.8	69	69-90 (67-89)	72-86 (80-84)	48-60 (55-63)	na
CC308	TH	-	170	57.0	54	67-70 (60-61)	71-83 (70-71)	56-82 (40-67)	na
CC326	TH	-	170	55.2	53	65-72 (54-60)	70-74 (72-74)	61-82 (78-79)	69-70
CC348	TH	-	187	53.8	59	67-76 (66-77)	63-86 (73-84)	68-86 (49-70)	70-85

Formation abbreviations are WH (Whakapapa), MA (Mangawhero), and TH (Te Herenga). Package abbreviations are SC (Saddle Cone), Turoa (TR), PT (Paretaitonga), RT (Rangataua), TK (Te Kohatu) and ME (Mangaehuehu). SiO₂ (in weight %) and values of Mg# [100Mg/(Mg + Fe)] are displayed for whole-rock lava. Range of Mg# values determined by EPMA are shown for Opx (orthopyroxene), Cpx (clinopyroxene) and Olv (olivine) phenocrysts and their rims (in parentheses). Anorthite % shown for analyses of Plg (plagioclase) phenocrysts and rims (in parentheses). NA indicates that olivine phenocrysts were not analysed for the sample.

4.4.6.1. Te Herenga Formation

The mineral assemblage of the 200–150 ka basaltic-andesites is dominated by subhedral pyroxene phenocrysts and glomerocrysts that range in size up to 14 mm and are readily visible in hand specimen. Orthopyroxene phenocrysts exhibit minimal compositional zonation ($\sim\text{Mg}\#_{70}$) but commonly have resorbed edges that are overgrown by coronas of orthopyroxene with $\text{Mg}\#_{55-60}$ (Fig. 4.10a). Clinopyroxene often displays complex multiple zoning outward of resorbed or mottled cores (Fig. 4.11a). Rims are typically more magnesian ($\text{Mg}\#_{75-80}$) than cores ($\text{Mg}\#_{70}$). Plagioclase phenocryst interiors are invariably sieved and often resorbed, whereas the outer $<200\ \mu\text{m}$ display faint cyclic zoning towards sub- or euhedral rims that are generally less calcic than the cores (Fig. 4.12a). Plagioclase crystals typically record more complex growth histories than pyroxene and olivine phenocrysts. Within CC348, the least evolved and oldest precisely dated Ruapehu sample collected in this study (see Chapter 3), olivine is relatively common as 100–500 μm -wide rounded crystals (either isolated or within clots) that display a gradual decrease from $\text{Mg}\#_{70-80}$ in cores towards $\text{Mg}\#_{<70}$ in rims (Fig. 4.13a). The rims are often resorbed (wavy) and overgrown by orthopyroxene with similar compositions to groundmass pyroxene ($\text{Mg}\#_{70}$).

4.4.6.2. Mangawhero Formation

Within the geochemically diverse Mangawhero Formation, the crystal-specific aspect of this study was restricted to lavas of the Mangaehuehu and Te Kohatu packages erupted during the early stage (50–35 ka).

Mangaehuehu package

Orthopyroxene and clinopyroxene phenocrysts and glomerocrysts dominate the mineral assemblage of lavas of this eruptive package. Accumulations of subhedral, unzoned and compositionally identical orthopyroxene form clusters $\leq 1.5\ \text{mm}$ across within Mangaehuehu package lavas (Fig. 4.10b). These clots commonly contain glass (which has often partially crystallised to form plagioclase) along grain boundaries, as well as symplectite veins and pools (up to 300 μm -wide accumulations) of Fe-Ti oxide phases (magnetite). Outermost rims that are in contact with groundmass have $<5\ \mu\text{m}$ -thick

reaction coronas composed of prismatic orthopyroxene with lower Mg#_{60–70}. Crystal shapes range from euhedral to resorbed and rounded, with common examples of mechanical breakage. The most conspicuous crystal type is reverse-zoned orthopyroxene (and minor clinopyroxene), which comprises ~8–17 % of the total phenocryst proportion (Fig. 4.10c). This crystal type exhibits rounded and unzoned cores with ~Mg#₇₀. Crystals display sharp transitions over 5–10 µm to dark rims with Mg#_{85–90}. The outer rims are generally euhedral, and average rim width varies between samples from 22–54 µm with widest rims observed in lavas with highest whole-rock Mg#. Outermost crystal margins typically have <5 µm-wide reaction coronas composed of orthopyroxene with similar Mg# values to the associated groundmass microcrystals (~Mg#₇₀). Reverse zoned orthopyroxene are present both as individual grains and within clusters. For clustered crystals, only the outermost grain edges that are in contact with groundmass have Mg-rich rims and rim width varies between adjacent crystals. Many individual crystals display broken edges along which there are thin orthopyroxene coronas but no high-Mg rims.

Clinopyroxene phenocrysts are subordinate in abundance compared to orthopyroxene and generally exhibit multiple compositional zones outward of resorbed or mottled cores with spongy textures (Fig. 4.11b). Core compositions range from Mg#_{65–85}; rim compositions lie within this range also. Clinopyroxene rarely (<5 % proportion of clinopyroxene) exhibit the strong reverse zoning displayed commonly by orthopyroxene: rounded cores (Mg#₇₀) are sharply overgrown by BSE-dark rims (Mg#₈₈) and the outermost edges are composed of orthopyroxene coronas.

Plagioclase phenocrysts generally lack the intensely sieved and cored interiors that are characteristic of plagioclase crystals within Te Herenga Formation lava flows. They are characterised by cyclic zoning in the outer half of the crystal area and outer rims define sub- to euhedral forms (Fig. 4.12b). Compositions dominantly lie between An_{50–60}, with rare calcic zones of An₈₀.

Interiors of olivine (Mg#_{78–84}) are unzoned or normally zoned toward grain edges that are strongly resorbed and overgrown by clusters of coalescing orthopyroxene crystals (Fig. 4.13b, c). Symplectite veins and 50–80 µm-wide patches of Fe-Ti oxide mineral phases are common at the interface between resorbed olivine and outer pyroxene crystals.

Figure 4.10. EPMA back-scattered electron images of orthopyroxene crystals in Ruapehu lavas. Mg# values are shown (in red) for analysis sites (red dots). Sample numbers and corresponding Formation and composition are labelled on each panel. Abbreviations are TH (Te Herenga), MA (Mangawhero), WH (Whakapapa), ba (basaltic-andesite), an (andesite), da (dacite). Patch of mnt (magnetite) is labelled in (b). Explanation of textures and features is provided in the text.

Figure 4.11. EPMA back-scattered electron images of clinopyroxene crystals in Ruapehu lavas. See caption of Figure 4.10 for explanation of abbreviations for sample labels.

Figure 4.12. EPMA back-scattered electron images of plagioclase crystals in Ruapehu lavas. See caption of Figure 4.10 for explanation of abbreviations for sample labels.

Figure 4.13. EPMA back-scattered electron images of olivine crystals with in Ruapehu lavas. In each example shown, ol (olivine) is bordered by rims of opx (orthopyroxene). Further explanation in text. See caption of Figure 4.10 for explanation of abbreviations for sample labels.

Te Kohatu package

As with Mangaehuehu package andesites, reverse-zoned orthopyroxenes (and minor clinopyroxenes) are present within Te Kohatu dacites, although in lower abundances (~7 % of total phenocryst proportion) compared to the andesites. Mg-rich rims (Mg#₈₂₋₈₈) have sharp boundaries with rounded cores (Mg#₇₀₋₇₆) and are overgrown by an outermost <5 µm-thick euhedral rim with compositions equivalent to groundmass pyroxene

microcrystals (Mg#_{60–70}). Unzoned orthopyroxene phenocrysts (Mg#_{60–70}) are present as sub- to euhedral grains as well as anhedral and broken crystals within the dacites. Clinopyroxene are generally sub- to euhedral and exhibit multiple compositional zoning patterns (Fig. 4.11c). Plagioclase phenocrysts display a range of complexly zoned types, often comprising sieved or spongy cores that have been resorbed and overgrown by multiple zones and subhedral rims. Anorthite contents range from 45–65 mol. %, and rims generally display less calcic compositions than cores. Rare euhedral apatite crystals (100–200 μ m-long) are present along pyroxene rims within glomerocryst clusters. Relict amphibole grains are identified based on their characteristic diamond-shaped cross-sectional forms but have been completely replaced by symplectite intergrowths of orthopyroxene + plagioclase + Fe-Ti oxides $\pm$ apatite $\pm$ minor glass. Clusters of crystals comprised of orthopyroxene, clinopyroxene, plagioclase and Fe-Ti oxides form clots up to 12 mm-wide within Te Kohatu dacite lavas. Interstitial glass is preserved between these phases within pockets that are not in immediate contact with groundmass.

4.4.6.3. Whakapapa Formation

Euhedral and subhedral grains of unzoned orthopyroxene with compositions of Mg#_{65–70} are the dominant crystal type within Whakapapa Formation lavas (Fig. 4.10a). Rare glomerocrysts of anhedral and unzoned orthopyroxene with Mg#_{65–70} occur within the lavas. Reverse zoned types with rim compositions of Mg#_{78–84} were observed in basaltic-andesite lava sample CC281 (~12 % of total phenocryst proportion) and rarely (<5 % phenocrysts) in samples CC193, CC260 and CC335. Clinopyroxene dominantly exhibits mottled cores, similar to those in the older formations (Fig. 4.11d). Resorbed olivine cores (Mg#_{70–75}) are overgrown by orthopyroxene (Mg#_{60–72}), and the boundary between olivine and orthopyroxene is often marked by magnetite symplectites (Fig. 4.13d). Plagioclase phenocrysts display resorbed cores that are often spongy or sieved. Outer zones of crystals exhibit fine-scale cyclic zoning (An_{60–90}) toward subhedral or euhedral rims.

4.5. DISCUSSION

The extended sample coverage and improved geochronological sequencing of lava flows presented here makes it possible to refine published models of the evolution of the Ruapehu magmatic system. The new data bring to light several key questions, including:

- What caused elevated levels of differentiation and diversity in magmas that were erupted between ~50 and 35 ka?
- What caused the reversion to more mafic whole-rock compositions (with less potassic melt inclusions) after 26 ka?
- What is the nature and origin of rhyolitic melts generated in the Ruapehu andesite-dacite magma system and what is their link to rhyolites from Taupo volcano?
- What is the petrogenetic significance of the eruption of a suite of high-magnesian andesites and dacites between ~50 and 35 ka?

4.5.1. Long-term whole-rock compositional trends

The eruptive products of composite volcanoes can cover the compositional spectrum from basalt to rhyolite, however, time-sequenced trends generally do not follow unique pathways of progressive evolution toward the silicic end of the spectrum (cf. Eichelberger et al., 2006). To explain non-systematic geochemical changes observed in volcanic sequences erupted over time periods ranging from <1 yr to >10 kyr, models of random tapping of individual batches of magma that have followed distinct lithospheric pathways of mixing and contamination have been invoked for Ruapehu and Tongariro (e.g. Hobden et al., 1999; Gamble et al., 1999; Shane et al., 2008; Price et al., 2012) as well as numerous composite volcanoes globally (e.g. Dungan et al., 2001; Frey et al., 2004). Over longer time periods of (>100 kyr), a common conception is that magma systems evolve toward producing more silicic eruptive products. This idea is founded on the association of non-evolved (mafic) eruptive products with stratigraphically old portions of volcanic edifices, and the eruption of more evolved lavas and, in some cases, the incidence of climactic explosive eruptions of silicic magma later in the history of composite volcanoes (e.g. Bacon and Lanphere, 2006; Hora et al., 2007; Singer et al., 2008; Escobar-Wolf et al., 2010). Throughout the cycle of volcanism represented by the eruptive products, the corresponding development of evolved, relatively low-density intrusive complexes in the

crust will impede higher-density, more mafic magmas from reaching the surface. This provides a feedback loop that may explain such evolutionary trends.

An alternative consideration is that the load imparted on a magma source region during the construction of a surficial volcanic edifice allows only the eruption of progressively more buoyant magmas as the load increases with cumulative growth of the volcano (Pinel and Jaupart, 2000). It then follows that destructive loss of mass from the edifice by sector collapse or erosion would enable the eruption of more dense magmas (Pinel and Jaupart, 2005). In this way, a composite volcano acts as a density filter for eruptible magma compositions.

4.5.1.1. Compositional evolution of Ruapehu lava flows

Investigating the time-sequenced variation of Ruapehu lavas enables assessment of the magmatic and crustal influences on the composition of eruptive products throughout the construction of a composite volcano in a continental arc setting. Ruapehu lavas display a gradual increase in SiO_2 , K_2O , incompatible trace element contents (represented here by Zr) and ratios (e.g. La/Yb) from ~200 to 80 ka (lavas of the Te Herenga and Wahianoa formations; Fig. 4.14). One of the oldest dated flows in this study is also the most mafic (sample CC348: ~190 ka; 53.8 wt. % SiO_2).

Following the gap between ~80 and 50 ka, during which no lavas were erupted that were captured by the intensive sampling undertaken previously and for this thesis, magma composition diversity was greatest during the eruptive period from ~50–35 ka (Fig. 4.14). Despite a compositional gap between lava flows with ~62 and 63 wt. % SiO_2 , effusion of dacite was prevalent during this time (Fig. 4.3). Lava flows that were erupted during this period display a wide range in incompatible trace element contents, which extend to the most continental crust-like values for Ruapehu samples, and generally does not overlap with the composition of lava flows in the Te Herenga Formation (Figs. 4.5, 4.14).

Lavas that have erupted since ~35 ka define a trend opposite to that in the earlier magmatic history: ~35–26 ka lava flows have a relatively narrow range of compositions intermediate within the range defined by ~50–35 ka lavas, and younger flows (<26 ka) exhibit progressively less silicic compositions with time (Fig. 4.14). An exceptions to this trend is the late Holocene Whangaehu flow (61.5 wt. % SiO_2) of the Crater Lake package.

Trends for incompatible major (K_2O) and trace (Zr) elements, as well as trace element ratios (La/Yb), display the same decreasing pattern as SiO_2 for post-35 ka lavas (Fig. 4.14).

Figure 4.14. Time-composition relationships for Ruapehu lavas. Lava ages are $^{40}Ar/^{39}Ar$ weighted mean plateau ages (WMPA) with associated 2sd uncertainties shown by bars. This figure is repeated here from Fig. 3.18 in Chapter 3 with additional trace element data. Grey diamonds are samples dated by Gamble et al. (2003) with corresponding compositional data presented by Price et al. (2012). Black diamonds are samples dated in this study. The timing of an apparent eruptive hiatus, the onset of deglaciation (d) and the sector collapse of the northern flank (s) are labelled in the top panel.

The matching trends for different elements suggest that some common process (or combination of processes) has controlled compositional variation through time. The linear relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and SiO_2 , K_2O , and incompatible trace elements indicates that assimilation of basement metasedimentary crust had a primary role, along with crystal fractionation, in the compositional development of post-Te Herenga Formation magmas. Crust-normalised multielement diagrams reflect this trend also. The most ‘crust-like’ compositions are observed for dacite lavas erupted at ~40 ka, whereas there are notably low values for lavas of the Te Herenga and Wahianoa formations, and a reversion to less crust-like values for Whakapapa Formation lavas (Fig. 4.14).

Previous bivariate major element plots revealed a scatter of overlapping data for lavas of variable age (e.g. Fig. 10 in Price et al., 2012). In light of the more comprehensive sample suite and better age control presented here, the covariance of molar K/Ca with SiO_2 contents is shown to be a particularly useful discriminant for lavas from the three broad periods of volcanism at Ruapehu (Fig. 4.3). Pre-80 ka lavas do not form a strong trend toward a unique end-member, but are tightly clustered around relatively low SiO_2 and K/Ca values (Fig. 4.3). Lavas that were erupted between ~50 and 26 ka and <26 ka define distinct SiO_2 -K/Ca compositional trends: Te Kohatu package dacite (sample CC508; 37.6 ± 1.4 ka) forms a silicic end-member for 50–26 ka lava flows; Whakapapaiti package member dacite (sample CC513; 25.7 ± 3.8 ka) forms a silicic end-member for <26 ka lavas (Fig. 4.3). Although the preserved portion of Whakapapaiti package dacite flows is volumetrically minor (see Chapter 3, Fig. 3.10), their eruptions delineate a significant change in the mechanics of magma genesis after ~26 ka.

As noted above, lavas erupted during the period from ~50–26 ka appear to be represented by a single silicic end-member in SiO_2 -K/Ca space (i.e. Te Kohatu package dacite; Fig. 4.4). However, examination of their MgO contents reveals a bimodal diversity. Mangaehuehu package andesites and Te Kohatu package dacites form a high-MgO trend when plotted against SiO_2 , whereas Ngahuinga package andesites and Mangaturuturu package dacites align with a lower-MgO compositional array (Fig. 4.15). The lower MgO trend is broadly representative of all other Ruapehu lavas except for the Whakapapaiti package dacite flows, which have distinctive K_2O concentrations (Figs. 4.3, 4.15).

Figure 4.15. Compositional characteristics (a, b) and spatial distribution (c) of early Mangawhero Formation lava flows. (a) MgO and (b) Al₂O₃ versus SiO₂ plots for lavas erupted from 50 to 35 ka. Colour key for lava packages is shown in (c). Shaded fields show compositional ranges for pre-80 ka Ruapehu lavas (i) and post-35 ka Ruapehu lavas (ii). Additional fields labelled for WH (~26 ka Whakapapaiti dacite package) and T2 (Type 2 plagioclase-phyric andesites of the Wahianoa Formation; Graham and Hackett, 1987)). Generalised trends (dashed lines) for the low- and high-MgO suites are projected towards K (Kakuki basalt) and W (Waimarino basalt), respectively. Basalt compositions from Gamble et al. (1993). Average compositions of P (Pukeonake andesite) and O (Ohakune andesite) shown for comparison; data from Cole (1978) and Hackett (1985). Locations of P and O labelled in (c).

Reasons for the high-MgO compositions are discussed in section 4.6.3., but the trends are here investigated to establish scales of heterogeneity within the magma system beneath Ruapehu. Preliminary comparisons are made between Ruapehu lavas and Waimarino and Kakuki basalts from the Taupo Volcanic Zone (Gamble et al., 1993), as well as Pukeoanake and Ohakune andesite lavas and scoria, which were erupted from small peripheral vents that are located ~20 km from the central vent area of Ruapehu (Fig. 4.15c). Eruptive activity at the peripheral vents pre-dates the deposition of the Oruanui tephra (25.4 ka; Vandergoes et al., 2013) as indicated by stratigraphic relations (Hackett, 1985; Froggatt and Lowe, 1990), and is likely to have occurred within the period ~40–30 ka, thus, making them broadly overlapping in time with the eruption of high-Mg lavas from Ruapehu. The discussion of the significance of these peripheral high-magnesian lavas is expanded in section 4.6.3.

Compositions for ~50–35 ka lavas span SiO₂ contents that equate to the range of all but the most mafic of pre-80 ka Ruapehu lavas whether sampled for this thesis or by previous work (Fig. 4.14). The compositional range of the high-MgO lineage is disrupted by a 1.5 wt. % gap in SiO₂ contents and a 0.5 wt. % gap in K₂O contents, which corresponds to a north-south spatial distinction between the two lava packages (Fig. 4.15). The high-MgO trend can be traced toward the composition of Waimarino basalt, and is approximately intercepted by the composition of Pukeonake and Ohakune andesites (Fig. 4.15).

The low-MgO suite (Ngahuinga and Mangaturuturu packages) displays a 1.9 wt. % gap in SiO₂ contents (Fig. 4.15) and a 0.5 wt. % gap in K₂O contents within lavas erupted at this time. This low-MgO group form a general trend from Mangaturuturu dacite toward Kakuki basalt, which is broadly intercepted by all post-35 ka and pre-80 ka lavas from the Ruapehu edifice. The striking geochemical association between the spatially discrete Mangaehuehu package andesite flows (to the south) and Te Kohatu package dacite flows (to the northwest) is notable given the eruption of low-MgO Ngahuinga package andesite and Mangaturuturu package dacite flows that were apparently also erupted from a vent focus that was proximal to that of Te Kohatu package dacites during the same period (Fig. 4.15c). Additionally, the unique geochemical characteristics of Mananui package dacite on northern Ruapehu indicate that this flow was sourced from a magma system separate to that of Te Kohatu and Mangaturuturu package dacites (Fig. 4.15).

These relationships imply that at least three magma types (Te Kohatu-Mangaehuehu high-MgO; Ngahuinga-Mangaturuturu low-MgO; Mananui mid-MgO) were feeding lavas to the south, west and north flanks of Ruapehu from spatially proximal vent foci during this time period (~50–35 ka) and yet were able to remain compositionally isolated. Mapping of compositionally distinct eruptive packages with overlapping time periods of emplacement for late (~35–26 ka) Mangawhero Formation lavas and Whakapapa Formation lavas (see Figs. 3.10, 3.14 in Chapter 3) is further evidence of magma heterogeneity within the magma system beneath the Ruapehu edifice. Despite this heterogeneity, the long-term compositional evolution remains broadly coherent (Fig. 4.14).

4.5.1.2. Potential role of density filtering of magma compositions

Here the possibility is investigated that the time-composition trends in the effusive volcanic record at Ruapehu are biased due to the ability of magmas of certain compositions to erupt is investigated. The mobility of magma depends on rheological properties governed by crystallinity, temperature, viscosity, and volatile content (Marsh, 1981), as well as regional tectonic stress regimes and mantle melt production. The compositions of erupted volcanic rocks are therefore ultimately biased towards those of magmas that overcome the opposing lithostatic load by ascending through the crust and ultimately being erupted. As lithostatic conditions that influence the ease of magma ascent through the crust change (e.g. regional rifting rates and addition or removal of overlying mass through edifice construction/destruction), so too will the potential for magmas of different composition to be erupted. The compositional variations within volcanic sequences at composite volcanoes can potentially trace these changes. One hypothesis that has been explored for the magmatic evolution of composite volcanoes through modelling (Pinel and Jaupart, 2000) and chemostratigraphic studies (Hora et al., 2007; Escobar-Wolf et al., 2010) is that cumulative edifice growth increases lithostatic pressure on magma chambers and inhibits the ascent of dense magmas, thus filtering the composition of erupted products toward more evolved types. With time the density of magmas will be lowered via crystal fractionation, enabling them to overcome the critical density threshold imposed by loading of the edifice in order to ascend and ultimately erupt (Pinel and Jaupart, 2000). Conversely, unloading of an edifice via deglaciation,

erosion or sector collapse will reduce the confining pressure on magma reservoirs and enable relatively dense magmas to ascend to the surface (Pinel and Jaupart, 2005).

In light of the hypothesised consequences of density filtering at growing volcanic edifices, two observations within the geochemical evolution of Ruapehu lavas are considered significant here. First, the prevalent effusion of dacite following >150 kyr of edifice construction by effusive eruption of basaltic-andesites and andesites of the Te Herenga and Wahianoa formations. Second, the reversion to more mafic lava compositions, which broadly overlaps with deglaciation of the edifice after ~18 ka and Holocene sector collapse events.

With respect to the first observation, the 50–35 ka effusive episode occurred after an apparent ~30 kyr hiatus in eruptive activity (Fig. 4.14). This followed the construction of a composite edifice comprising the Te Herenga and Wahianoa formations that contributed a $\geq 110 \text{ km}^3$ volume of total eruptive products to the lithosphere above the Ruapehu magmatic system, during which time lava compositions generally became gradually more evolved (Fig. 4.14). The eruptive hiatus may represent the development of a density barrier for the eruption of basaltic-andesite and andesite magmas that had been ongoing for the prior ~100 kyrs (Fig. 4.14).

Mangawhero Formation dacite lavas were erupted following the apparent hiatus, but basaltic-andesites were also erupted at the beginning of the 50–35 ka eruptive period (within the Mangaehuehu and Ngahuinga packages) with SiO_2 contents comparable to pre-80 ka lavas. The eruption of basaltic-andesite appears to contradict the hypothesis that a density filter biased the eruptible magma compositions at this time. The connection between the apparent compositional gap for lavas with SiO_2 between 61.9–63.4 wt. % erupted at ~50–35 ka (Figs. 4.3, 4.15) and a density control on eruptible magma compositions is ambiguous. The compositional gap was, however, partially filled by the subsequent eruption of Manganuioteao package lavas between ~35 and 26 ka (Table 4.2).

With respect to the second observation, there is a conspicuous trend toward more mafic lavas erupted since ~26 ka and Holocene lava flows are exclusively andesites to basaltic-andesites with SiO_2 contents ≤ 59 wt. % (excepting the late Holocene Whangaehu flow with 61.5 wt. % SiO_2). Although not exactly coincident with the onset of this compositional change, wholesale glacial retreat on Ruapehu from ~18 ka is inferred from regional paleoclimate records (Newnham et al., 2003), and corroborated by local moraine

geochronology (Eaves, 2015) and lava-ice interaction features (Chapter 2; Conway et al., 2015). Furthermore, sector collapse of the northwest summit and upper flank at ~10.5 ka (Palmer and Neall, 1989; Eaves et al., 2015) and the southeast summit at ~4.6 ka (Donoghue and Neall, 2001) would have also contributed to a reduction of the vertical component of stress on the sub-volcanic system. From the preserved extents of the resultant debris avalanche deposits, the volume of collapsed material is calculated to be ~1 km³.

The positive relationship between SiO₂ and ⁸⁷Sr/⁸⁶Sr values for Ruapehu lavas indicates that crustal assimilation during magma genesis was a fundamental control on the eruptive products (Graham and Hackett, 1987; Price et al., 2012). This does not preclude the influence of a density filter (cf. Pinel and Jaupart, 2000) but is interpreted here to reflect a coupling between magma diversity and crustal assimilation, which relates more to the thermal condition of the crust than the load imposed by construction (or destruction) of a surficial edifice. Moreover, the volume of material reduced from the edifice due to sector collapse (~1 km³) and superficial ice cover is minor compared to total edifice volume (~150 km³). Factors such as tectonic activity and flux of melt from the mantle, although hard to quantify, are also primary influences on the timescales of magma generation and residence in the crust (e.g. Schmidt and Gruner, 2009). To conclude this section of the discussion, it is here considered to be unlikely that systematic trends within the ~200 kyr-long chemical evolution of Ruapehu lavas were influenced primarily by density filtering of eruptible magma compositions. Instead, eruptions tapped magmas that had undergone variable degrees of differentiation in the crust via mechanisms of crystal fractionation and crustal assimilation. The extent of magma differentiation has apparently varied systematically (Fig. 4.14) from minimal degrees at 190 ka that increased gradually for lavas erupted between ~160 and 80 ka, to maximum (though variable) degrees at ~50–35 ka, followed by a reversion to lower degrees since 26 ka. Thus, despite evidence for short-term heterogeneity within individual eruptive sequences on annual to 10 kyr timescales (e.g. Gamble et al., 1999, 2003), this study has defined a broadly coherent geochemical trend for Ruapehu eruptive products over the ~200 kyr lifetime of the exposed edifice. The mechanisms of magma differentiation and the reasons for their varied influence through time are now explored in the following sections.

4.5.2. Nature and origin of silicic melts in Ruapehu lavas

Silicic glass compositions (often rhyolite) for groundmass and melt inclusions in arc andesite-dacite volcanic rocks have been widely reported (Reubi and Blundy, 2009; Kent, 2013; Lee and Bachmann, 2014). Determining the origin of silicic melts within volcanic arc systems is of key importance for understanding the distinctive continental signature of arc rocks and element recycling through the mantle and crust. Silicic melts can originate via fractionation of mantle-derived primary basaltic magmas (e.g. Sisson et al., 2005), partial melting of subducted oceanic lithosphere and sediment (e.g. Tatsumi, 2001), partial melting of crustal source rocks (e.g. Jackson et al., 2003) or plutonic crystal cumulates from prior magmatism (Reubi and Blundy, 2008) or some combination of these possibilities. The compositions of melt inclusion glasses that represent trapped portions of melt from the Ruapehu magma system are reviewed and compared to regional and global examples in this section.

Dacite to rhyolite glass compositions (~67–78 wt. % SiO₂) are reported for Ruapehu lava groundmass and pyroxene melt inclusions in this chapter (Fig. 4.8). The range in SiO₂ contents broadly overlaps with previously reported data for inclusions in samples from historical eruptions (Gamble et al., 1999; Kilgour et al., 2013) and edifice-forming lavas from the Whakapapa and Wahianoa formations (Price et al., 2005, 2012). The first melt inclusion data from Te Herenga Formation lava flows are presented here, in addition to those for newly defined Mangaehuehu andesite and Te Kohatu dacite eruptive packages of the Mangawhero Formation.

The silicic composition of Te Herenga Formation lava melt inclusions may not be a surprising result considering the ubiquity of such inclusion compositions in younger Ruapehu lavas (Price et al., 2005) and arc volcanic rocks globally (Reubi and Blundy, 2009). However, the new data highlight the notion that even the most basic eruptive products erupted at Ruapehu cannot be considered primary magmas and should be used with caution in petrogenetic models (e.g. Price et al., 2012). The low-K/Ca whole-rock composition of Te Herenga Formation lavas matches the relatively low K₂O contents of their phenocryst-hosted melt inclusions. Combined with their unique whole-rock ¹⁴³Nd/¹⁴⁴Nd isotopic compositions, these results provide further evidence that distinct petrogenetic processes operated to generate melts and derivative magmas in the ~200–150 ka time period compared to subsequent magmatism.

Melt inclusions and groundmass glasses within the Mangaehuehu and Te Kohatu packages of the Mangawhero Formation have significantly higher K₂O contents in comparison to Te Herenga samples (Fig. 4.8). In particular, K₂O contents of up to 5–6 wt. % were measured for groundmass glasses, melt inclusions and xenolith-hosted glasses within Te Kohatu dacite lavas. The characteristics of these melts can be best explained by partial melting and assimilation of a meta-sedimentary crustal source with a significant contribution from melting of a K-bearing mineral. Such rocks exist within the Torlesse Terrane that forms the basement and upper to mid-crust beneath Ruapehu, and biotite and K-feldspar are present within the greywacke-argillite mineral assemblage (Graham and Hackett, 1987; Graham et al., 1990; Adams et al., 2009) and is inferred to have provided the high K₂O in the melt. This process was fortuitously captured by the discovery and analysis of xenolith-hosted glass within dacite sample CC415. Similarly high K₂O contents were measured in these melt pockets that also display Rb contents of up to 250 ppm, which further implicates the preferential partial melting of biotite out of the crustal source rocks and into the melt. High ⁸⁷Sr/⁸⁶Sr values for Mangawhero Formation dacites (Fig. 4.6; Price et al., 2012) further underlines the elevated level of crustal contamination of these magmas. The role of assimilation of continental crust within the genesis of post-Te Herenga Formation magmas has been widely documented (Graham and Hackett, 1987; Price et al., 2005; Price et al., 2012). The new data in this thesis reveal that this process was most pronounced during the period from ~50–35 ka.

Melt inclusions in Whakapapa Formation lava flows exhibit a range of compositions that notably return to lower K₂O contents (Fig. 4.8). The compositions presented here are consistent with groundmass glass and melt inclusion data for historically erupted samples (Gamble et al., 1999; Kilgour et al., 2013) and previous analyses from Whakapapa Formation lavas (Price et al., 2012) and ~11 ka pyroclastic deposits (Donoghue et al., 1995b). Furthermore, the glass data match the lower K₂O contents within whole-rock compositions and the lower K/Ca trends defined by <26 ka lavas compared to earlier Mangawhero Formation lavas (Fig. 4.4). ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr systematics indicate that Whakapapa Formation lavas were derived from magmas that were contaminated by a continental crust assimilant, although to a lesser degree than the earlier Mangawhero Formation lavas (see section 4.5.1). The glass data indicate that these crustal melts were less enriched in K₂O than earlier melts trapped within lavas erupted at ~50–35 ka. This may reflect a lesser contribution from K-rich mineral phases to the partial melts and/or

higher degrees of partial melting in the crustal source region for the younger eruptive products.

The documentation of silicic melts within Ruapehu eruptive products led to comparisons by Price et al. (2005) with the products of rhyolitic volcanism at Taupo volcano where the basement crust is thinner and hotter than it is beneath Ruapehu (Harrison and White, 2004). Price et al. (2005) postulated that andesitic volcanism at Ruapehu represents a thermally immature stage of arc magmatism that might eventually evolve toward voluminous production of silicic magma (Price et al., 2005).

Eruptions at Taupo volcano evacuated extremely large volumes of silicic magma assembled within upper crustal mush systems where fractionated melts were pooled at shallow levels in the crust (e.g. Allan et al., 2013; Barker et al., 2015). Considering the difference in crustal characteristics beneath Taupo and Ruapehu, are the rhyolitic glasses produced within the two settings comparable?

Figure 4.16. SiO₂-K₂O compositions for Ruapehu lava whole-rock and glass compared to glass from Taupo volcano. Arrows indicate generalised whole-rock trends for 50–35 ka lavas towards TK (Te Kohatu package dacite) and for post-26 ka lavas towards WH (Whakapapaiti package dacite). Glass data are shown for xg (xenolith glass) and mi (melt inclusions) in TK lavas for Ruapehu. Field for TV gl (Taupo volcano glass, post-Oruanui) based on data from Barker et al. (2015).

Glass compositions from Whakapapa Formation lavas broadly overlap with matrix glass and melt inclusion compositions from Oruanui and post-Oruanui eruptive products from Taupo volcano (Barker et al., 2015), whereas glasses from Mangawhero Formation lavas contain substantially higher K₂O contents (TK in Fig. 4.16). Light rare earth element (LREE) contents in rhyolite glass and whole-rock samples from post-Oruanui eruptives

from Taupo are similar to those of contents for Ruapehu whole-rock dacite lavas of the Mangawhero Formation (Fig. 4.17). The trace element patterns for the eruptives from the two settings are divergent for heavy REE, with Taupo eruptives displaying relatively higher concentrations. The xenolith-hosted glass from Ruapehu sample CC415 displays slightly elevated contents for LREE compared to Taupo rhyolites (Fig. 4.17). Lower K₂O contents and higher HREE contents in glasses from post-Oruanui eruptives from Taupo volcano compared to Mangawhero Formation lavas from Ruapehu are interpreted to reflect higher degrees of partial melting of assimilated continental crust in the Taupo silicic magma system, which is reflected by generally high ⁸⁷Sr/⁸⁶Sr values compared to Ruapehu lavas (Price et al., 2005).

Figure 4.17. Chondrite-normalised Rare earth element plot for Ruapehu lava whole-rock and glass compared to Waimarino and Kakauki basalts, and post-Oruanui dacites and rhyolites from Taupo volcano. Basalt data are from Gamble et al. (1993). Taupo glass data are from Barker et al. (2015). Normalising values are from Sun and McDonough (1989).

Compared to younger lavas at Ruapehu, the high-K nature of glasses within the Mangaehuehu and Te Kohatu eruptive packages of the Mangawhero Formation are considered to represent products of the incipient stages of assimilation of middle to upper continental crust. Lava flows of the Whakapapa Formation encapsulate melts generated in a crustal melting scenario that is more advanced than at ~40 ka beneath Ruapehu. Progressive heating and melting of the crustal column prior to 26 ka is interpreted to have produced melts that were less enriched than at ~50–35 ka because of either or both of: (1) the exhaustion of fertile, K- and Rb-rich phases (e.g. biotite) that were readily fused during early stages of upper crust assimilation; and (2) higher degrees of partial melting as magma flux continued for the magma system beneath Ruapehu.

The compositional similarity between a crustal partial melt analysed in-situ within its host xenolith fragment that was captured by the derivative magma (i.e. xenolith-hosted glass within dacite sample CC415) and the groundmass of that lava highlights the concept that crustal assimilation has a significant bearing on the geochemical characteristics of eruptive products at continental arc volcanoes. The continental crust-like compositions of arc magmas may reflect either or both of the processes of fluid flux melting of the mantle wedge and crustal assimilation. Resolving the origin of the signature has important implications for tracing the recycling of elements through the ‘subduction factory’ (Davidson et al., 2005). The addition of ‘exotic’ melts formed through preferential melting of fusible phases within assimilated xenolithic or antecrystic material has been shown to contribute significantly to the trace element budget of andesitic magmas (e.g. Reubi and Blundy, 2008). In particular, the budget of large-ion lithophile elements (LILE: K, Rb, Cs, Sr, Ba) in arc magmas, which has been traditionally linked to a subducted slab and entrained sediment component (e.g. McCulloch and Gamble, 1991), may be augmented by partial melts from crustal source rocks in the arc lithosphere. A contribution of LILE from partial melts of continental crust to Ruapehu magmas is shown here to also be significant, particularly during the period from ~50–35 ka. The contribution from the primary mantle source of Ruapehu magmas is much more difficult to ascertain, because melts from this region have not been sampled.

4.5.3. A case for mafic recharge recorded in high-Mg andesite-dacites at Ruapehu

High-magnesian andesites (HMAs) are intermediate arc volcanic rocks (54–65 wt. % SiO₂) with high Mg# (≥ 50) and high Cr and Ni concentrations (Kelemen et al., 2003a). At an extreme, the eruption of primitive HMAs with Mg# ~70, although rare, is of particular importance because such magmas may be produced by partial melting of hydrous mantle peridotite (e.g. Grove et al., 2002, 2005; Wood and Turner, 2009) and play a fundamental role in the genesis of arc magmas and continental crust (Kelemen et al., 2003b). Other models for the petrogenesis of HMAs invoke equilibration of slab-derived melts with ultramafic mantle wedge material (e.g. Kay, 1978; Shimoda et al., 1998; Tatsumi, 2001; Yogodzinski et al., 2001) and felsic-mafic magma mixing combined with entrainment of ultramafic crystal material within arc lithosphere (e.g. Kawabata and Shuto, 2005; Streck et al., 2007). HMAs have been extensively studied at Mt Shasta in the Cascade arc

(Anderson, 1973; Grove et al., 2002; Streck et al., 2007) and the Setouchi volcanic belt in southwest Japan (Shimoda et al., 1998; Kawabata and Shuto, 2005). Previously studied New Zealand examples have erupted at White Island volcano (Mg#₇₀: Heyworth et al., 2007) and Hauhungatahi volcano (Mg#₇₀: Cameron et al., 2010).

Andesite and dacite lavas of the Mangaehuehu and Te Kohatu eruptive packages, respectively, can be classified as HMAs: whole-rock Mg# for the lavas range from 60–69 (andesites) and 54–57 (dacites). Mangaehuehu andesites exhibit high MgO contents over a ~5 wt. % SiO₂ range, and Te Kohatu dacites (~64–65 wt. % SiO₂) have MgO contents that are notably higher than other Ruapehu dacite lavas (Fig. 4.3, 4.15). Other remarkable characteristics of Ruapehu HMAs are the elevated Cr and Ni contents of up to 470 ppm and 148 ppm, respectively, compared to other eruptive products at equivalent SiO₂ contents (Fig. 4.3). An important petrographic feature that distinguishes these HMA lavas from lower MgO flows at Ruapehu is the high proportion within the mineral assemblage of resorbed orthopyroxene crystals that are mantled by euhedral rims with high Mg# values (~88–90; Fig. 4.18). The HMAs also contain xenolithic material, indicating that their source magmas assimilated crustal rocks. Moreover, crustal partial melts are inferred to have contributed to the high-K compositions of groundmass glasses and melt inclusions within these lavas. The petrographic and geochemical characteristics indicate that derivative magmas underwent substantial fractionation and assimilation processes in the lithosphere and do not represent near-primary melting products from the mantle wedge.

Ruapehu HMAs are interpreted to have been produced via an influx of a deeper-sourced mafic magma that interacted with an upper crustal-level felsic magma. Hotter mafic magma is interpreted to have reactivated stalled crustal reservoirs, mingled and mixed with melts and entrained the cargo of crystalline material. Clusters of orthopyroxene crystals appear to have been incorporated from the felsic magma as evidenced by their resorbed cores (cf. Nakagawa et al., 2002; Fig. 4.18). Subsequent crystal growth occurred within the hotter magma to account for the higher MgO rims. The rims maintain consistently high MgO contents across their widths, which measure up to 54 μm (Fig. 4.18). Clusters of orthopyroxene preserved in the HMAs display high-MgO rims only on the outermost exposed margins of the crystal clots (Fig. 4.18), indicating that the mafic magma encountered a crystal-rich felsic magma and interacted with crystal margins that were in contact with the mafic magma during disaggregation of the crystal assemblage.

Mechanically broken edges on reverse-zoned orthopyroxene do not display high-Mg rims, indicating that breakage occurred after the crystals had undergone rim growth in the more mafic magma. Outermost crystal edges have thin coronas of orthopyroxene (Mg#₆₅₋₇₂), which represent reaction rims formed as grains were reincorporated into the final host magma.

Figure 4.18. EPMA back-scattered electron images of reverse zoned orthopyroxene in high-magnesian andesite lavas in the Mangaehu package. (a) Cluster of resorbed crystals that are overgrown by darker, Mg-rich zones and outermost rims in equilibrium with groundmass orthopyroxene microcrystals. (b) Reverse zoned orthopyroxene with broken edge, along which there is no Mg-rich rim. (c) Reverse zoned crystal with rounded core and euhedral Mg-rich rim. (d) Mg# values along an EPMA traverse along red line marked in (c).

Evidence for interaction between recharging higher temperature magmas and stagnant more felsic magmas has been reported in pyroclasts ejected in the 1995-1996 Ruapehu eruptions (Nakagawa et al., 2002). Whole-rock Mg# values of ~60 for the pyroclast samples are not as high as those reported in this study for Ruapehu HMAs of equivalent SiO₂ contents, which may reflect a greater contribution from the mafic end-member within the Mangawhero Formation HMAs. The comparable crystal zonation features are interpreted to reflect a similar process for older lavas and younger pyroclasts, however,

and has been documented in other continental arc settings. In particular, near-identical pyroxene zoning features are displayed in HMAs from Mt Shasta (see Fig. 2 in Streck et al., 2007) and the Setouchi volcanic belt (see Fig. 7 in Kawabata and Shuto, 2005). In both cases, magma mixing processes played a primary role in generating the HMA magmas. Mafic recharge and mafic-felsic interactions have been widely recognised as key processes at numerous arc volcanoes (see review by Kent, 2013). In some cases, this process results in the generation of HMA. It must be noted, however, that different types of HMA correspond to distinct petrogenetic origins and magma mixing is not required in every case. The Ruapehu type presented here lacks the high Sr/Y values that are characteristic of many examples, including those from neighbouring ~1.0 Ma Hauhangatahi volcano (Cameron et al., 2010), and are interpreted as being sourced from a melted slab component (e.g. Defant and Drummond, 1990).

Constraining the nature of primitive magmas within the southern end of the Taupo Volcanic Zone is difficult because even relatively primitive basaltic-andesites have generally undergone textural and chemical modification in the crust. The reverse zoned crystal cargo of HMAs provides only a cryptic record of mafic magma intrusion into the crust beneath Ruapehu. Comparison to regional primitive lavas, however, provides an indication of the composition of the mafic end-member involved in their generation and, moreover, yields insight into the spatial distribution of such an end-member with respect to regional volcanism. The high-MgO lineage of Ruapehu HMAs forms a trend towards the composition of Waimarino basalt (Fig. 4.15), which is a rare magnesian type of basalt erupted within the Taupo Volcanic Zone (Gamble et al., 1993). This trend is approximately intercepted by the average compositions of Pukeonake and Ohakune andesites (Fig. 4.15), which were erupted from vents located ~20 km to the north and southwest, respectively, of the central vent area of Ruapehu (Fig. 4.15). Pukeonake lavas have been described as hybrid andesites and their compositions can be modelled by mixing between Ruapehu dacite and Waimarino basalt (Graham and Hackett, 1987). A similar model of petrogenesis is invoked here for the formation of Ruapehu HMAs (Fig. 4.15). The shared petrogenetic origin of hybrid andesites at Ruapehu and within its periphery indicate the incidence of a common mafic end-member, which may be of key importance to fuelling volcanism within the Tongariro Volcanic Centre as well as the broader Taupo Volcanic Zone.

4.5.4. Evolutionary model of the magma system at Ruapehu

New petrological, geochemical and microanalytical data are here integrated with existing data and placed within a new high-resolution eruptive chronology to present an overview model for the evolution of the Ruapehu magma system over the last ~200 kyrs. Key stages of this evolution are summarised below.

Te Herenga Formation lavas that were erupted from ~200–150 ka represent magmas that transited through the lithosphere without significant assimilation of meta-sedimentary basement rocks as indicated by Sr-Nd isotopic systematics (Fig. 4.6; Price et al., 2005, 2012). Low whole-rock K/Ca values and incompatible element concentrations, and the low K₂O contents of silicic melt inclusions within these lavas reflect assimilation of altered Phanerozoic oceanic crust that is interpreted to underlie the greywacke-argillite sequence of mid-upper crustal rocks (Graham, 1987; Price et al., 2012). This is interpreted to represent the early stages of thermal development of the magma system beneath Ruapehu as captured by the sampling for this thesis and previous studies of the exposed edifice.

The magma system beneath Ruapehu was progressively fluxed by magmas that sourced the eruption of ≥ 74 km³ of Wahianoa Formation lavas from ~166 to 80 ka. Over this time period, erupted lava compositions generally evolved to more silicic compositions (Fig. 4.14), although geochemical variations throughout a ~300 m-thick lava sequence exposure reflect non-systematic changes (Gamble et al., 1999, 2003). Compositional characteristics of Wahianoa Formation lavas erupted between ~166 and 80 ka indicate their source magmas were contaminated by greywacke-argillite basement (Fig. 4.6; Gamble et al., 2003; Price et al., 2012), although normalised trace element diagrams indicate that this effect was not pronounced (Fig. 4.5). Emplacement of Wahianoa Formation lavas may have been punctuated by an eruptive hiatus from 80 to 50 ka, as reflected by the absence of eruption ages for the comprehensive suite of previous and new geochronology samples from the edifice.

Following the apparent hiatus, magma compositional diversity was greatest in lavas of the early Mangawhero Formation erupted during the period from ~50–35 ka. The basaltic andesite to dacite lavas erupted over this interval define an elevated K/Ca trend compared to all other eruptive products from Ruapehu and, accordingly, record a distinct and discrete stage of magmatic differentiation within the overall evolution of the magma

system. The most evolved of the lavas erupted during this time exhibit crust-like whole-rock trace element compositions and contain K₂O- and Rb-rich melts preserved within melt inclusions and interstitial glass patches (Fig. 4.7d). Within ~40 ka dacite lavas sampled in this study, fused portions of meta-sedimentary xenoliths that have encapsulated in-situ veins of K- and Rb-rich partial melts were analysed (Fig. 4.7c). These observations essentially record the process of crustal melting and assimilation within the derivative magmas at this time. Assimilation of these melts contributed to the high K/Ca trends, LILE contents and ⁸⁷Sr/⁸⁶Sr values of the derivative magmas and sampled lavas. The enrichment in LILE is inferred to reflect either or both of low degree partial melting and preferential melting of biotite within the metasedimentary crustal source rocks.

During the same ~50–35 ka period, recharging mafic magmas interacted with crustal level silicic magmas to produce hybrid highly-magnesian andesites and dacites erupted onto the southern and northwestern flanks of Ruapehu. Evidence for crustal assimilation in these lavas and petrographic features reflecting mafic-felsic interaction indicate Ruapehu high-Mg andesites-dacites are complex magmatic products arising from middle to upper crustal-level assimilation and mixing processes (cf. Mt Shasta, Setouchi volcanic belt). Other andesite and dacite lava packages that were erupted from spatially proximal vents (<1 km) during the same 50–35 ka period were not affected by mafic recharge processes and indicate that distinct magma types were able to remain compositionally isolated beneath Ruapehu.

Mid-Mangawhero Formation lavas were erupted onto the western flank of Ruapehu between ~35 and 26 ka. The composition of these andesites coincides with an apparent gap for lavas with ~62–63 wt. % SiO₂ erupted from ~50 to 35 ka. In contrast to prior conclusions by Graham and Hackett (1987) and Price et al. (2012), the revised chemical stratigraphy of Ruapehu lavas reveals a reversion since 26 ka to less silicic and less potassic eruptive products with lower incompatible element contents within the late Mangawhero Formation (~26–15 ka) and Whakapapa Formation. Melt inclusion compositions also revert to lower K₂O contents relative to Mangawhero Formation lavas and maximum values of ⁸⁷Sr/⁸⁶Sr are comparatively lower (Fig. 4.6; Price et al., 2012). Post-26 ka magmas are interpreted to have assimilated less enriched melts due to the exhaustion of fertile phases in the middle to upper crustal column and/or higher degrees of melting of crust associated with ongoing magma and heat flux through the magma

system. Alternatively, the crustal column may have become resistant to cumulative crustal assimilation through injection and crystallisation of a complex of dikes and sills.

4.5.5. Occurrence and formation of cristobalite in Ruapehu lava flows

Cristobalite is a high-temperature, low-pressure polymorph of crystalline silica. Despite the temperatures of magmatic systems being substantially lower than that of the stability field for cristobalite ($>1470^{\circ}\text{C}$; Deer et al., 1992), it has been widely observed in volcanic products (e.g. Baxter et al., 1999; Horwell et al., 2003; Schipper et al., 2015), and is therefore a key example of metastable crystallization in volcanic systems. Cristobalite most commonly occurs in rhyolitic or dacitic lava, where it grows from a silica-saturated vapour phase (e.g. Baxter et al., 1999; de Hoog et al., 2005; Horwell et al., 2013) or forms by devitrification of glass (e.g. Damby et al., 2014). The two processes are inferred to operate coevally but semi-independently of each other, with the latter contributing to the majority of total cristobalite content in a given sample (Schipper et al., 2015).

Figure 4.19. Bivariate plots for composition of cristobalite in Ruapehu lavas. Values were measured by EPMA and are normalised to 100 weight %. Distinct trends are evident for cristobalite within vesicles and within the groundmass.

This study presents the first recognition and definition of cristobalite in edifice-forming eruptive products at Ruapehu volcano. In addition to SiO₂ (96–99 wt. %), minor oxides with relative abundances of Al₂O₃ > Na₂O > TiO₂, K₂O comprise the bulk composition of cristobalite analysed by EPMA in this study. Divergent K₂O trends for cristobalite within vesicles and groundmass suggest that two distinct processes operated to form each type, with groundmass cristobalite incorporating greater amounts of K₂O (Fig. 4.19).

It is inferred here that cristobalite formed from a silica-saturated vapour related to dissolution of glass within Ruapehu lava flows as they were emplaced and cooled on the flanks of the edifice. Cristobalite was sparse or absent in glassy flows, thus, rapid quenching of the margins of flows emplaced against ice is inferred to have precluded the formation of cristobalite in glass Te Kohatu package dacite lavas studied here. In contrast, slower cooling in flow interiors increased the potential for cristobalite formation.

Despite a general association with silicic pyroclastic and lava dome-forming eruptions, the results of this study suggest that cristobalite may also be widespread in mafic-intermediate effusive products from continental arcs due to the high frequency of dacitic to rhyolitic groundmass compositions in such rocks. At Ruapehu, glacial erosion and explosive magmatic and phreatomagmatic eruptions are likely to have made cristobalite readily available to the environment.

A modern motivation for studying the occurrence and formation of cristobalite is its potential to cause respiratory health hazards to populations living proximal to volcanic areas (Baxter et al., 1999). The discovery of cristobalite at Ruapehu and the potential for its widespread occurrence in the central North Island of New Zealand is a significant and unique finding. The reactivity of crystalline silica in human lungs is dependent on its chemical, physical and structural characteristics (Horwell et al., 2012), and the toxicity of pure cristobalite remains under investigation (Damby et al., 2013). Whether cristobalite poses a serious health risk to North Island populations is therefore unknown and requires further investigation.

4.6. CONCLUSIONS

Previous workers established a broad distinction between Te Herenga (≥ 150 ka) and post-Te Herenga periods of magmatism at Ruapehu, with magmas of the latter stage

undergoing progressively increasing levels of assimilation and fractional crystallisation with time since ~ 150 ka (Gamble et al., 2003; Price et al., 2005, 2012). This chapter has utilised existing isotopic data and petrogenetic models from these workers to further elucidate the evolution of the Ruapehu magma system. New whole-rock, mineral and glass compositions have been characterised for edifice-forming effusive products and sequenced within a high-resolution eruption chronology for Ruapehu (Chapter 3). The long-term compositional variability of lava flows displays systematic changes over the ~200 kyr lifetime of the exposed Ruapehu edifice and offers valuable snapshots into the crustal mechanics of an arc magma system. Major new findings are summarised as follows.

- The relatively low K₂O contents of melt inclusions from Te Herenga Formation lava flows are consistent with low whole-rock K/Ca values. Combined with their unique whole-rock ¹⁴³Nd/¹⁴⁴Nd isotopic compositions, the results provide further evidence that petrogenetic processes generating melts and derivative magmas at ~200–150 ka were distinct when compared to subsequent magmatism.
- Magma composition diversity was greatest during the period from ~50–35 ka. The range of basaltic-andesite to dacite lavas erupted during this time define an elevated K/Ca trend compared to all other eruptive products from Ruapehu. The most evolved of the lavas (high ⁸⁷Sr/⁸⁶Sr and crust-like trace element abundances) erupted during this time contain high-K₂O, high-Rb melts preserved within melt inclusions, interstitial glass patches and xenolith-hosted melt pockets. These melts were generated via low degrees of partial melting and/or preferential melting and assimilation of biotite-bearing greywacke-argillite source rocks in the continental crust basement. Taken in geochronological context, this suggests a ‘bottom-up’ heating of the crust beneath Ruapehu.
- Two eruptive packages of high-magnesian andesites and dacites were produced via interaction between crustal level felsic magmas and Mg-rich mafic magmas between ~50 and 35 ka. Clusters of pyroxene were thermally eroded from existing more felsic magma reservoirs by the influx of hotter, more mafic magma, and were then resorbed and overgrown by Mg-rich rims. Ruapehu high-Mg andesites-dacites represent magmas resulting from middle to upper crustal-level assimilation and mixing processes rather than primary magmas derived directly from mantle melting (cf. Mt Shasta, Setouchi volcanic belt).

- In contrast to conclusions from prior workers, the geochemical data from Ruapehu lavas presented here reveals a reversion to less silicic and less potassic eruptive products with lower incompatible element contents after 26 ka. Post-26 ka magmas are interpreted to have assimilated less enriched melts due to exhaustion of fertile phases in the crustal column and/or higher degrees of melting of continental crust associated with ongoing magma and heat flux through the axial magma system.
- Cristobalite was discovered and described within lava flows that span the ~200 kyr eruptive history of the exposed Ruapehu edifice. Cristobalite occurs as prismatic crystals on vesicle walls within relatively glassy samples and is felted through holocrystalline groundmass in slowly cooled samples. Imaging and compositional data acquired by EPMA for this thesis suggest that cristobalite may be widespread in lava flows with basaltic-andesite through dacite bulk compositions from other continental arc settings due to the high frequency of dacitic to rhyolitic groundmass compositions in such rocks.

CHAPTER 5

5. SYNTHESIS: GLACIOVOLCANIC AND PETROGENETIC PROCESSES PLACED WITHIN A HIGH-RESOLUTION LAVA CHRONOLOGY FOR RUAPEHU VOLCANO

5.1. Key findings

This thesis has presented a high-resolution geochronological framework for studying and interpreting processes and products of volcano-ice interaction, edifice growth and magma genesis at Ruapehu. Insights from these varied fields of research have been combined here to provide a detailed case study overview of arc volcanism at a glaciated composite edifice. The following synthesis revisits the questions that were introduced in Chapter 1 and presents key findings that resulted from testing these hypotheses. Each question turned out to present challenging limitations and open up new avenues for research, therefore, directions for future work are also suggested under the relevant sections.

5.1.1. Were ridge-top lava flows eroded by glaciers or emplaced against ice at Ruapehu?

Ruapehu presents an ideal locality to investigate volcano-ice interaction processes because of the long-term overlap between effusive volcanic activity (Gamble et al., 2003) and glaciation (Eaves, 2015), particularly from ~50 and 15 ka. Except for small summit region glaciers, the edifice is now almost entirely ice-free and offers excellent exposure of lava flows above the tree-line. Extensive pre-historical glaciation of the Ruapehu edifice is evidenced by the deep glacial valleys that indent the flanks of the volcano. However, the work of Lescinsky and Sisson (1998) indicates that high volcanic ridges adjacent to glacially eroded valleys can also be constructional volcanic features formed by impoundment and constraint of lava against ice margins during glacial periods. I sought to test this hypothesis for Ruapehu by conducting an edifice-wide reconnaissance of glaciovolcanic features (Chapter 2).

Lava flows located adjacent to formerly glaciated valleys display grossly overthickened margins (50–100 m) indicating flows were obstructed from being emplaced within valleys and grew thicker within a confined space as a result of this impoundment. The margins of these flows exhibit fracture networks that comprise column-forming joints, pseudopillow fractures, kubbaberg joints, crease structures and platy joints that are diagnostic of quenching against ice and/or impounded meltwater. These morphological and fracture characteristics indicate that the ridge-bounded flows formed as a result of emplacement against formerly extensive glaciers on the flanks of Ruapehu. Moraine crests that overlie ice-bounded flows indicate that some post-emplacement erosion of flow edges may have occurred. The primary morphology of the flows reflects, however, the syn-eruptive interaction between lava and ice.

Lava-ice interaction features at Ruapehu were first recognised by Spörli and Rowland (2006) for a limited areal extent of the eastern flank of the edifice. The work in this thesis has established that widespread volcano-ice interaction during edifice growth from ~50 to 15 ka has resulted in complex lateral and vertical contacts between lava flows. These complexities can now be accounted for by deflection and impoundment of lava away from valleys filled with ice during glacial periods, compared to flow emplacement within valleys during interglacial times (e.g. Lescincky and Sisson, 1998).

While the evidence for glaciovulkanism at Ruapehu is most clearly manifested for ice-marginal effusive activity during the period from ~50–15 ka, reconciliation of the timing of edifice growth with periods of global glaciation led to a reinterpretation of volcanic breccias within the Te Herenga and Wahianoa formations. The thick mounds of tuff breccias that underlie the corresponding sequences of lavas flows for each formation are classified in Chapter 3 as sub-glacial hyloclastites, which implies the presence of a pre-existing glaciated edifice as early as ~200 ka. Further investigation of the fragmentation and deposition mechanisms involved in sub-glacial andesite eruptions will provide an interesting case study to contrast with published work that has dominantly described rhyolitic and basaltic eruptive products from Iceland and Antarctica (e.g. Smellie et al., 2011; Tuffen et al., 2001).

The results presented in Chapter 2 and published by Conway et al. (2015) have been recently cited by local (Tost and Cronin, 2015) and international researchers (Lachowycz et al., 2015) and are applicable to other studies of composite volcanoes in New Zealand

and globally. It is critical that future researchers at Tongariro and Taranaki composite volcanoes of New Zealand investigate and integrate volcano-ice interaction processes within their eruptive histories.

5.1.2. Can ice-marginal lava flows be used to inform paleoclimate reconstructions of former glacier extents?

Having established a link between the distribution of ice-marginal lava flows and the presence of glaciers on Ruapehu, constraining the timing of lava emplacement with $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology presents a potentially powerful paleoclimate proxy. Traditional terrestrial ice extent reconstructions that are based on exposure age dating of moraines have been used widely to constrain the timing glacial advances in the South Island of New Zealand (e.g. Putnam et al., 2013a, 2013b; Kelley et al., 2014). Eaves (2015) applied ^3He exposure-age dating of lateral moraines in a similar way at Ruapehu to establish that a period of advanced ice extent occurred on the edifice between ~31–17 ka, during which time glaciers reached as low as ~1200 m elevation. Moraines indicate the ultimate extent of a glacier's advance, thus recording a unique aspect of local ice volume fluctuation during a glacial cycle. In contrast, the timing of eruption of glaciovulcanic products occurs independently of a glacier's position. Therefore, sequences of ice-marginal lava flows have the potential to act as valuable conservative records of glacier volume fluctuations for times when moraines were not formed, or have since been eroded.

$^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages of ice-bounded flows were utilised to interpret glacial extents on Ruapehu since ~50 ka in Chapter 3. Glacial impoundment and the associated overthickening and slow cooling of the interior zones of thick flows of the Mangawhero Formation have combined to produce favourable groundmass textures for $^{40}\text{Ar}/^{39}\text{Ar}$ dating at Ruapehu. These zones have been exposed via erosion of the steep and finely fractured quenched margins of many flows. Consequently, the precision of the ages measured in this study permit ice extent reconstructions that are resolvable on timescales of 2–5 kyr.

Full-glacial conditions equating to valley-filling volumes of ice are indicated by the elevation above formerly glaciated valley floors of ice-bounded flows erupted between ~50 and 25 ka. The results are consistent with synchronous cooling between Antarctica

and New Zealand at ~42 ka as constrained by moraine evidence in the Pukaki glacier region in South Island, New Zealand (Kelley et al., 2014). Age data for ice-marginal dacite lava flows on northwest Ruapehu indicate this period of cooling may have lasted until at least 38 ka. This information is not recorded by moraine formation at Ruapehu and serves as an example of the value of glaciovolcanic products for reconstructing past terrestrial ice extents. On the basis of their relatively lower heights within valleys and lesser thicknesses, lavas erupted at ~25–18 ka were apparently impounded by smaller volumes of ice than were present at ~31 ka. Estimating thicknesses and volumes of ice responsible for impounding lava flows relies on discerning the elevation difference between the lava flows and the floor of the formerly glaciated valley that was. This approach is limited by the uncertainty of how much the valley floor has been subsequently lowered through down-cutting and glacial erosion or raised by fluvial aggradation and volcanic construction since the timing of lava-ice interaction.

Figure 5.1. Volcano-ice interaction features on southwest Ruapehu. Location of valley labelled (red star) and direction of view noted by arrow in the inset map. Peaks of Tahurangi (T) and Girdleston (G) are labelled. $^{40}\text{Ar}/^{39}\text{Ar}$ ages are labelled for ice-bounded lavas within the glacial valley catchment for the southwest flank. The ^3He exposure age indicate moraine formation at ~13 ka (Eaves, 2015), following retreat of the local ice volume that had previously impounded lava flows.

Studies that combine constraints from dated ice-marginal lava flows and moraine exposure ages represent the best approach to accurately interpret glacial histories in

volcanic settings (Fig. 5.1). This PhD research has contributed to one such study (Eaves et al., 2016b), in which ages of ice-marginal flows are used to provide temporally constrained tie-points for glacial extents in catchments for which no moraine exposure ages were acquired. In order to provide quantitative paleo-temperature information from ice flow models, the pre-existing topography of Ruapehu at ~20 ka was reconstructed using the eruptive history outlined in Chapter 3.

Changes in the distribution and morphology of lava flows erupted since ~15 ka are linked to deglaciation at Ruapehu. On the upper flanks (>2200 m a.s.l.) of the edifice <15 ka lava flows display evidence (i.e. localised ice-contact fracture networks, metre-scale overthickening, superficial glacial striae) for minor interaction with glaciers similar in extent to those present ~50 years ago (Heine, 1963). At lower elevations (<1700 m a.s.l.) <15 ka lava flows were emplaced on the floors of the previously glaciated valleys. While eruption ages for these lavas provide valuable constraints for the timing of wholesale glacier retreat at Ruapehu, glacial fluctuations in response to short-term climate variability since ~18 ka on Ruapehu are complex (Eaves, 2015) and beyond the resolution of the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology dataset.

5.1.3. Did Ruapehu grow via discrete episodes of construction punctuated by erosion, or are apparent eruptive hiatuses biased by non-preservation of volcanic products?

A central objective of this research was to establish a high-resolution geochronological framework in order to investigate the growth history of Ruapehu. The traditional model of edifice evolution at composite volcanoes invokes that constructive volcanism occurs via pulses of effusive activity that are separated by periods of erosion and sector collapse (e.g. Hackett and Houghton, 1989; Hildreth and Lanphere, 1994; Hobden et al., 1999). I tested this model by assembling a comprehensive lava flow eruption chronology using previous data from Gamble et al. (2003) and collecting new data from portions of the edifice that had previously been only sparsely sampled. Major findings from this aspect of my thesis are discussed here.

1. The previously interpreted hiatus in effusive activity defined by Gamble et al. (2003) for the period from ~115–60 ka has been readjusted to a ‘potential’ eruptive hiatus at ~80–50 ka (Fig. 5.2). Lavas erupted between ~115 and 80 ka have low preservation and exposure potentials because they were emplaced within valleys during the last interglacial

period and have subsequently been either eroded, or buried beneath till and younger volcanic products. These processes may result in a common bias towards non-preservation of lavas of this age at glaciated continental composite volcanoes globally. The discovery of flows of this age (coincident with interglacial marine isotope stage 5, 129–71 ka; Fig. 5.2) situated deep within valleys rather than exposed on adjacent ridges is further justification of the model proposed by Lescinsky and Sisson (1998; see section 5.1.1). Caution is given to labelling the revised period as a hiatus, because glaciation at this time (MIS 4; Fig. 5.2) may have eroded eruptive products or precluded emplacement of lavas on flanks because of minimal emergent topography adjacent to glaciated valleys.

2. Detailed sampling of lava flows within the Mangawhero Formation yielded ages that define a continuity in effusive activity from ~50–15 ka at Ruapehu (Fig. 5.2), rather than pulses centred at ~45 ka and ~22 ka (cf. Gamble et al., 2003). Due to the presence of flank glaciers within valleys throughout this period, growth of the edifice flanks occurred via construction of high ridges and planèzes. The geomorphic distinction between ice-bounded lavas of the syn-glacial Mangawhero Formation and intra-valley lavas of the post-glacial Whakapapa Formation is in concordance with the new geochronology data reported in this study.

3. The continuity of effusive activity over the last 50 kyr at Ruapehu has formed a volcanic stratigraphy that is now well-calibrated enough such that a high-resolution secular geomagnetic record in the southwest Pacific region can be acquired. This thesis research has contributed to two current projects within this field. A total of 17 eruption ages were measured for lava flows emplaced during the period from 50–35 ka that encompasses the Laschamp geomagnetic excursion event (~41 ka; Guillou et al., 2004; Singer, 2014). New geomagnetic data collected for the flows in a collaborative study has revealed the existence of an excursionsal magnetic field in New Zealand during the emplacement of Mangaehuehu package lava flows with $^{40}\text{Ar}/^{39}\text{Ar}$ ages ranging from 45.4 ± 2.0 ka to 41.8 ± 1.8 ka, but not for Ngahuinga package and Te Kohatu package lava flows with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 39.6 ± 2.8 ka and 39.1 ± 1.4 ka (Ingham, 2015).

Consequently, the ages of the lavas provide a high-precision constraint on the timing and nature of the excursion in the Southern Hemisphere. New $^{40}\text{Ar}/^{39}\text{Ar}$ ages presented in this thesis have also been used in a co-authored study of secular geomagnetic variation in New Zealand over the last 10 kyr by Greve et al. (2016).

Figure 5.2. Summary diagram of the effusive growth history of Ruapehu. Diamonds are $^{40}\text{Ar}/^{39}\text{Ar}$ weighted mean plateau ages (WMPA) and bars are the associated 2 σ uncertainties. Samples from Gamble et al. 2003 (grey) and this study (black) are arranged along the y-axis in chronological order of the WMPA. Timing of marine isotope stages (MIS) and data for the $\delta^{18}\text{O}$ curve are from Lisiecki and Raymo (2005). Eruptive volumes (km^3) for Te Herenga (TH), Wahianoa (WA), Mangawhero (MA) and Whakapapa (WH) formations, calculated in this thesis are provided in the top row.

4. Effusive products that form composite edifices provide the best opportunity to define the growth history of a volcano through studying the exposed intercalation of primary volcanic products. Complete eruption histories, however, should integrate the records of explosive volcanism and edifice destruction provided by distal deposits on the ring plain. Apart from a preliminary comparison between the compositions of post-50 ka lavas and pyroclastic deposits in Chapter 3, integration of explosive and effusive volcanic records has not been investigated in this thesis. It is, however, part of the wider collaborative mapping project (Townsend et al., 2016) and will receive further attention therein. The well-defined compositional characteristics of lavas for individual eruptive packages presented in this thesis provides the potential to geochemically correlate distal deposits with periods of effusive activity. This is particularly pertinent for the period from ~50–15 ka, for which lava packages have distinct compositions and the dynamics of ring plain

aggradation adjacent to the Ruapehu edifice have received little attention (cf. Tost and Cronin, 2015).

5. A further feature of the growth history of Ruapehu that can be illuminated from ring plain studies is the relationship between volcanism and tectonic activity. Comparison of the revised chronology of effusive activity at Ruapehu to slip rates on local faults would allow an investigation of this relationship. At present, however, the uncertainties on slip rate reconstructions for the period >20 ka preclude a thorough test of the coupling between extension and magma flux rates (cf. Villamor and Berryman, 2006a, 2006b). This is a fundamental concept that should be further investigated for Ruapehu by refining the constraints on fault displacement rates.

6. A comprehensive study of the growth history of Tongariro composite volcano constrained by new $^{40}\text{Ar}/^{39}\text{Ar}$ ages should be undertaken. Considering the close proximity to Ruapehu, and the similarity of the timescales of eruptive (Hobden et al., 1999) and glacial histories (Eaves et al., 2016a), similar approaches to those used in this thesis are applicable.

5.1.4. What are the ages of the oldest and youngest lava flows exposed on the edifice, and can the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer be applied to Holocene andesite flows?

The oldest indication of volcanism in the Ruapehu region is manifested by the ~1 Ma basaltic-andesite lavas of Hauhangatahi (Cameron et al., 2010). Early volcanism at the location of the modern Ruapehu edifice has been connected to distal andesitic clasts in ~340 ka marine terraces located ~200 km to the southwest by Tost and Cronin (2015). However, dating of eruptive deposits within the deepest exposures of the edifice by Gamble et al. (2003) yielded maximum ages of ~200 ka. I tested whether the Ruapehu edifice exposes any older record of volcanism by sampling deep exposures of Te Herenga Formation eruptive products on the northern flank. The oldest constraint presented in this study is an imprecise weighted mean plateau age (WMPA) of 187.9 ± 34.4 ka (Fig. 5.2). A more precise measurement with a comparable WMPA was determined for sample CC348 (186.2 ± 6.8 ka). These results did not extend the age constraints earlier than those set by Gamble et al. (2003) for the timing of eruptive activity relating to the construction of the exposed edifice. The age determined for CC348 which is from the least evolved basaltic-andesite lava sampled at Ruapehu is significant, however, because this lava had

previously been assigned an erroneous eruption age within the Mangawhero Formation (Price et al., 2012; i.e. 50–15 ka). The new age provides an important temporal tie-point for the geochemical evolution of eruptive products throughout the lifetime of Ruapehu.

At the other end of the age spectrum, I tested whether the $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometer could be applied to dating Holocene age andesite lavas. WMPA eruption ages of <5 ka determined for this study are consistent with late Holocene ages from field evidence for the relevant flows. Three experiments on Holocene lavas produced 2σ uncertainties of 2.2–2.8 ka, which are comparable to those for Mangawhero Formation lava flows and permitted the discrimination of lava flows into early (10–5 ka) or late Holocene (<5 ka) timeframes. This level of precision has previously not been achieved in other studies of such young andesite lavas (e.g. Jicha et al., 2012). The results support using the $^{40}\text{Ar}/^{39}\text{Ar}$ technique to date Holocene andesite lavas and indicate that optimal 2σ uncertainties can be as small as ~2 kyr.

Several Holocene flows on Ruapehu were, however, unable to be dated because emplacement and erosion of the lavas had not generated or exposed holocrystalline interior zones. These include andesite lava flows of the Rangataua and Saddle Cone eruptive packages. An alternative technique that could be used to constrain ages for these lavas is ^3He exposure dating. The local production rate of ^3He has recently been calibrated (Eaves et al., 2015) and used to constrain exposure ages of moraines at Tongariro volcano (Eaves et al., 2016a). The fresh margins of the Saddle Cone and Rangataua lavas, their location at low elevations (~1000 m) that have been minimally affected by seasonal snow and ice, and their pyroxene-dominated mineral assemblages make them suitable targets for ^3He exposure dating (cf. Eaves et al., 2015).

5.1.5. What processes controlled the timing of two major Holocene sector collapse events?

Major collapses of Ruapehu's northern and southern summit sectors occurred respectively at ~10.5 ka (Palmer and Neall, 1989; Eaves et al., 2015) and ~4.6 ka (Donoghue and Neall, 2001). These events generated debris avalanche deposits that inundated the flanks and adjacent ring plain in areas that now coincide with ski fields, small townships and state highways. Understanding the causes of edifice instability that led to these events is

fundamental for determining the future hazard potential at Ruapehu and other composite volcanoes.

The interpretation put forward in this thesis invokes deglaciation to have played a primary role in controlling the timing of Holocene sector collapses at Ruapehu. Wholesale retreat of glaciers is inferred to have occurred from 18–15 ka, although upper flank glaciers and a summit ice cap are likely to have remained for several kyrs. Rapid climate amelioration from ~11 ka is indicated by regional records (e.g. Newnham et al., 2003), which broadly coincides with the cessation of construction of summit cones composed of Paretaitonga (14.8 ± 3.0 ka), Tureiti (11.9 ± 2.8 ka) and Turoa (11.9 ± 2.2 ka) package flows. The retreat of glaciers and summit ice debutressed the pre-collapse summit cones and exposed parts of the supporting steep, hydrothermally altered edifice that had been under ice. While deglaciation conditioned the instability of the edifice, disruption via seismic or volcanic activity may have provided the eventual trigger for collapse of the cones.

Post-20 ka warming is inferred to have been a global factor in generating sector collapses at glaciated volcanoes (Capra, 2006). Other steep, hydrothermally altered and fractured portions of the Ruapehu (and Tongariro) edifice remain prone to collapse if destabilised by volcanic or tectonic activity and present a real threat to recreational users and local populations of the Tongariro National Park at the current time.

5.1.6. Has edifice erosion, sector collapse and deglaciation since ~20 ka cause elevated eruption rates?

Constraining feedback mechanisms between glaciation and volcanism at ice-clad volcanoes is an important question for understanding and reconciling global volcanic records and climate drivers. Moreover, it is a relevant question in light of the rapid thinning and recession of alpine glaciers on many volcanoes in response to contemporary global climate change (e.g. Rivera et al., 2006). Eruptive volumes were calculated and compared for the periods from 50–15 ka and 15–0 ka to test whether the removal of a lithospheric load on the magma storage system at Ruapehu due to deglaciation, sector collapse and erosion led to enhanced eruption rates. Revised eruption rate estimates that were calculated based on the new chronostratigraphy are approximately constant at $0.8 \text{ km}^3 \text{ ka}^{-1}$ since ~50 ka, indicating that deglaciation of the edifice did not lead to a heightened magma production rate at Ruapehu.

Calculating lava flow volumes is an inherently complex process that must take into account numerous complicating factors, particularly the post-emplacement erosion of lava flows. Estimating volumes of syn-glacial lavas for Ruapehu were compounded by several limitations, including the unknown volume of lava transported to the ring plain by glaciers both during (due to supra-glacial emplacement of lava) and following effusive eruptions is difficult to quantify. However, the widespread presence of ice-bounded knuckles of overthickened lava suggests that the latter process of lateral erosion was less significant. Nevertheless, generalised thickness estimates that were used for eruptive packages may be biased by outcrops at flow margins where lavas were impounded and overthickened against ice. Conversely, the recognition of ice-marginal flow emplacement improves the accuracy of the estimate by discounting the back-calculation of eruptive volumes inferred to have been lost via valley incision.

The limitations of defining accurate eruptive rates at glaciated composite volcanoes are illuminated in this study as they have been in many preceding attempts (e.g. Singer et al., 1997; Frey et al., 2004). A note for future workers is that integration of the syn- and post-eruptive impacts of glaciation should be considered when undertaking such studies.

5.1.7. How has the varying magma flux through the lithosphere influenced the composition of erupted products over time?

New and existing petrological and geochemical data were sequenced into a ~200 kyr-long record of the compositional evolution of Ruapehu lavas in Chapter 4. The resolution provided by a more comprehensive sample suite and absolute age constraints for lava flows erupted since 50 ka has revealed compositional trends that were not observed by previous workers (Fig. 5.3). An overview evolution model for the Ruapehu magmatic system constrained by new results and existing petrogenetic models and isotopic data is outlined below.

Time-composition trends reveal a general increase in the degrees of crustal assimilation and crystal fractionation involved in magma genesis from ~200 to 80 ka (Fig. 5.3). Following the apparent 30 kyr-long eruptive hiatus, lavas erupted at ~50–35 ka exhibit wide compositional heterogeneity ranging from high-magnesian andesite (Mangaehuehu package) to evolved high-K dacite (Te Kohatu package). The latter type defines a discrete

end-member for all 50–35 ka lavas in SiO₂ versus K/Ca or Rb bivariate diagrams when compared to older and younger flows. Analysis of glass hosted within xenolithic fragments of fused metasedimentary basement indicate that Te Kohatu package lavas assimilated highly enriched partial melts of continental crust basement rocks. If a hiatus did precede this period of magmatism it may have provided a time period of progressive intrusion and stalling of magmas from the lower crust that consequently facilitated partial melting and assimilation in the middle to upper crust. This scenario is supported by existing Sr- and Nd-isotopic data that indicate elevated levels of crustal assimilation in 50–35 ka Mangawhero Formation lavas, relative to other time periods. A distinct reversion to less silicic, less potassic compositions is defined by lava flows erupted since 26 ka (Fig. 5.3). These magmas are inferred to have assimilated less enriched melts due to the progressive exhaustion of fertile phases in the crustal column from prior melting and ongoing magma and heat flux through the volcanic plumbing system beneath Ruapehu.

Figure 5.3. Age-SiO₂ evolution diagrams for Ruapehu lavas. Top panel displays new data from this study; bottom panel displays data from Gamble et al. (2003).

The coherent evolution of whole-rock compositions therefore appears to reflect the long-term thermal conditioning of the magma system beneath Ruapehu. Superimposed on this general trend are short-term geochemical heterogeneities preserved within lava flow sequences that exhibit non-systematic variability on timescales of 1–10 kyr. These heterogeneities reflect the unique combination of varied extents of melting, mixing,

fractionation and assimilation that each sequentially erupted magma batch undergoes within the complex crustal plumbing system (Price et al., 2012).

Microanalytical work undertaken in this study has contributed new constraints for the composition of key ingredients that produce the crust-like geochemical signatures of arc andesites and dacites. Preliminary characterisation of glass compositions within a temporal framework was undertaken, but further data are required to detail the evolution of the magma system, particularly for the period from 50–0 ka. The scarcity of pristine melt inclusions and areas of groundmass glass larger than $>10\text{ }\mu\text{m}$ -wide in even the most glassy of Ruapehu lavas is a limiting factor for such work.

This thesis did not present petrogenetic models to attempt quantification of the roles of melting, mixing, crustal assimilation and fractionation processes, but has provided a framework within which such models can now be developed. As noted by Dungan et al. (2001), the meaningful modelling of the origin and evolution of magmas requires high-resolution volcanic records with precise temporal constraints. Such a record is now available for Ruapehu lava flows and will contribute to the advancement of researching one of Earth Science's fundamental concepts: the formation of continental crust within the root zones beneath arc volcanoes.

5.1.8. Are high-magnesian andesites the products of primary mantle-derived magmas or mafic-felsic interaction?

High-density sampling of the previously sparsely sampled southern and western flanks yielded samples of lavas with distinct geochemical characteristics (Chapter 4). The Mangaehuehu (~47–40 ka) and Te Kohatu (~44–36 ka) packages of andesite and dacite lavas, respectively, exhibit elevated MgO, Cr and Ni contents compared to other Ruapehu eruptive products (Fig. 5.4). Based on the corresponding whole-rock Mg# values (60–69 for Mangaehuehu package and 54–57 for Te Kohatu package) the lavas are classified as high-magnesian andesites (HMAs; Kelemen et al., 2003a).

The eruption of HMAs at arc volcanoes is intriguing because such rocks may be the direct products of partial melting of hydrous mantle peridotite (e.g. Grove et al., 2002, 2005; Wood and Turner, 2009). This model is seemingly contradicted, however, by the irrefutable evidence for crustal assimilation in the Ruapehu HMAs, including the

presence of xenolithic fragments with metasedimentary assemblages and crust-like $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values. Alternative models invoke mixing between felsic and mafic magmas (e.g. Kawabata and Shuto, 2005; Streck et al., 2007), for which, in turn, there is strong evidence in Ruapehu HMAs. A population of orthopyroxene with rounded and resorbed $\text{Mg}_{\#70-72}$ cores that are mantled by euhedral rims with $\text{Mg}_{\#88-90}$ (Fig. 5.4) is prevalent in the lavas. The crystals occur in clots where only outermost crystal margins are mantled by high-Mg# rims and as single phenocrysts that are often broken (Fig. 5.4). The characteristics are consistent with a model of interaction between a hot recharging mafic magma and a stalled felsic magma in the crust (cf. Nakagawa et al., 2002).

Constraining the nature of primitive magmas within the southern end of the Taupo Volcanic Zone is difficult because even relatively primitive basaltic-andesites have generally undergone textural and chemical modification in the crust. Cryptic records of mafic magma intrusion into the crust beneath Ruapehu are provided by the reverse zoned crystal cargo of HMAs. Mafic magmas may represent important regulators of not only the composition of arc magmas but also the timing of their eruption and the involvement of mafic recharge events in eruptive episodes at arc volcanoes have been widely cited (see review by Kent, 2013). Future microanalytical efforts should be undertaken to document the composition of mafic magmas and their crystal cargoes that have fed eruptions from the central vent focus at Ruapehu as well as periphery vents (e.g. Ohakune and Pukeonake andesites). Such work will provide further information on the composition of primitive magmas that ultimately fuel arc magmatism.

5.1.9. Cristobalite in Ruapehu lavas

A fortuitous finding from this research was the discovery of cristobalite within lava flow samples that cover a wide spatial and temporal range, which represents the first recognition and definition of cristobalite in edifice-forming eruptive products at Ruapehu. Cristobalite occurs as prismatic crystals on vesicle walls within relatively glassy samples and is felted through holocrystalline groundmass in slowly cooled samples. Despite a general association with rhyolitic lava domes (e.g. Schipper et al., 2015), this study indicates that cristobalite may be widespread in lava flows with basaltic-andesite to dacite bulk compositions from continental arcs due to the dominance of dacitic to rhyolitic groundmass compositions in such rocks (Reubi and Blundy, 2009). At Ruapehu, glacial

erosion and explosive magmatic and phreatomagmatic eruptions are likely to have made cristobalite readily available to the environment. Cristobalite is also likely to be present within other andesite composite cones (e.g. Tongariro) as well as the voluminous rhyolite products throughout the Taupo Volcanic Zone. Physical weathering, mining for construction materials and geothermal energy exploration are likely to have disturbed these volcanic products and, potentially, caused dispersal of cristobalite across North Island, New Zealand. Whether this presents a serious health risk regional populations is unknown and requires further investigation.

5.2. Epilogue

This thesis has established a high-resolution chronostratigraphic framework through the collection and integration of geological, geochronological and geochemical datasets. This has permitted investigations of the interrelated magmatic, volcanic and glacial processes that shape glaciated composite edifices. In doing so, I have addressed key questions relating to the growth history and geochemical evolution of Ruapehu. New questions have been suggested in this synthesis and can be tested by future interdisciplinary research at Ruapehu and elsewhere along Earth's active volcanic arcs.

As a final thought, the multi-stage processing of volcanic rocks that originate as partial melts of the mantle wedge above subduction zones, transit through the lithosphere and are eventually emplaced on the flanks of a volcano, can be summarised as follows:

*The mantle proposes,
the crust imposes,
the edifice juxtaposes,
the glacier exposes,
the ring plain disposes,
the student supposes.*

The life history of arc andesites

After Hildreth (2007).

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APPENDICES

Appendix 1. Location of ice-marginal lava flows and fractures

Locations of fracture types identified and measured at outcrops of ice-marginal lava flows during fieldwork between 2012 and 2014 are displayed in Figure A1.1 and Table A1.1. Initial sites of interest, particularly steep ridges and bluffs, were identified from digital terrain models (DTMs) and aerial photographs, and subsequently reconnoitred. Locations were logged using a Garmin GPS unit in the field.

Figure A1.1. Location map of lava outcrops where fractures were identified and measured in the field (black squares). Tick marks are metres in the NZTM projection. Locations are provided in Table A1.1. Measurement data available in Appendix 2.

Table A1.1. Locations of lava outcrops of where ice-contact fractures were measured.

Flow type	E	N	CO	PP	CR	PL	KB
Ice-dammed	1818539	5652739	x				
	1818602	5652785			x		
	1818588	5652210			x		
	1818510	5652662				x	
	1818431	5652479				x	
	1817581	5650627	x	x	x		
	1817515	5651414				x	
	1817444	5651189				x	
	1817307	5650972				x	
	1816776	5650850				x	
	1816992	5651161	x	x			
	1824201	5651576				x	
Ice-bounded	1820524	5649986	x				
	1822604	5645717				x	
	1821834	5645497				x	
	1818196	5651218	x				
	1818287	5651253		x			
	1818465	5650989			x		
	1817898	5651701				x	
	1817855	5651482				x	
	1819363	5651820		x			
	1818263	5650621		x			
	1818066	5650558	x	x			
	1818528	5650394	x				
	1817362	5649446	x				
	1818127	5650145	x			x	
	1819009	5650243			x		
	1816307	5649444				x	
	1816973	5648753	x				
	1817346	5649043	x				
	1818580	5649177	x				
	1818580	5649177			x		
	1818392	5649274				x	
	1817495	5648804				x	
	1818585	5648075				x	
	1818815	5647389	x	x	x		
	1817710	5648384	x				x
	1817808	5647564	x	x			x
	1819177	5645252				x	
	1819351	5646290				x	
	1823279	5648634	x				
	1824505	5648629	x	x		x	
	1824201	5648476	x				
	1826472	5650407				x	
	1827232	5650071				x	
	1827524	5650644				x	
	1825768	5652155	x				
Sub-glacial	1823995	5646228	x	x			
	1818756	5645587					x
	1818688	5648627					x
Post-glacial	1823195	5644854				x	
	1822135	5651262		x			
	1822302	5653514				x	
	1819093	5651828		x			
	1821403	5652371	x				
	1821196	5652670		x			

Easting (E) and Northing (N) values are given in metres for the NZTM projection. Abbreviated fracture types are: CO (column-forming joints); PP (pseudopillow fractures); CR (crease structures); PL (platy joints); KB (kubbaberg joints).

Appendix 2. Fracture measurements for ice-marginal lava flows

This appendix provides measurement data for fracture types on ice-marginal lava flows at Ruapehu. Fracture types and attributes are shown in Figure A2.1. (repeated from Chapter 2) as a reference for measurement data in Table A2.1.

Figure A2.1. Characteristics of fracture types formed by interaction between lava flows and ice at Ruapehu.

Table A2.1. Measurement data for fracture types formed by interaction between lava and ice at Ruapehu.

Type	E	N	Position on flow	Orientation	Spacing	Length	Striation spacing
CO	1818539	5652739	front face	sub-horizontal	10-20 cm	2-3 m	n/a
	1817581	5650627	lower lateral	horizontal	10-20 cm	0.5-2 m	n/a
	1816992	5651161	front face	vertical	10-20 cm	0.5-2 m	n/a
	1818196	5651218	colonnade	fanning	10-20 cm	<30 m	2-4 cm
	1818066	5650558	colonnade	fanning	10-20 cm	<20 m	n/a
	1818528	5650394	lateral	horizontal	10-20 cm	1-3 m	n/a
	1817362	5649446	lateral	horizontal	10-30 cm	1 m	n/a
	1818127	5650145	front face	fanning	10-20 cm	1-3 m	2-4 cm
	1816973	5648753	lateral	fanning	10-20 cm	0.5-5 m	n/a
	1817346	5649043	lateral	horizontal	10-20 cm	1-2 m	n/a
	1818580	5649177	lateral	horizontal	10-20 cm	1 m	n/a
	1818815	5647389	lateral	sub-horizontal	10-20 cm	1-2 m	n/a
	1817710	5648384	lobe	fanning	10-20 cm	0.5-5 m	n/a
	1817808	5647564	colonnade	fanning	10-20 cm	<20 m	1 - 5 cm
	1823279	5648634	lateral	horizontal	10-20 cm	1-2 m	n/a
	1824505	5648629	front face	fanning	10-20 cm	<5 m	n/a
	1824201	5648476	lateral	fanning	10-20 cm	1-2 m	n/a
	1825768	5652155	lobe	sub-vertical	10-20 cm	1-3 m	2 cm
	1823995	5646228	colonnade	fanning	10-20 cm	<30 m	n/a
	1821403	5652371	lateral	horizontal	10-20 cm	<1m	n/a
	1820524	5649986	lateral	horizontal	10-20 cm	1 m	n/a

Fracture types are: CO (column-forming joints); PP (pseudopillow fractures); CR (crease structures); KB (kubaberg joints); PL (platy joints).

Table A2.1.1. (cont.) Measurement data for fracture types formed by interaction between lava and ice at Ruapehu.

Type	E	N	Position on flow	Orientation	Spacing	Length	Striation spacing
PP (M; S)	1817581	5650627	lateral	vert; hor	<5 m; <20 cm	<20 m; <30 cm	5 cm; n/a
	1816992	5651161	lateral	vert; hor	<2 m; <20 cm	<5 m; <30 cm	n/a
	1818287	5651253	colonnade	vert; hor	<5 m; <30 cm	<20 m; <30 cm	n/a
	1819363	5651820	front face	vert; hor	<5 m; <30 cm	<10 m; <30 cm	n/a
	1818263	5650621	lateral	vert; hor	<2 m; <20 cm	<4 m; <30 cm	n/a
	1818066	5650558	colonnade	vert; hor	<5 m; 30 cm	<5 m; <30 cm	n/a
	1818815	5647389	lateral	vert; hor	<5 m; <30 cm	<15 m; <30 cm	n/a
	1817808	5647564	colonnade	vert; hor	<5 m; 30 cm	<10 m; <30 cm	n/a
	1824505	5648629	front face	vert; hor	<5 m; 30 cm	<10 m; <30 cm	n/a
	1823995	5646228	colonnade	vert; hor	<2 m; <20 cm	<15 m; <30 cm	n/a
	1822135	5651262	lateral	vert; hor	<2 m; <20 cm	1 m; <20 cm	n/a
	1819093	5651828	lateral	vert; hor	<2 m; <20 cm	1 m; <20 cm	n/a
	1821196	5652670	front face	vert; hor	<2 m; <20 cm	1 m; <20 cm	n/a
CR	1818602	5652785	lateral	sub-vertical	<30 cm	<1 m	<2 cm
	1818588	5652210	lateral	sub-vertical	<30 cm	<2 m	<5 cm
	1817581	5650627	lateral	sub-vertical	<20 cm	<1 m	<2 cm
	1818465	5650989	colonnade	sub-horizontal	<20 cm	<50 cm	<2 cm
	1819009	5650243	lobe	sub-vertical	<20 cm	<50 cm	<2 cm
KB	1818580	5649177	lateral	sub-horizontal	<20 cm	<50 cm	<2 cm
	1818815	5647389	lateral	sub-horizontal	<50 cm	<2 m	<10 cm
	1817710	5648384	lobe	random	<10 cm	<10 cm	n/a
	1817808	5647564	colonnade	random	<10 cm	<10 cm	n/a
	1818756	5645587	top of esker	random	<10 cm	<10 cm	<2 cm
	1818688	5648627	lateral	random	<10 cm	<10 cm	n/a

For PP, measurement data are given for both M (master) and (S) subsidiary fracture planes.

Table A2.1.1. (cont.) Measurement data for fracture types formed by interaction between lava and ice at Ruapehu.

Type	E	N	Position on flow	Orientation	Spacing	Length	Striation spacing
PL	1818510	5652662	front face	horizontal	<5 cm	<1 m	n/a
	1818431	5652479	front face	horizontal	<5 cm	<1 m	n/a
	1817515	5651414	front face	horizontal	<5 cm	<1 m	n/a
	1817444	5651189	front face	horizontal	<5 cm	<1 m	n/a
	1817307	5650972	front face	horizontal	<5 cm	<1 m	n/a
	1816776	5650850	front face	horizontal	<5 cm	<1 m	n/a
	1824201	5651576	front face	sub-horizontal	<5 cm	<1 m	n/a
	1822604	5645717	front face	horizontal	<10 cm	<1 m	n/a
	1821834	5645497	lateral	horizontal	<10 cm	<1 m	n/a
	1817898	5651701	lateral	fanning	<5 cm	<1 m	n/a
	1817855	5651482	lateral	horizontal	<5 cm	<1 m	n/a
	1819363	5651820	lateral	horizontal	<5 cm	<1 m	n/a
	1816307	5649444	lateral	horizontal	<5 cm	<1 m	n/a
	1818392	5649274	lateral	fanning	<10 cm	<1 m	n/a
	1817495	5648804	front face	sub-vertical	<10 cm	<1 m	n/a
	1818585	5648075	lateral	sub-horizontal	<5 cm	<1 m	n/a
	1819177	5645252	front face	fanning	<5 cm	<1 m	n/a
	1819351	5646290	front face	fanning	<5 cm	<1 m	n/a
	1824505	5648629	front face	sub-vertical	<5 cm	<1 m	n/a
	1826472	5650407	lateral	horizontal	<5 cm	<1 m	n/a
	1827232	5650071	front face	sub-vertical	<5 cm	<1 m	n/a
	1827524	5650644	lateral	sub-horizontal	<5 cm	<1 m	n/a
	1823195	5644854	top of esker	fanning	<5 cm	<1 m	n/a
	1822302	5653514	lateral	horizontal	<5 cm	<1 m	n/a

Appendix 3. Sample list

A total of 413 lava samples were collected during fieldwork from 2012 to 2015. A subset of these samples were used for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and whole-rock and microanalytical geochemical analyses. Remaining sample material has been archived at Victoria University of Wellington. A full list of sample locations and the methods of analysis is provided in Table A3.1. Sample locations are shown in Figure A3.1.

Figure A3.1. Sample location map. Pink diamonds are samples for which eruption ages, and whole-rock major and trace element data were measured. Samples with major and trace element data (green diamonds) and only major element data (purple diamonds) are shown. White diamonds are samples that were not analysed by the above methods during this study. Map projection and grid coordinates are in NZTM metres.

Table A3.1. Locations for lava samples collected during this study.

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC050	1823033	5645038				
CC051	1823021	5644930		X		
CC052	1822999	5644882				
CC054	1822981	5644697				
CC055	1822953	5644666				
CC058	1824390	5643756				
CC059	1824706	5643624				
CC060	1824789	5642918				
CC061	1825141	5642398		X		
CC062	1824684	5642488		X		
CC063	1824440	5642030				
CC064	1824134	5642249		X	X	
CC065	1824029	5642286				
CC066	1824013	5641776				
CC067	1823873	5641387		X		
CC069	1823539	5641265		X		X
CC070	1823099	5641179				
CC071	1823066	5641352		X	X	
CC073	1823176	5643241				
CC074	1823088	5643550		X		
CC075	1823043	5644160		X		
CC077	1822829	5644731		X		X
CC078	1822608	5645149				
CC080	1822756	5645478		X		
CC081	1822604	5645717	X	X	X	
CC082	1822285	5645802				
CC083	1821699	5645996		X		
CC084	1821555	5645914		X		
CC085	1821604	5645626				
CC087	1821834	5645497		X		
CC088	1821653	5645115				
CC089	1821623	5644960	X	X	X	X
CC090	1823909	5643370				
CC091	1823537	5643237		X		
CC093	1823376	5642667		X		
CC095	1823060	5641683				
CC096	1823043	5641569		X		
CC097	1822774	5641712				
CC099	1822540	5642057				
CC100	1822820	5642430		X		
CC101	1823132	5642541				
CC102	1822461	5642803		X	X	
CC103	1822281	5643079				
CC104	1822110	5643137				
CC107	1822105	5642690				
CC108	1821834	5642936		X		
CC109	1821741	5643080				
CC110	1821595	5642985				
CC111	1821506	5643297		X		
CC112	1821730	5643322				
CC114	1822202	5643288		X	X	
CC115	1821966	5643855		X		

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC116	1820096	5643347		X		
CC117	1820386	5644444				
CC119	1820841	5644880	X	X	X	
CC121	1821139	5645231				
CC123	1821305	5645838				
CC125	1820706	5646278		X	X	X
CC126	1820503	5646099		X		
CC127	1820258	5645899	X	X	X	
CC129	1819670	5645177				
CC130	1820063	5646806	X	X	X	
CC134	1818530	5645414				
CC135	1818618	5645440		X	X	
CC136	1818722	5645352				
CC139	1819028	5645499		X		
CC140	1819256	5645213	X	X	X	
CC141	1819260	5645200				
CC143	1818544	5644352	X	X	X	
CC144	1818540	5644273				
CC145	1818684	5644556				
CC147	1818801	5644608				
CC148	1818771	5644657				
CC149	1819335	5645320		X	X	
CC150	1819513	5645421		X		
CC152	1819812	5645692		X	X	
CC154	1819901	5646086		X		X
CC155	1816930	5645350		X		
CC156	1817001	5645283		X		
CC157	1818107	5644618		X		
CC158	1818528	5645125				
CC159	1818052	5645431				
CC160	1817953	5645491		X		
CC161	1815488	5643704		X		
CC162	1816367	5643385		X		
CC163	1816612	5643102		X		
CC164	1817179	5642198		X		
CC165	1815260	5643802		X		
CC166	1825551	5649136				
CC167	1825165	5649263				
CC168	1825695	5649700				
CC169	1826707	5650941				
CC170	1826932	5650294				
CC171	1827524	5650644				
CC172	1827566	5650476				
CC173	1828822	5650623				
CC174	1813193	5641806		X		
CC175	1813001	5641741				
CC181	1820593	5648304		X	X	
CC182	1820427	5648303				
CC184	1820199	5648112		X		
CC185	1820050	5648202				
CC186	1819779	5648078		X	X	
CC187	1819239	5647907				

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC188	1818359	5647405		X		
CC189	1817194	5643265		X		
CC191	1820156	5645665				
CC193	1820086	5645232		X		X
CC195	1819954	5643956		X		
CC196	1825651	5647038		X		
CC197	1825342	5647375	X	X	X	
CC198	1825355	5647559		X		
CC199	1825018	5647417				
CC200	1824783	5647288		X	X	
CC201	1824612	5647519		X		
CC202	1824270	5647584		X		
CC203	1824028	5647642				
CC205	1824304	5647014		X		
CC206	1824527	5646658				
CC207	1826896	5646125				
CC208	1826832	5645828				
CC209	1826814	5645788	X	X	X	
CC210	1826607	5645770		X		
CC211	1826477	5646193				
CC212	1825386	5645031		X		
CC213	1824299	5644796	X	X	X	
CC214	1823974	5644885		X		
CC215	1823974	5644885				
CC216	1823738	5645080	X	X	X	
CC217	1823564	5645212		X		
CC218	1823323	5645440				
CC219	1822885	5646025		X		
CC221	1823050	5645369		X		
CC222	1824212	5644556				
CC224	1823995	5646228		X	X	
CC225	1823808	5646277		X		
CC226	1823673	5646350	X	X	X	
CC228	1823433	5646377		X		
CC229	1823275	5646504		X		
CC230	1823076	5646747		X		
CC231	1822984	5646960				
CC232	1823123	5646871		X		
CC234	1816829	5647409				
CC235	1817751	5647605		X		
CC236	1817546	5647853	X	X	X	
CC237	1817648	5647851				
CC238	1818307	5648503		X	X	
CC239	1818509	5648577		X		
CC240	1818688	5648627		X	X	
CC241	1819273	5648548		X		
CC245	1817090	5648073		X		
CC246	1817585	5648373				
CC247	1817710	5648384				
CC248	1817912	5648256		X		
CC253	1824023	5648179				
CC254	1822904	5648513				

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC260	1819749	5647008		X		X
CC261	1820646	5647442				
CC262	1820980	5647752				
CC263	1820997	5647975		X		
CC264	1821509	5650597				
CC267	1821858	5650968				
CC268	1822058	5651140				
CC269	1822135	5651262		X		
CC270	1822266	5651273				
CC271	1822435	5651359				
CC273	1823240	5652876				
CC274	1822159	5656503				
CC275	1822646	5653643				
CC276	1822853	5653306	X	X	X	
CC277	1823359	5653397				
CC278	1820923	5650325				
CC279	1822302	5653514	X	X	X	
CC280	1822448	5652627				
CC281	1823297	5652634		X	X	X
CC282	1819195	5653075				
CC284	1818639	5653131				
CC287	1818486	5644720				
CC289	1818802	5644269				
CC291	1819648	5642572		X	X	
CC292	1816747	5645013		X		
CC300	1821722	5651633				
CC301	1821847	5651610		X		
CC302	1821863	5651276				
CC303	1821970	5651673				
CC304	1821780	5651840				
CC305	1817884	5653257		X	X	
CC306	1818460	5652994	X	X	X	
CC307	1818543	5653013		X		
CC308	1818174	5652988		X		X
CC309	1818500	5652794				
CC310	1818599	5652850				
CC311	1818591	5652789				
CC313	1818532	5652698	X	X	X	X
CC314	1818223	5653599				
CC315	1821700	5655342				
CC316	1822060	5654611		X		
CC317	1822059	5654683				
CC318	1821719	5653665		X		
CC319	1821789	5654203				
CC320	1821728	5654479				
CC321	1821670	5654774				
CC322	1821672	5654821	X	X	X	
CC324	1821440	5655195				
CC325	1821364	5655483		X		
CC326	1820996	5655249		X	X	X
CC327	1821045	5655460				
CC328	1821080	5655514		X		

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC330	1819823	5655089		X		
CC331	1819823	5655089		X		
CC332	1818208	5652540				
CC333	1818222	5652419		X		
CC334	1818352	5652075				
CC335	1818570	5651957	X	X	X	X
CC336	1819168	5652000		X		
CC337	1819309	5652158		X		
CC338	1822189	5654931		X		
CC339	1822567	5654120		X		
CC340	1822624	5653651				
CC341	1822659	5653585				
CC342	1822770	5653498				
CC343	1822652	5653016				
CC344	1822642	5652989				
CC345	1822664	5652940		X		
CC346	1822737	5653101				
CC347	1823481	5654138				
CC348	1823483	5654189	X	X	X	X
CC349	1823175	5654366				
CC350	1823117	5654452	X	X	X	
CC351	1839661	5675104				
CC352	1839658	5675044				
CC353	1839416	5674947				
CC355	1822434	5652920				
CC356	1822569	5652893		X		
CC357	1822603	5652856		X		
CC358	1822576	5654077				
CC360	1822664	5654505		X		
CC361	1819022	5645839				
CC362	1818814	5645655				
CC363	1818783	5645596				
CC364	1828642	5653187	X	X	X	
CC365	1827946	5653266				
CC366	1827061	5653131		X		
CC367	1826904	5652569				
CC368	1826779	5652497				
CC369	1826484	5652346		X	X	
CC370	1826255	5652230		X		
CC371	1826296	5652264				
CC372	1825889	5652107		X		
CC373	1825768	5652155		X		
CC374	1825738	5652193		X		
CC375	1825383	5651844	X	X	X	
CC376	1825523	5651787		X	X	
CC378	1826258	5650801				
CC379	1822270	5650863		X		
CC381	1822564	5650927		X		
CC382	1822747	5650989		X		
CC383	1822886	5651056				
CC384	1822910	5651172				
CC386	1823110	5651891		X		

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC387	1823289	5652012				
CC389	1823266	5652149				
CC390	1823318	5652097		X		
CC391	1823717	5652356				
CC392	1823971	5652613		X		
CC393	1824391	5652896	X	X	X	
CC394	1825022	5654221				
CC396	1823636	5651680				
CC397	1823616	5651806	X	X	X	
CC399	1823862	5652186				
CC400	1824849	5653075		X		
CC401	1824907	5653373				
CC402	1825456	5653620		X		
CC403	1825776	5653660		X		
CC404	1825731	5653888		X		
CC405	1825984	5654050		X		
CC406	1827503	5654197		X		
CC408	1819238	5645274	X	X	X	
CC410	1819439	5644463				
CC411	1817542	5652140		X		
CC413	1817926	5651815		X		
CC414	1817885	5651710	X	X	X	
CC415	1818006	5651290		X		X
CC417	1818070	5651189				
CC422	1818090	5651564		X		
CC423	1818146	5651562		X		
CC424	1818213	5651592	X	X	X	
CC425	1817990	5651824		X		
CC426	1819936	5647798		X		
CC428	1819787	5648150				
CC429	1819461	5648128				
CC430	1819461	5648128		X		
CC431	1819360	5648211				
CC432	1819073	5648401		X		
CC433	1817349	5646279				
CC434	1817685	5647357		X	X	
CC435	1817753	5647275				
CC436	1817783	5647423				
CC438	1817784	5647604				
CC440	1817879	5647669				
CC441	1817672	5647593	X	X	X	
CC442	1820524	5649986		X		
CC443	1820463	5649915		X		
CC444	1820613	5649527		X	X	
CC445	1820440	5649931		X		
CC446	1820420	5650261				
CC447	1820497	5653024		X		
CC448	1819789	5651259		X		
CC449	1819378	5650933		X		
CC450	1818861	5650724				
CC451	1818724	5650762		X	X	
CC452	1818271	5650595		X		

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC453	1819270	5651833	X	X	X	
CC454	1815985	5650091		X		
CC455	1816239	5650269		X		
CC456	1816510	5650166				
CC458	1817151	5650302				
CC459	1817494	5650379				
CC460	1818227	5650299		X		
CC462	1818169	5650151	X	X	X	
CC463	1818573	5649911				
CC464	1818670	5649741		X		
CC465	1818648	5649584		X		
CC466	1818224	5649696		X		
CC467	1817342	5650093		X		
CC468	1815977	5649551		X		
CC469	1816044	5649580		X		
CC470	1816307	5649444	X	X	X	
CC471	1816488	5649472				
CC472	1816520	5649450		X		
CC473	1816520	5649450		X		
CC474	1816908	5649413		X		
CC475	1816908	5649413		X		
CC476	1817126	5649355				
CC477	1816909	5649915		X		
CC478	1816893	5649902				
CC479	1819009	5650243		X	X	X
CC480	1819059	5650129		X		
CC481	1818949	5650028		X		
CC482	1818653	5650362		X		
CC483	1818528	5650394		X		
CC484	1818100	5650510		X		
CC485	1818022	5650505				
CC486	1817971	5650555		X		
CC500	1818773	5653238		X		
CC503	1818793	5652631				
CC504	1818640	5652207				
CC506	1818562	5652221				
CC507	1818609	5652813				
CC508	1817506	5651423	X	X	X	
CC509	1816822	5651038				
CC510	1816866	5650981		X		
CC511	1816776	5650850	X	X	X	
CC512	1817567	5650625				
CC513	1819987	5650387		X	X	
CC514	1820170	5649430		X		
CC515	1819734	5649877		X		
CC516	1821253	5653765				
CC517	1821268	5653684				
CC518	1821154	5653389	X	X	X	
CC519	1821140	5653233		X	X	
CC520	1819308	5631051				
CC521	1821274	5636222		X		
CC522	1822529	5636146		X		

Table A3.1. continued

Sample number	Location NZTM		Analysis method			
	East	North	Ar/Ar	XRF	ICPMS	EPMA
CC523	1823155	5640122				
CC524	1822967	5639972		X		
CC525	1825392	5640863		X		
CC526	1814089	5662959				
CC528	1813894	5664267				
CC529	1817751	5651586				
CC531	1821066	5649986		X		
CC532	1821778	5649631		X		
CC533	1822108	5649887		X		
CC534	1821678	5650481		X		
CC535	1808791	5642539		X		
CC536	1809808	5641867				
CC537	1809899	5641243				
CC538	1810134	5642905		X		
CC539	1811311	5645002		X		
CC540	1809224	5643422		X		
CC541	1836234	5655610				
CC542	1835384	5651562		X		
CC543	1816574	5648360		X		
CC545	1817495	5648804	X	X	X	
CC546	1817346	5649043		X		
CC547	1817623	5649236	X	X	X	
CC548	1818392	5649274		X		
CC549	1818580	5649177		X		
CC550	1818537	5649122				
CC551	1818381	5649099				
CC552	1818005	5648964	X	X	X	
CC553	1817994	5648883	X	X	X	
CC554	1816973	5648753				
CC555	1818815	5647389		X		
CC556	1818585	5648075	X	X	X	
CC557	1818219	5648009				
CC558	1818296	5648027				
CC559	1818220	5648039				
CC560	1822468	5657994		X		
CC561	1827131	5647968				
CC562	1826576	5648175	X	X	X	
CC563	1825672	5649778		X	X	
CC564	1825627	5649836		X	X	
CC565	1824967	5650125		X		
CC566	1824551	5650286		X		
CC567	1823593	5650103		X		
CC568	1823938	5650134				
CC569	1824756	5648844	X	X	X	
CC570	1822913	5654199	X	X	X	
CC571	1822913	5654199				
CC572	1823099	5654616		X		
GL1030	1821050	5652015	X	X	X	
GL1983	1828506	5647559	X	X	X	

Appendix 4. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data

Radiometric $^{40}\text{Ar}/^{39}\text{Ar}$ dating was undertaken using crystalline groundmass material from lava flows. Sample preparation and analysis procedures are outline in Chapter 3. The full experiment information for age measurements is provided in this appendix.

Total gas, isochron and weighted mean plateau ages (WMPA) were calculated for each sample experiment. Total gas ages were calculated from the sums of all radiogenic ^{40}Ar and potassium-derived ^{39}Ar in all step-heating increments of the analysis. Isochron ages were calculated from $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{39}\text{Ar}/^{36}\text{Ar}$ correlation using the algorithm of York (1968). WMPA are the inverse-variance weighted means that were calculated for the steps of an age spectrum comprising contiguous gas fractions that represented >50% of the total ^{39}Ar released from the sample.

WMPA represent the best age estimates for 43 samples, based on their concordant age spectra, and are indicated in bold as the accepted lava flow eruption ages in Table A4.1.

The isochron age was preferred as the accepted eruption age for one sample (CC545).

Two experiments resulted in recoil spectra patterns indicative of loss of ^{39}Ar during the nuclear irradiation procedure. To preclude an underestimation of the eruption age due reduced $^{40}\text{Ar}/^{39}\text{Ar}$ values at high temperature increments, recoil model ages were calculated from the entire spectra (100% fraction of ^{39}Ar released) of the two affected samples (CC306, CC350) using the method outlined in Fleck et al. (2014).

This appendix provides the experiment information for each of the 46 age determinations recorded on the following sample sheets. Each sheet is divided into two main parts:

1. The age spectrum: values of Cl/K, radiogenic ^{39}Ar %, K/Ca and apparent age for each heating step during the experiment are plotted against the cumulative amount of ^{39}Ar released during heating. The temperature of the heating step is labelled beside each box. The range of heating steps used to calculate the weighted mean plateau age (WMPA) is indicated by the coloured arrows. The WMPA calculated from these is displayed beside the arrow, as is the proportion of ^{39}Ar % released over the steps used and the mean square weighted deviation (MSWD). The total gas age is displayed in black text.
2. The isochron diagram: the coloured line and text represents the isochron age calculated taking into account the number of steps used to calculate the corresponding WMPA in the age spectrum diagram (1). The black text and line is the isochron age calculated for 100 % ^{39}Ar .

This information is summarised in Table A4.1.

Table A4.1. Summary of $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data.

Sample	Fmtn-Package	N	Plateau age			Total gas age (ka, $\pm 2\sigma$)	Isochron age (ka, $\pm 2\sigma$)	$^{40}\text{Ar}/^{36}\text{Ar}_i$ ($\pm 2\sigma$)
			^{39}Ar %	MSWD	(ka, $\pm 2\sigma$)			
GL1983	WH-Crater Lake	10	79.8	1.06	0.2 $\pm$ 2.2	1.8 $\pm$ 2.2	1.4 $\pm$ 8.8	294.3 $\pm$ 9.9
CC564	WH-Iwikau	7	86.0	0.67	0.8 $\pm$ 5.6	-0.8 $\pm$ 5.6	4 $\pm$ 13.4	293.3 $\pm$ 9.5
GL1030	WH-Iwikau	11	100.0	1.10	6.0 $\pm$ 2.4	6.5 $\pm$ 2.4	1.4 $\pm$ 7.4	298.4 $\pm$ 5.2
CC279	WH-Iwikau	12	63.9	0.79	8.8 $\pm$ 2.8	8.6 $\pm$ 3.0	10.5 $\pm$ 17.2	294.4 $\pm$ 12.1
CC569	WH-Iwikau	4	60.8	0.13	9.2 $\pm$ 8.0	-.03 $\pm$ 8.6	22.2 $\pm$ 47.8	287.6 $\pm$ 33.9
CC236	WH-Turoa	12	62.7	0.61	11.9 $\pm$ 2.2	9.3 $\pm$ 2.2	15.4 $\pm$ 15.2	291.8 $\pm$ 19.1
CC393	WH-Tureiti	10	100.0	0.65	11.9 $\pm$ 2.8	12.3 $\pm$ 2.8	11.9 $\pm$ 8.8	295.4 $\pm$ 6.9
CC397	WH-Tureiti	10	83.9	0.90	12.5 $\pm$ 2.6	10.2 $\pm$ 2.6	14.4 $\pm$ 5.0	293.2 $\pm$ 6.0
CC335	WH-Paretaitonga	10	79.8	0.80	14.8 $\pm$ 3.0	22.1 $\pm$ 3.0	10.8 $\pm$ 12.4	299.5 $\pm$ 14.7
CC130	WH-Turoa	11	100.0	0.46	15.1 $\pm$ 2.4	15.2 $\pm$ 2.4	13.9 $\pm$ 6.0	296.3 $\pm$ 2.9
CC226	MA-Makotuku	10	100.0	0.34	17.8 $\pm$ 2.2	18.1 $\pm$ 2.6	16.8 $\pm$ 4.2	296.7 $\pm$ 5.2
CC408	MA-Makotuku	10	94.7	0.39	20.9 $\pm$ 2.8	19.6 $\pm$ 3.0	22.7 $\pm$ 7.4	293.9 $\pm$ 7.3
CC143	MA-Waitonga	11	99.5	0.80	23.0 $\pm$ 1.6	23.0 $\pm$ 1.8	22.2 $\pm$ 4.6	296.4 $\pm$ 5.7
CC513	MA-Whakapapaiti	3	67.9	0.50	25.7 $\pm$ 3.8	6.7 $\pm$ 4.4	39.4 $\pm$ 28.6	265.6 $\pm$ 72.9
CC441	MA-Manganuioteao	10	86.6	1.34	25.7 $\pm$ 2.6	20.3 $\pm$ 2.8	34.1 $\pm$ 8.2	286.6 $\pm$ 9.9
CC553	MA-Manganuioteao	10	100.0	0.40	27.2 $\pm$ 4.8	25.8 $\pm$ 5.8	29.0 $\pm$ 7.2	294.0 $\pm$ 3.2
CC547	MA-Manganuioteao	6	72.6	0.77	30.7 $\pm$ 5.2	43.9 $\pm$ 4.6	28.6 $\pm$ 10.4	296.6 $\pm$ 21.5
CC462	MA-Manganuioteao	10	94.6	0.54	30.9 $\pm$ 2.2	30.4 $\pm$ 2.6	30.8 $\pm$ 5.4	295.6 $\pm$ 6.4
CC508	MA-Te Kohatu	3	57.4	1.11	37.6 $\pm$ 1.4	46.2 $\pm$ 1.4	37.8 $\pm$ 21.8	294.4 $\pm$ 109.2
CC556	MA-Ngahuinga	7	90.8	0.53	38.3 $\pm$ 3.4	30.0 $\pm$ 4.0	37.9 $\pm$ 8.4	295.9 $\pm$ 13
CC414	MA-Te Kohatu	10	100.0	1.78	39.1 $\pm$ 1.4	40.7 $\pm$ 1.4	36.5 $\pm$ 2.0	302.2 $\pm$ 5.1
CC511	MA-Te Kohatu	9	97.7	0.44	39.2 $\pm$ 2.0	40.2 $\pm$ 2.4	38.4 $\pm$ 3.6	297.3 $\pm$ 9.9
CC424	MA-Ngahuinga	10	100.0	0.96	39.6 $\pm$ 2.8	40.3 $\pm$ 3.2	38.6 $\pm$ 5.2	296.2 $\pm$ 4.0
CC570	MA-Mananui	8	91.7	0.28	40.3 $\pm$ 2.2	37.7 $\pm$ 2.6	41.7 $\pm$ 3.6	291.5 $\pm$ 9.6
CC545	MA-Mangaturuturu	8	91.6	1.33	38.4 $\pm$ 2.4	35.9 $\pm$ 2.6	40.7 $\pm$ 4.6	290.0 $\pm$ 10.9
CC470	MA-Mangaturuturu	10	99.4	0.96	41.3 $\pm$ 1.8	41.2 $\pm$ 2.0	42.9 $\pm$ 4.2	292.9 $\pm$ 6.7
CC140	MA-Mangaehuehu	11	100.0	0.52	41.8 $\pm$ 1.8	41.2 $\pm$ 2.0	44.6 $\pm$ 4.0	293.3 $\pm$ 3.3
CC313	MA-Te Kohatu	10	70.5	1.73	42.6 $\pm$ 1.8	39.5 $\pm$ 1.4	49.6 $\pm$ 7.0	273.3 $\pm$ 25.8
CC127	MA-Mangaehuehu	11	84.4	0.66	42.8 $\pm$ 1.0	43.9 $\pm$ 1.0	42.9 $\pm$ 2.2	295.1 $\pm$ 5.9
CC216	MA-Mangaehuehu	12	100.0	1.32	43.1 $\pm$ 1.4	43.8 $\pm$ 1.4	41.5 $\pm$ 2.6	298.1 $\pm$ 4.3
CC119	MA-Mangaehuehu	11	100.0	1.46	43.3 $\pm$ 1.6	42.6 $\pm$ 1.6	45.3 $\pm$ 2.4	292.7 $\pm$ 3.1
CC552	MA-Mangaturuturu	6	91.8	0.68	43.4 $\pm$ 2.4	45.1 $\pm$ 3.0	41.9 $\pm$ 6.0	300.0 $\pm$ 20.7
CC081	MA-Mangaehuehu	11	86.7	1.17	44.2 $\pm$ 1.8	46.8 $\pm$ 1.8	41.9 $\pm$ 6.2	300.6 $\pm$ 15.6
CC453	MA-Ngahuinga	10	96.7	1.43	44.8 $\pm$ 3.0	45.4 $\pm$ 2.8	45.8 $\pm$ 5.8	294.3 $\pm$ 5.9
CC089	MA-Mangaehuehu	11	96.9	1.72	45.4 $\pm$ 2.0	46.0 $\pm$ 1.6	47.2 $\pm$ 8.0	293.2 $\pm$ 10.2
CC562	WA	6	83.7	0.51	88.1 $\pm$ 6.4	85.2 $\pm$ 9.0	85.0 $\pm$ 19.4	296.9 $\pm$ 10.5
CC350	WA	10	100.0	recoil	95.9 $\pm$ 7.0	95.5 $\pm$ 4.2	98.6 $\pm$ 16.8	293.8 $\pm$ 9.3
CC209	WA	10	98.9	0.75	120.7 $\pm$ 4.0	119.5 $\pm$ 5.0	123.6 $\pm$ 5.4	293.8 $\pm$ 2.5
CC213	WA	11	54.2	1.25	121.4 $\pm$ 2.8	122.2 $\pm$ 2.4	123.7 $\pm$ 16.0	292.2 $\pm$ 25.2
CC375	WA	10	89.2	1.64	121.7 $\pm$ 4.2	119.6 $\pm$ 3.4	125.8 $\pm$ 9.8	292.2 $\pm$ 9.2
CC197	WA	11	97.2	0.72	133.6 $\pm$ 6.4	136.0 $\pm$ 6.8	138.1 $\pm$ 13.6	293.6 $\pm$ 5.7
CC518	TH	10	100.0	0.36	158.8 $\pm$ 8.2	157.6 $\pm$ 9.6	158.9 $\pm$ 13.4	295.3 $\pm$ 7.5
CC322	TH	10	99.1	2.02	169.4 $\pm$ 7.8	171.0 $\pm$ 6.0	176.4 $\pm$ 17.2	291.0 $\pm$ 10.7
CC276	TH	12	94.5	0.86	174.6 $\pm$ 3.4	171.0 $\pm$ 5.8	169.2 $\pm$ 7.2	300.9 $\pm$ 7.3
CC348	TH	10	81.5	1.00	186.2 $\pm$ 6.8	173.1 $\pm$ 7.2	203.3 $\pm$ 22.4	287.7 $\pm$ 11.5
CC306	TH	10	100.0	recoil	187.9 $\pm$ 34.4	146.6 $\pm$ 11.4	207.5 $\pm$ 22.2	289.8 $\pm$ 2.9

Formation abbreviations are: WH (Whakapapa); MA (Mangawhero); WA (Wahianoa); TH (Te Herenga). N is number of heating steps, % ^{39}Ar is the proportion of released radiogenic gas, and MSWD is the mean standard weighted deviation of each age plateau calculation. Bold numbers are the preferred ages for each sample, which are all mean weighted plateau ages, except for CC545 where the isochron age was preferred.

Figure A4.1. Sample sheets for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology data. All sample sheets are provided on the following pages.

Appendix 5. Whole-rock XRF standard data

Lava samples were crushed and then milled using an agate or tungsten-carbide ring mill to form a whole-rock powder. Up to 400 mg of material was powdered for each sample, from which a homogeneous aliquot was used for analysis.

Major element compositions for 238 whole-rock powder samples were determined using an ARL[®] 8420+ dual goniometer wavelength dispersive X-ray fluorescence (XRF) spectrometer at the Open University, U.K. Fused lithium metaborate glass discs were prepared for each powder and analysed following the methods of Ramsey et al. (1995). Glass disks were formed by mixing 1 part by weight (0.70 g) of rock powder (dried at 110 °C) with 5 parts by weight of dried lithium metaborate flux and fusing in a muffle furnace for 15 minutes at 1100 °C in 95% Pt - 5% Au crucibles. Loss-on-ignition (LOI) measurements were undertaken on dried rock powders by heating in a pre-ignited aluminium crucible to 1000 °C for 1 hr and recording percentage weight loss. John Watson prepared the discs and undertook the XRF analyses. In addition to major oxides, concentrations were measured for trace elements Ba, Cr and Ni.

Internal standards WS-E (Whin Sill Dolerite) and OU-3 were analysed repeatedly throughout analysis sessions. Approximate 2 standard deviation (2 sd) analytical precisions are <2 relative % for major oxides (excepting those with concentrations <0.5 wt. %) for the 22 replicate analyses of each standard. There is a close agreement (generally within ~1 % offset) between average values for the repeated standard analyses and recommended values for each element. Trace element analyses were accurate to <4 % for WS-E and relative 2 sd precisions are 5–7 %. Standard data for analyses of WS-E and OU-3 are provided in Tables A5.1 and A5.2.

Duplicate analyses of samples were undertaken during separate sessions to monitor instrument accuracy and check the homogeneity of sample powders and reliability of their preparation procedures (Table A5.3). Duplicate analyses yielded results that were accurate to within ~2 % offset of each other. Trace element analyses were accurate to <6 % for duplicate analyses, except Ni (<12 %).

Full sample data are provided in the electronic appendix files.

Table A5.1.1. Precision and accuracy for the XRF internal standard WS-E.

WS-E	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Ba	Cr	Ni
1	51.26	2.42	13.83	13.17	0.17	5.56	9.15	2.45	0.99	0.30	0.85	100.2	351.6	101.7	52.2
2	51.27	2.43	13.87	13.18	0.17	5.57	9.16	2.42	0.99	0.30	0.85	100.2	332	100.3	55.3
3	51.21	2.42	13.88	13.19	0.17	5.57	9.05	2.43	1.00	0.30	0.85	100.1	335	100.4	52.8
4	51.22	2.43	13.90	13.17	0.17	5.57	9.04	2.46	1.00	0.30	0.85	100.1	330.9	105.4	52.4
5	51.22	2.43	13.99	13.14	0.17	5.56	8.95	2.46	1.00	0.30	0.85	100.1	320.6	104.7	51.2
6	51.24	2.42	13.94	13.15	0.17	5.58	8.96	2.44	1.00	0.30	0.85	100.1	335.7	102.9	53.6
7	51.16	2.42	13.89	13.16	0.17	5.57	8.98	2.44	1.00	0.30	0.85	99.9	332.4	105.4	53.6
8	51.24	2.43	13.87	13.16	0.17	5.57	8.99	2.44	1.00	0.30	0.85	100.0	330.6	104.6	52.7
9	51.23	2.43	13.84	13.16	0.17	5.56	8.98	2.40	1.00	0.30	0.85	99.9	341.8	100.5	51.7
10	51.26	2.43	13.84	13.17	0.17	5.55	8.97	2.42	1.01	0.30	0.85	100.0	327.2	100.6	54
11	51.18	2.43	13.96	13.16	0.17	5.53	9.04	2.45	1.00	0.30	0.85	100.1	324	106.5	55.9
12	51.19	2.42	13.98	13.15	0.17	5.57	9.01	2.45	0.99	0.31	0.85	100.1	330.5	104.3	57.4
13	51.17	2.41	13.94	13.16	0.17	5.55	8.99	2.44	1.00	0.30	0.85	100.0	329.2	101.8	51
14	51.16	2.42	13.93	13.17	0.17	5.57	8.98	2.43	1.00	0.30	0.85	100.0	348.5	102.6	53.3
15	51.27	2.44	13.96	13.16	0.17	5.57	9.04	2.43	1.00	0.30	0.85	100.2	315.6	103	53.7
16	51.30	2.43	13.96	13.17	0.17	5.59	9.07	2.44	1.00	0.31	0.85	100.3	318.1	105.1	53.7
17	51.13	2.44	13.84	13.16	0.17	5.56	8.96	2.44	1.00	0.30	0.85	99.9	343.8	101	52.8
18	51.17	2.43	13.81	13.17	0.17	5.58	8.97	2.44	1.00	0.31	0.85	99.9	337.1	99.2	52.9
19	51.13	2.43	13.84	13.14	0.17	5.59	8.94	2.44	1.00	0.30	0.85	99.8	336.7	107.1	50.6
20	51.20	2.44	13.85	13.16	0.17	5.57	8.95	2.44	1.00	0.31	0.85	99.9	328.3	105.2	54.9
21	51.15	2.43	13.83	13.13	0.17	5.59	8.97	2.45	1.00	0.30	0.85	99.9	337.2	99.7	50.6
22	51.08	2.44	13.87	13.15	0.17	5.56	8.97	2.43	1.00	0.31	0.85	99.8	329.4	101	54.7
avg	51.20	2.43	13.89	13.16	0.17	5.57	9.01	2.44	1.00	0.30	0.85	100.02	332.55	102.86	53.23
max	51.30	2.44	13.99	13.19	0.17	5.59	9.16	2.46	1.01	0.31	0.85	100.28	351.60	107.10	57.40
min	51.08	2.41	13.81	13.13	0.17	5.53	8.94	2.40	0.99	0.30	0.85	99.84	315.60	99.20	50.60
2sd	0.11	0.01	0.11	0.03	0.00	0.03	0.12	0.02	0.01	0.01	0.00	0.25	17.97	4.77	3.46
2sd %	0.21	0.57	0.80	0.20	1.66	0.48	1.36	1.01	0.72	1.91	0.00	0.25	5.40	4.63	6.50
Rec	51.10	2.43	13.78	13.15	0.17	5.55	8.95	2.47	1.00	0.30	0.85	99.75	338.00	99.00	55.00
% off.	0.20	0.19	0.82	0.08	0.53	0.30	0.62	-1.31	-0.06	0.13	0.00	0.27	-1.61	3.90	-3.22

Oxide abundances given in wt. % and normalised to 100 % on a volatile free basis, with original analytical totals given. Ba, Cr, and Ni concentrations are in ppm. LOI (loss on ignition) is weight loss of sample after ~1 hour of 1000°C heating. Reference values are from Govindaraju et al. (1994) except SiO₂, TiO₂ and Fe₂O₃, which are from Thompson et al. (2000).

Table A5.2. Precision and accuracy for the XRF internal standard WS-E.

OU-3	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Ba	Cr	Ni
1	74.10	0.22	11.02	3.87	0.09	0.02	0.21	3.73	4.56	0.02	1.82	99.66	29	22.8	7
2	74.16	0.22	10.97	3.86	0.09	0.03	0.21	3.70	4.56	0.02	1.82	99.64	36.1	21.3	5.5
3	74.15	0.22	11.05	3.86	0.09	0.03	0.20	3.72	4.57	0.02	1.82	99.74	41.1	22.2	7.3
4	74.12	0.22	11.04	3.86	0.09	0.03	0.20	3.73	4.57	0.02	1.82	99.70	37.2	24.5	5.4
5	74.15	0.22	11.08	3.87	0.09	0.02	0.21	3.70	4.59	0.02	1.82	99.76	29	25.6	9.7
6	74.11	0.22	11.06	3.87	0.09	0.03	0.21	3.75	4.55	0.02	1.82	99.73	31.3	28.3	10.6
7	74.13	0.22	11.02	3.86	0.09	0.03	0.20	3.75	4.57	0.01	1.82	99.69	24.8	22.5	7.5
8	74.25	0.22	11.07	3.86	0.09	0.03	0.20	3.75	4.54	0.01	1.82	99.85	30.8	23.8	8.1
9	74.13	0.23	11.00	3.86	0.09	0.03	0.21	3.74	4.54	0.01	1.82	99.65	36.7	22.5	7.7
10	74.11	0.23	10.97	3.86	0.09	0.03	0.20	3.71	4.56	0.01	1.82	99.59	25.6	21.4	7.5
11	74.04	0.22	11.09	3.88	0.09	0.03	0.20	3.75	4.57	0.01	1.82	99.71	39.8	26.4	7.4
12	74.06	0.22	11.09	3.86	0.09	0.03	0.20	3.74	4.56	0.01	1.82	99.68	29.1	29.4	7.6
13	74.04	0.22	11.11	3.89	0.09	0.03	0.22	3.69	4.54	0.02	1.82	99.67	24.1	25.8	7.3
14	74.09	0.22	11.13	3.88	0.09	0.03	0.21	3.73	4.54	0.02	1.82	99.77	33.6	27.3	8.6
15	74.05	0.22	11.09	3.87	0.09	0.03	0.20	3.74	4.55	0.01	1.82	99.69	24.3	28.2	7.3
16	74.05	0.23	11.08	3.88	0.09	0.03	0.20	3.73	4.56	0.01	1.82	99.68	28.9	26	7.3
17	74.11	0.22	11.01	3.84	0.09	0.03	0.21	3.72	4.57	0.02	1.82	99.65	26.4	23.5	5.3
18	74.29	0.23	11.00	3.86	0.09	0.04	0.21	3.70	4.55	0.02	1.82	99.80	32	16.8	4.2
19	74.01	0.23	11.01	3.85	0.09	0.04	0.21	3.71	4.52	0.02	1.82	99.51	22.7	25.5	6.6
20	74.16	0.23	10.98	3.84	0.09	0.04	0.21	3.73	4.54	0.02	1.82	99.65	32.2	25.9	9.1
21	74.07	0.23	11.01	3.84	0.09	0.04	0.21	3.72	4.54	0.02	1.82	99.57	39.3	22.9	6.5
22	74.13	0.22	11.01	3.84	0.09	0.05	0.21	3.72	4.53	0.02	1.82	99.63	26.4	19.8	7.3
avg	74.11	0.22	11.04	3.86	0.09	0.03	0.21	3.73	4.55	0.02	1.82	99.68	30.9	24.2	7.3
max	74.29	0.23	11.13	3.89	0.09	0.05	0.22	3.75	4.59	0.02	1.82	99.85	41.1	29.4	10.6
min	74.01	0.22	10.97	3.84	0.09	0.02	0.20	3.69	4.52	0.01	1.82	99.51	22.7	16.8	4.2
2sd	0.13	0.01	0.09	0.03	0.00	0.01	0.01	0.03	0.03	0.00	0.00	0.15	11.1	6.0	2.9
2sd %	0.18	2.37	0.84	0.69	2.21	38.98	3.85	0.93	0.70	24.82	0.00	0.15	35.8	24.9	39.7
Rec.	74.09	0.22	11.11	3.83	0.09	-	0.20	3.68	4.55	-	1.82	99.59	29.00	19.00	-
% off.	0.03	0.11	-0.62	0.82	1.05	-	2.96	1.23	0.07	-	0.00	0.09	6.65	27.37	-

Oxide abundances given in wt. % and normalised to 100 % on a volatile free basis, with original analytical totals given. Ba, Cr, and Ni concentrations are in ppm.

LOI (loss on ignition) is weight loss of sample after ~1 hour of 1000°C heating. Reference values are long-term running averages from the Open University XRF lab.

Table A5.3. Repeated samples analysed by XRF.

CC216	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Ba	Cr	Ni
a	60.50	0.76	15.17	6.49	0.10	5.52	6.25	3.20	2.04	0.17	-0.03	100.18	407.00	239.10	71.60
b	60.61	0.75	15.19	6.50	0.10	5.44	6.23	3.21	2.03	0.17	-0.02	100.22	411.20	233.90	63.20
% diff.	0.18	-1.07	0.08	0.11	0.35	-1.34	-0.39	0.35	-0.35	0.45	-33.33	0.04	1.03	-2.17	-11.73

CC276	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Ba	Cr	Ni
a	56.44	0.65	17.41	8.85	0.14	4.83	7.69	3.24	0.65	0.09	0.15	100.14	182.40	61.40	26.60
b	56.29	0.65	17.42	8.73	0.13	4.70	7.82	3.24	0.66	0.09	0.13	99.88	181.30	58.70	29.30
% diff.	-0.28	0.91	0.09	-1.30	-3.93	-2.62	1.72	-0.24	1.99	1.85	-13.33	-0.26	-0.60	-4.40	10.15

CC408	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	Ba	Cr	Ni
a	60.37	0.77	17.14	6.37	0.10	2.62	5.98	3.71	1.95	0.17	-0.10	99.08	407.10	19.20	13.10
b	60.85	0.79	17.30	6.44	0.10	2.63	5.98	3.77	1.97	0.17	-0.07	99.93	420.40	20.30	13.20
% diff.	0.78	2.27	0.93	1.08	2.51	0.36	0.09	1.48	0.90	1.84	-30.00	0.85	3.27	5.73	0.76

Oxide abundances are given in wt. % and normalised to 100 % on a volatile free basis, with original analytical totals and LOI given.

Ba, Cr and Ni concentrations are in ppm.

Appendix 6. Whole-rock solution ICP-MS trace element standard data

A subset of whole-rock powders were selected for trace element analysis. Samples were prepared for analysis in a PicoTrace Class 10 laminar flow workstation within the positively pressured ultra-clean chemical separation laboratory of the geochemistry facility at Victoria University of Wellington (VUW), New Zealand. SeaStar™ (SS) grade ultrapure acids (all key metals <10 ppt) were used for trace element sample preparation. Analytical reagent (AR) grade acids, distilled to produce sub-boiled (SB) distilled acids were used in final stages of beaker preparation. Milli-Q water was used during beaker cleaning and acid dilution.

Aliquots of whole-rock powders prepared for XRF major element analysis were taken for trace element analysis. Approximately 50 mg of sample was weighed on a high-precision balance to ± 0.0001 g in pre-cleaned 23 mL Savillex screw-top Teflon beakers. Samples and international reference materials were dissolved by conventional digestion methods using ~2 mL concentrated hydrofluoric acid (29 M HF) and 0.5 mL HNO₃ (16 M HNO₃) in sealed beakers heated on a hotplate to 120 °C for 3-4 days. Once the sample was completely digested, the solution was evaporated to incipient dryness, refluxed twice in ~2 mL of concentrated HNO₃ and evaporated again to incipient dryness. The sample cake was then refluxed in ~5 mL of 6M HCl overnight and the solution was checked to make sure the sample had completely dissolved. The HCl was evaporated and the sample cake was taken up again in ~2 mL of concentrated HNO₃ for two days. The sample was once again evaporated and then taken up in 9 mL of 1M HNO₃ to reflux for a further 2-3 days to form a final solution. The final solution was carefully and completely transferred from beakers into pre-cleaned 10 mL polyethylene centrifuge tubes and weighed on a high-precision balance. To form a dilution of the sample. A 50 μ L aliquot was transferred into another clean 10 mL centrifuge tube and weighed. The tube was then topped up with ~9 mL of 1% HNO₃ and weighed again so that a final dilution of the sample could be accurately calculated.

Whole-rock trace element analysis was carried out by solution inductively coupled plasma mass spectrometry (ICP-MS), using a Thermo-Fisher Element2 sector-field ICP-MS equipped with an ESCI auto sampler at VUW using methods similar to those of Eggins *et al.* (1997). In this study ⁴³Ca was used for an internal correction, as CaO concentrations of sample powders had previously been determined to ± 2 % by XRF. This method allows correction for any major changes or inconsistencies, which may be caused by sample loss during sample preparation. The ICP-MS was tuned using a 10 ppb multi element standard diluted to 1 ppb, where instrumental conditions such as torch position and carrier/make-up gas flow were adjusted to achieve the lowest relative standard deviation (RSD), typically <1-2%, and to optimise sensitivity. This step was then repeated for the calibration standard, BHVO-2. Oxide generation was monitored during the tuning procedure using measured UO⁺/U⁺ ratios (<7 %), BaO⁺/Ba⁺ (<0.2 %) and

Ba⁺⁺/Ba⁺ (<5 %). To assess the quality of the data, multiple isotopes from some elements (e.g. ⁹⁰Zr and ⁹¹Zr) were included in the analysis, generally producing concentrations within ±0.5%. The Element2 was operated at increased mass resolution for selected isotopes to resolve the elemental peak from common spectral interferences (e.g. ⁴⁵Sc, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga) or to reduce counts in highly abundant isotopes (e.g. ²³Na, ²⁵Mg, ²⁷Al, ⁴³Ca, ⁵⁵Mn). Each sample solution was measured for a total time of 240 s. Prior to introduction of each sample the background counts were measured and assessed for the same count time using a 1% SS HNO₃ acid blank.

Following sample analyses, the auto sampler lines and ICP-MS were washed out in two consecutive rinse cycles in 1% SS HNO₃ for 240 s. Concentrations were calculated by sample-standard bracketing, thus the analysis sequence followed an order starting with the primary standard (BHVO-2), followed by 3 samples, the secondary standard (USGS standard BCR-2), and finishing back on the primary standard. Total procedural blanks for solution ICP-MS were within background count levels on all measured elements.

Trace element abundances in samples were calculated relative to the bracketing standard (BHVO-2) according to equations 1 and 2:

$$1. \text{ Sample } C_i = (\text{Sample } CPS / BHVO \text{ CPS}) \times (\text{Sample } Dil / BHVO \text{ Dil}) \times C_{ref}$$

$$2. \text{ Sample } C_i (\text{Ca corrected}) = eq. 1. \times (C_{Ca \text{ XRF}} / C_{Ca \text{ ICP-MS}})$$

Where C_i , C_{ref} and C_{Ca} are the concentrations of the measured isotope, the reference value for the bracketing standard and Ca, respectively, the latter of which was determined by XRF and ICP-MS. Reference values for BHVO-2 were acquired from Georem preferred values (<http://georem.mpch-mainz.gwdg.de/>). X_{Dil} is the concentration of material in the aliquot dilution.

International standard BCR-2 was analysed throughout analysis sessions in order to monitor the precision and accuracy of data acquired by solution ICP-MS (Table A6.1). Approximate 2 sd analytical precisions calculated from 18 replicate analyses of BCR-2 are <13 relative % for all elements (most are ~8–10 %) except Nb (~24 %). Analyses of BCR-2 are accurate to within 5 % of preferred values for all elements (most are within 1–2 %), except Cr, U (~6 %), Cu (~18 %) and Ni (~30 %). The bulk powder (TPI) of a single large clast from Taupo ignimbrite was used as an additional secondary standard throughout analysis sessions. Approximate 2 sd analytical precisions calculated from 8 replicate analyses of TPI are 5–10 relative % for most elements (Table A6.2) Separate dilutions from the same sample powders were also analysed to monitor reliability of the sample preparation procedure and homogeneity of powders. Values of 5–10 % offset for all elements from analyses of duplicate digestions further indicate high levels of reproducibility of the solution ICP-MS technique used in this study (Table A6.3). Sample data are displayed in Table A6.4.

Table A6.1. Precision and accuracy of solution ICP-MS trace element analysis for standard BCR-2.

BCR-2	1a-1	1a-2	1a-3	1a-4	1b-1	2a-1	2b-1	3a-1	3a-2	3b-1	3b-2	4a-1	4a-2	4a-3	4b-1	4b-2	4b-3	4b-4	Avg	2sd	2sd %	Ref.	%off
Li7	8.5	8.6	8.9	8.7	8.9	9.2	9.2	10.5	9.6	10.2	8.5	9.8	9.5	9.5	9.6	10.0	10.1	9.8	9.4	1.2	13.1	9.0	4.4
Sc45	34.2	33.9	33.8	33.9	33.8	34.0	33.4	34.4	32.7	34.1	32.5	34.1	33.9	33.8	34.3	34.7	33.4	34.0	33.8	1.1	3.3	33.0	2.5
V51	424	424	419	426	416	418	420	425	399	415	395	425	418	415	432	414	422	416	418	17.7	4.2	416.0	0.5
Ni60	11.8	11.8	11.8	12.0	11.1	18.2	17.8	11.8	11.8	12.0	11.6	12.9	12.7	12.4	12.4	12.1	12.8	12.3	12.7	3.9	30.9	18.0	-29.2
Co63	17.0	16.8	16.9	16.8	16.7	21.0	21.0	16.7	17.2	17.2	16.6	15.7	16.4	16.6	16.3	16.0	17.3	16.9	17.2	2.9	16.9	21.0	-18.3
Zn66	140	136	136	138	139	123	123	135	132	132	130	122	124	124	137	136	142	129	132	13.1	9.9	127.0	4.1
Ga69	23.3	22.6	23.2	22.5	22.6	22.4	22.3	22.4	22.8	22.8	22.3	21.9	22.5	22.1	22.9	22.3	22.4	22.8	22.6	0.7	3.2	23.0	-1.9
Rb85	47.6	46.3	48.1	46.8	47.6	47.4	47.6	50.1	45.6	47.3	42.3	45.8	51.6	46.3	46.7	47.6	48.2	47.1	47.2	3.8	8.0	46.9	0.7
Sr88	346	335	351	339	346	352	347	366	343	344	304	329	337	328	334	330	330	331	338	26.3	7.8	340.0	-0.5
Y89	36.6	35.5	36.7	35.7	36.4	37.2	37.4	37.8	35.3	37.0	31.5	35.3	36.0	34.8	35.5	35.3	34.8	35.0	35.8	2.8	7.9	37.0	-3.3
Zr91	192	188	195	188	192	181	182	204	186	190	165	184	188	185	188	182	183	185	187	15.5	8.3	184.0	1.4
Nb93	12.6	12.3	12.7	12.3	12.5	12.2	13.7	11.4	10.2	10.2	8.9	11.9	12.3	13.5	13.5	12.6	14.1	14.8	12.3	2.9	23.7	12.6	-2.2
Cs133	1.2	1.1	1.2	1.2	1.1	1.1	1.1	1.3	1.2	1.2	1.1	1.2	1.1	1.2	1.2	1.2	1.1	1.1	1.2	0.1	8.9	1.1	5.1
Ba137	697	670	705	686	685	690	676	741	676	691	617	688	662	701	662	684	686	777	688	65.6	9.5	677.0	1.7
La139	25.3	24.8	25.7	24.9	25.3	25.2	24.9	27.5	24.5	25.4	21.5	25.0	24.6	23.9	24.8	24.4	24.1	25.4	24.8	2.3	9.2	24.9	-0.3
Ce140	53.8	53.4	54.7	52.6	53.5	53.7	53.3	58.0	52.0	52.7	45.9	51.5	50.8	50.4	52.5	51.5	50.6	52.6	52.4	4.8	9.2	52.9	-0.9
Pr141	6.9	6.8	7.1	6.8	7.0	6.8	6.8	7.2	6.8	6.8	5.9	6.5	6.9	6.6	6.6	6.7	6.7	6.7	6.8	0.5	8.1	6.7	0.9
Nd146	28.9	28.1	29.5	28.5	28.8	29.3	28.9	30.2	29.0	28.8	24.7	26.9	27.5	27.6	28.4	27.8	27.9	28.6	28.3	2.4	8.4	28.7	-1.4
Sm147	6.6	6.3	6.7	6.5	6.7	6.6	6.6	7.1	6.4	6.5	5.6	6.3	6.4	6.3	6.4	6.4	6.5	6.3	6.5	0.6	8.9	6.6	-1.9
Eu151	2.0	2.0	2.1	2.0	2.0	2.0	2.0	2.2	2.1	2.1	1.8	1.8	2.0	1.9	1.9	2.0	2.0	2.0	2.0	0.2	9.6	2.0	1.0
Gd157	7.1	6.7	7.2	6.9	7.0	6.8	7.1	7.4	7.1	7.1	6.2	6.9	6.8	6.4	6.6	6.6	6.6	6.7	6.8	0.6	8.9	6.8	1.3
Tb159	1.1	1.0	1.1	1.0	1.0	1.1	1.1	1.1	1.1	1.0	0.9	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.1	9.5	1.1	-3.6
Dy163	6.5	6.3	6.7	6.3	6.5	6.6	6.5	6.7	6.5	6.4	5.6	6.1	6.3	6.2	6.2	6.1	6.3	6.0	6.3	0.5	8.5	6.4	-1.3
Ho165	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.4	1.3	1.3	1.1	1.2	1.3	1.2	1.2	1.2	1.3	1.2	1.3	0.1	8.9	1.3	-0.7
Er166	3.8	3.6	3.7	3.6	3.7	3.7	3.7	3.9	3.7	3.7	3.1	3.5	3.6	3.6	3.4	3.3	3.7	3.5	3.6	0.4	10.3	3.7	-1.9
Tm169	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.0	8.4	0.5	-4.7
Yb173	3.4	3.3	3.5	3.3	3.4	3.4	3.4	3.6	3.5	3.4	3.0	3.2	3.3	3.1	3.2	3.1	3.2	3.3	3.3	0.3	9.7	3.4	-2.4
Lu175	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.4	0.5	0.5	0.5	0.5	0.0	9.4	0.5	-4.2
Hf178	4.9	4.8	5.0	4.8	4.8	4.9	4.8	5.2	5.0	4.8	4.4	4.7	4.6	4.5	4.7	4.5	4.7	4.6	4.8	0.4	8.6	4.9	-2.7
Pb208	10.7	10.2	10.8	10.1	10.3	11.4	11.0	12.2	11.5	10.9	10.2	9.5	9.8	9.8	9.7	9.9	10.8	10.4	10.5	1.4	13.4	11.0	-4.4
Th232	6.0	5.9	6.1	6.0	5.9	5.8	5.7	6.4	6.1	6.0	5.3	5.6	5.7	5.7	5.6	5.6	5.7	5.7	5.8	0.5	8.6	5.7	2.0
U238	1.7	1.6	1.7	1.6	1.6	1.7	1.7	1.7	1.7	1.6	1.4	1.5	1.6	1.4	1.5	1.5	1.5	1.6	1.6	0.2	12.6	1.7	-5.8

Values are concentrations in ppm. Labels in top row indicate sample number; first number is individual digestion; letters are separate dilutions; final numbers indicate repeated analysis of same dilution. Reference values for BCR-2 are from Georem website (<http://georem.mpch-mainz.gwdg.de/>).

Table A6.2. Precision of solution ICP-MS trace element analysis for standard TPI.

TPI	A-1	B-1	C-1	C-2	C-3	D-1	D-2	D-3	Avg	2sd	2sd %
Li7	30.4	26.9	27.7	26.6	27.6	32.9	32.5	35.5	30.0	6.6	22.0
Sc45	10.4	10.2	10.5	10.6	10.5	10.7	10.9	11.0	10.6	0.5	4.9
V51	2.3	2.2	2.4	2.4	2.4	2.5	2.5	2.5	2.4	0.1	6.2
Ni60	1.3	0.9	1.1	1.1	1.0	1.1	1.0	1.1	1.1	0.2	16.9
Cu63	1.4	1.5	1.2	1.2	1.2	1.2	1.2	1.1	1.2	0.2	19.1
Zn66	64.1	68.1	70.1	69.6	71.3	72.5	69.3	69.4	69.3	5.0	7.2
Ga69	15.3	14.7	16.0	15.8	15.3	16.8	16.4	16.6	15.9	1.4	9.0
Rb85	90.6	86.2	91.4	85.8	88.7	95.4	88.3	91.2	89.7	6.3	7.0
Sr88	163	155	165	155	159	170	161	164	161	10.4	6.4
Y89	32.1	28.7	31.2	29.2	30.1	31.4	30.2	31.2	30.5	2.3	7.5
Zr91	203	194	212	199	206	213	207	219	207	16.2	7.8
Nb93	8.6	7.4	8.1	7.7	7.9	8.6	8.7	9.0	8.3	1.1	13.6
Cs133	4.4	4.5	4.6	4.2	4.5	4.9	4.5	4.6	4.5	0.4	9.2
Ba137	554	540	568	533	545	578	556	557	554	29.6	5.3
La139	23.5	21.6	24.1	22.7	23.7	24.1	23.2	24.7	23.5	1.9	8.1
Ce140	50.9	46.7	51.4	48.7	50.1	52.7	49.8	52.4	50.3	4.0	7.9
Pr141	6.0	5.7	6.1	5.7	6.0	6.4	6.0	6.2	6.0	0.4	7.4
Nd146	24.2	22.4	24.0	22.7	23.2	25.7	23.7	24.0	23.7	2.0	8.6
Sm147	5.2	4.9	5.1	5.0	5.1	5.4	5.0	5.3	5.1	0.4	6.9
Eu151	1.2	1.2	1.3	1.2	1.3	1.4	1.2	1.3	1.2	0.1	8.6
Gd157	5.3	5.5	5.5	5.2	5.3	5.8	5.2	5.5	5.4	0.4	7.7
Tb159	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.0	5.8
Dy163	5.2	4.9	5.3	4.9	5.0	5.5	5.0	5.2	5.1	0.4	7.8
Ho165	1.1	1.0	1.1	1.0	1.1	1.1	1.0	1.1	1.1	0.1	7.0
Er166	3.2	3.0	3.3	3.0	3.1	3.4	3.2	3.1	3.2	0.3	9.1
Tm169	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.0	6.7
Yb173	3.3	3.1	3.3	3.1	3.0	3.5	3.1	3.4	3.2	0.4	11.1
Lu175	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.0	8.7
Hf178	5.5	5.1	5.5	5.2	5.3	5.9	5.4	5.7	5.4	0.5	9.3
Pb208	18.7	17.1	17.8	17.2	17.6	19.9	17.9	19.3	18.2	2.0	11.1
Th232	9.1	8.9	9.6	9.0	9.3	10.2	9.2	9.6	9.4	0.9	9.1
U238	2.3	2.1	2.1	2.0	2.1	2.3	2.2	2.2	2.2	0.2	10.9

Values are concentrations in ppm. See Table A5.1 for explanation of sample number notation.

Table A6.3. Repeated samples analysed in this study by solution ICP-MS

Dup.	CC305			CC364			CC376			CC064			CC408			CC127			CC348			CC552			CC553		
	1	2	% off	1	2	% off	1	2	% off	1	2	% off	1	2	% off	1	2	% off	1	2	% off	1	2	% off	1	2	% off
Li7	14.4	15.5	7.5	13.6	14.0	2.6	19.5	20.2	3.6	21.3	22.6	5.9	25.7	26.9	4.5	31.2	32.8	5.2	8.3	8.0	-4.3	33.4	33.7	1.0	20.1	19.9	-1.0
Sc45	29.8	30.1	1.0	27.2	27.4	0.6	25.3	26.2	3.4	25.1	25.6	1.9	17.9	18.2	1.8	19.7	19.4	-1.2	34.5	35.0	1.6	15.6	15.3	-1.5	24.7	25.0	1.0
V51	236	238	1.2	205	205	0.4	201	203	0.9	173	173	-0.2	172	170	-1.7	154	158	2.0	249	248	-0.5	135	134	-0.5	202	200	-0.9
Ni60	27.4	28.4	3.6	41.0	42.0	2.3	30.9	30.8	-0.4	123.5	122.6	-0.7	7.7	8.2	6.6	85.2	85.7	0.7	54.7	54.3	-0.7	13.0	13.3	2.3	18.9	19.4	2.6
Cu63	66.1	66.6	0.7	50.8	50.4	-0.7	48.5	48.9	0.7	63.4	62.9	-0.7	32.7	31.8	-3.0	28.3	29.3	3.6	38.3	37.7	-1.7	26.8	27.1	1.2	24.7	27.4	9.8
Zn66	81.6	81.7	0.0	68.4	69.7	1.9	74.0	74.8	1.2	62.3	61.6	-1.1	66.7	64.9	-2.8	59.7	60.4	1.1	81.4	82.1	0.8	61.8	61.1	-1.1	77.3	75.8	-2.0
Ga69	18.4	18.4	0.3	16.9	16.8	-0.6	18.5	19.2	3.8	15.7	16.0	2.0	19.4	18.9	-2.5	17.1	17.8	3.7	17.5	17.2	-1.4	18.5	18.2	-1.7	17.7	17.6	-0.4
Rb85	19.9	19.5	-1.9	57.4	56.1	-2.2	40.5	40.2	-0.5	54.2	56.5	4.3	69.0	70.8	2.5	99.4	96.1	-3.3	17.5	16.3	-6.4	111.8	115.1	2.8	56.0	56.3	0.5
Sr88	249	248	-0.4	225	220	-2.1	231	235	1.7	263	272	3.4	305	315	3.4	230	213	-7.5	226	210	-7.0	250	248	-0.8	229	225	-1.8
Y89	16.5	16.4	-0.4	19.8	19.3	-2.3	19.1	19.7	3.1	17.5	18.1	3.7	19.6	20.1	2.5	20.2	19.5	-3.6	18.7	17.4	-7.2	22.9	23.0	0.7	19.4	19.4	0.2
Zr91	55.3	54.9	-0.7	112.7	109.8	-2.6	92.2	94.6	2.7	108.5	116.0	6.9	135.9	137.7	1.3	180.6	167.3	-7.4	58.5	55.1	-5.9	184.4	186.1	0.9	110.8	111.3	0.5
Nb93	1.8	1.8	-0.2	4.5	4.4	-2.9	3.7	3.8	2.5	4.4	4.8	9.0	5.1	5.3	2.3	7.7	7.4	-3.5	1.9	1.8	-5.1	8.0	9.1	12.0	5.1	4.9	-4.3
Cs133	1.7	1.6	-6.3	2.1	2.0	-4.4	1.3	1.3	0.8	3.5	3.3	-3.8	2.1	2.3	7.9	4.0	3.7	-8.4	0.4	0.4	-4.8	3.8	3.9	4.4	2.4	2.4	0.3
Ba137	220	215	-2.1	311	300	-3.6	305	307	0.8	335	342	1.8	417	433	3.9	475	445	-6.3	222	207	-6.6	496	514	3.4	301	305	1.1
La139	4.4	4.4	-0.9	12.2	12.0	-2.1	10.9	11.3	3.5	12.2	13.0	6.3	14.9	15.1	1.1	15.8	15.0	-4.6	6.0	5.6	-6.0	20.2	19.6	-3.1	10.9	11.0	0.2
Ce140	10.4	10.2	-1.7	26.7	26.0	-2.7	23.2	24.2	4.1	26.2	27.1	3.3	32.9	33.0	0.2	33.5	32.3	-3.7	13.5	12.5	-7.5	44.0	43.0	-2.3	24.4	24.2	-0.7
Pr141	1.5	1.5	-1.7	3.3	3.3	-2.7	3.0	3.1	2.8	3.3	3.4	3.4	3.9	4.1	3.5	4.3	4.0	-8.8	1.9	1.8	-7.3	5.3	5.4	2.1	3.2	3.1	-2.8
Nd146	6.9	6.7	-1.9	13.6	13.2	-3.1	12.4	12.7	2.1	13.2	14.0	6.5	16.1	16.4	1.9	17.6	16.2	-7.7	9.0	8.3	-7.9	20.4	20.9	2.3	12.9	12.6	-2.4
Sm147	2.0	1.9	-5.2	3.1	3.0	-2.6	2.9	3.0	1.7	3.0	3.1	1.6	3.6	3.7	2.7	3.9	3.7	-3.1	2.4	2.3	-4.0	4.6	4.5	-1.4	2.9	2.9	-0.9
Eu151	0.7	0.7	-4.3	0.8	0.8	-4.1	0.8	0.9	3.5	0.9	0.9	-2.3	1.0	1.0	3.0	1.0	0.9	-8.1	0.8	0.7	-7.5	1.1	1.0	-8.5	0.9	0.8	-2.6
Gd157	2.3	2.3	-0.9	3.5	3.3	-7.3	3.3	3.2	-0.9	3.4	3.4	-0.2	3.7	4.0	7.3	4.1	3.9	-6.7	2.8	2.5	-9.7	4.7	4.4	-8.1	3.3	3.2	-1.3
Tb159	0.4	0.4	-3.3	0.5	0.5	-3.3	0.5	0.5	-0.5	0.5	0.5	-1.3	0.5	0.6	6.3	0.6	0.6	-4.8	0.5	0.4	-7.2	0.7	0.6	-3.0	0.5	0.5	-6.3
Dy163	2.8	2.7	-3.6	3.4	3.2	-5.1	3.2	3.3	1.4	3.0	3.1	4.3	3.4	3.5	2.4	3.6	3.5	-4.4	3.1	2.9	-6.7	4.1	3.9	-4.1	3.5	3.3	-6.7
Ho165	0.6	0.6	-3.5	0.7	0.7	-5.5	0.7	0.7	1.2	0.6	0.7	4.6	0.7	0.7	0.7	0.8	0.7	-6.6	0.7	0.6	-9.1	0.8	0.8	-7.0	0.7	0.7	-4.7
Er166	1.8	1.7	-5.3	2.1	1.9	-7.0	2.0	2.0	1.7	1.8	1.8	0.0	2.0	2.1	4.4	2.1	2.0	-5.8	2.0	1.8	-8.8	2.2	2.3	3.7	2.1	1.9	-9.3
Tm169	0.3	0.3	-4.3	0.3	0.3	-7.1	0.3	0.3	3.0	0.3	0.3	2.2	0.3	0.3	3.4	0.3	0.3	-8.8	0.3	0.3	-6.1	0.4	0.3	-6.3	0.3	0.3	-4.3
Yb173	1.8	1.7	-2.3	2.0	1.9	-6.2	1.9	1.9	1.7	1.8	1.8	2.0	1.9	2.0	4.3	2.2	2.0	-10.2	1.9	1.8	-6.5	2.2	2.1	-5.5	2.0	1.9	-4.8
Lu175	0.3	0.3	-6.6	0.3	0.3	-6.5	0.3	0.3	2.0	0.3	0.3	6.2	0.3	0.3	2.7	0.3	0.3	-10.4	0.3	0.3	-8.3	0.3	0.3	2.0	0.3	0.3	-8.6
Hf178	1.7	1.6	-3.8	3.1	2.9	-5.7	2.5	2.6	2.6	3.0	3.2	7.4	3.6	3.7	2.4	4.9	4.6	-5.8	1.7	1.6	-7.8	5.1	4.7	-8.0	3.2	2.9	-8.5
Pb208	6.4	6.1	-3.5	7.5	7.2	-3.6	8.7	8.7	0.6	9.2	9.8	6.7	9.5	10.0	5.5	10.9	10.1	-6.9	3.6	3.4	-5.2	12.3	12.4	0.4	8.9	8.3	-7.0
Ta232	1.3	1.2	-2.0	5.4	5.1	-4.4	3.9	3.9	-1.0	4.9	5.2	6.4	6.5	6.7	3.8	9.2	8.6	-6.0	1.6	1.5	-5.4	9.8	9.7	-0.6	5.2	5.0	-2.8
U238	0.5	0.5	-1.0	1.4	1.3	-6.0	1.0	1.0	-3.4	1.2	1.4	15.3	1.6	1.8	8.4	2.5	2.3	-6.1	0.4	0.4	-5.4	2.6	2.4	-7.4	1.4	1.3	-4.6

Values are concentrations in ppm.

A7. EPMA: glass major element standard and sample data

Major element compositions for glass in 8 lava samples were analysed by electron probe microanalysis (EPMA) using the JEOL JXA 8230 instrument at VUW. This instrument is equipped with 5 wavelength dispersive X-ray spectrometers (WDS), an energy dispersive X-ray spectrometer (EDS) and highly sensitive detectors for acquisition of back-scattered electron (BSE) images. Thin sections were prepared from lava samples and coated with a ~25 nm film of carbon before analysis. For quantitative measurements of glass the instrument was calibrated using international glass standard VG-568 and synthetic oxides for elements in low abundance (<1 wt. %). The instrument was operated using a 15 kV accelerating voltage and 8 nA probe current. Due to the commonly small sizes of melt inclusions and interstitial glass patches, a 5 µm-diameter beam was used (rather than 10 µm). For each element, calibration was undertaken during a 30 seconds peak-search and a 15 seconds background measurement. Counting times for Na were reduced to 15 seconds on the peak and 10 seconds for the background to minimise potential devolatilisation. Na and K were measured first during glass analysis sequences also to minimise alkali loss. Element concentrations were calculated using the ZAF correction method (where Z is atomic number, A is absorption and F is fluorescence; Carpenter, 2008 and references therein).

Values of approximate 2sd measured from repeated analysis of glass standard VG-568 are within 1–5 relative % for major element oxides SiO₂, Al₂O₃ and K₂O, and ~14 % for Na₂O. Analyses are accurate to ≤ 2 % for SiO₂, Al₂O₃ and K₂O, and to 4 % for Na₂O of the preferred values of the standard. The level of analytical precision and accuracy is comparable to that obtained using a 10 µm-wide beam (Barker, 2015) and indicates that using a beam width of 5 µm does not result in significant alkali loss under the analytical conditions used.

Table A7.1. Precision and accuracy of major element analyses of glass VG-568

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	Total
Avg	77.3	0.1	12.1	1.0	0.0	0.0	0.4	3.6	5.0	0.1	99.6
Max	78.3	0.1	12.4	1.6	0.1	0.1	0.5	4.1	5.3	0.1	101.3
Min	75.5	0.0	11.7	0.7	0.0	0.0	0.4	2.8	4.6	0.1	98.0
2sd	1.1	0.0	0.3	0.2	0.0	0.0	0.0	0.5	0.3	0.0	1.3
2sd %	1.4	55.8	2.3	23.9	173.0	68.1	9.5	13.8	5.4	23.6	1.3
Ref	76.7	0.1	12.1	0.8	0.0	0.1	0.5	3.8	4.9	0.1	99.6
Off %	-0.7	34.8	-0.5	-28.1	32.3	37.4	10.6	4.0	-2.0	38.1	-0.1

Reference values from Jarosewich et al. (1980).

Abbreviations for over page: F-P (Formation-Package); WH (Whakapapa); MA (Mangawhero); TH (Te Herenga); RT (Rangataua); SC (Saddle Cone); PT (Paretaitonga); TR (Turoa); TK (Te Kohatu); ME (Mangaehuehu); Sam (sample number); mi (melt inclusion); gm (groundmass); ig (interstitial glass); xg (xenolith glass).

Table A7.2. Major element data for glass in Ruapehu lava samples

F-P	Sam	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	Total
WH-RT	193	mi	72.56	0.61	16.36	1.89	0.03	0.14	2.15	3.40	2.86	0.00	99.79
WH-RT	193	mi	70.92	0.67	15.89	2.00	0.03	0.03	1.17	4.44	4.85	0.00	100.45
WH-RT	193	mi	71.09	0.69	16.02	1.99	0.02	0.04	1.21	4.09	4.85	0.00	100.37
WH-RT	193	mi	70.27	0.37	17.01	1.12	0.02	0.19	3.18	4.54	3.31	0.00	100.52
WH-RT	193	mi	75.78	0.35	14.04	0.66	0.02	0.09	1.00	3.08	4.86	0.13	98.35
WH-RT	193	mi	73.85	0.50	14.99	0.54	0.06	0.11	1.24	3.46	5.14	0.15	99.80
WH-RT	193	mi	73.61	0.30	15.33	0.62	0.02	0.15	1.41	3.74	4.72	0.13	99.54
WH-RT	193	mi	70.59	0.44	17.32	1.03	0.04	0.24	3.32	4.36	2.55	0.13	100.22
WH-RT	193	mi	70.66	0.43	17.34	1.13	0.00	0.24	3.39	4.04	2.67	0.13	100.02
WH-SC	281	mi	71.47	0.61	19.00	2.21	0.04	0.15	3.62	0.80	2.09	0.00	98.67
WH-SC	281	mi	75.03	0.39	14.18	1.85	0.04	0.46	2.52	2.82	2.73	0.00	99.05
WH-SC	281	mi	75.01	0.77	13.29	0.81	0.04	0.07	1.06	3.32	5.62	0.00	100.05
WH-SC	281	mi	75.49	0.63	13.14	0.85	0.03	0.07	1.11	3.22	5.45	0.00	99.26
WH-SC	281	mi	75.32	0.49	13.79	1.02	0.03	0.09	1.29	3.57	4.40	0.00	99.58
WH-SC	281	mi	76.52	0.53	14.07	0.91	0.05	0.08	1.30	2.31	4.22	0.00	99.41
WH-SC	281	mi	75.52	0.57	13.90	0.97	0.02	0.07	1.36	3.31	4.27	0.00	99.17
WH-SC	281	mi	74.52	0.57	13.65	0.93	0.04	0.13	1.13	3.59	5.44	0.00	99.23
WH-SC	281	mi	74.49	0.57	13.54	1.04	0.00	0.18	1.11	3.67	5.39	0.00	99.57
WH-SC	281	mi	75.99	0.72	14.19	0.85	0.00	0.16	1.78	3.93	2.37	0.00	98.39
WH-SC	281	mi	75.74	0.70	14.18	0.83	0.02	0.27	1.98	3.92	2.36	0.00	98.75
WH-SC	281	mi	74.39	0.57	14.61	1.19	0.00	0.98	1.99	4.17	2.09	0.00	99.29
WH-SC	281	mi	75.21	0.59	15.09	0.92	0.07	0.18	2.02	3.79	2.13	0.00	99.68
WH-SC	281	mi	75.55	0.66	14.74	0.93	0.07	0.23	2.18	3.87	1.77	0.00	99.26
WH-SC	281	mi	76.70	0.70	14.99	0.95	0.06	0.17	2.13	2.48	1.81	0.00	99.04
WH-SC	281	mi	75.15	0.27	14.04	1.65	0.06	0.08	2.11	3.41	3.09	0.17	100.42
WH-SC	281	mi	74.51	0.37	14.18	1.87	0.07	0.11	2.14	3.36	3.25	0.19	100.32
WH-SC	281	mi	74.36	0.36	15.07	0.80	0.02	0.22	1.66	3.87	3.50	0.18	99.68
WH-SC	281	mi	74.26	0.42	14.64	0.80	0.05	0.10	1.90	3.07	4.62	0.18	100.29
WH-SC	281	mi	72.85	0.67	15.01	1.16	0.04	0.21	1.80	3.79	4.32	0.20	98.85
WH-SC	281	mi	73.08	0.75	14.79	1.15	0.07	0.16	1.85	3.78	4.20	0.20	99.17
WH-SC	281	mi	71.68	1.36	15.03	1.59	0.01	0.18	2.05	3.83	4.10	0.22	98.83
WH-SC	281	mi	73.63	0.81	14.63	1.10	0.03	0.14	1.67	3.58	4.26	0.22	99.19
WH-SC	281	mi	74.22	0.42	15.23	0.79	0.06	0.18	2.31	4.08	2.61	0.16	98.78
WH-SC	281	mi	75.67	0.23	13.42	1.56	0.06	0.12	1.80	3.26	3.77	0.15	100.15
WH-SC	281	mi	77.01	0.42	12.99	0.95	0.03	0.04	1.06	3.30	4.08	0.16	98.74
WH-SC	281	mi	76.80	0.48	13.05	0.86	0.03	0.06	1.00	3.04	4.56	0.16	99.25
WH-SC	281	mi	72.75	0.83	15.01	1.00	0.05	0.25	1.92	3.77	4.23	0.23	100.27
WH-SC	281	mi	73.68	0.46	14.87	0.81	0.04	0.14	1.78	3.76	4.29	0.20	100.06
WH-SC	281	mi	74.01	0.88	14.37	0.77	0.02	0.14	1.70	3.55	4.39	0.23	100.25
WH-SC	281	mi	74.00	0.48	15.20	0.81	0.09	0.17	2.43	3.99	2.71	0.16	100.47
WH-PT	335	mi	75.78	0.35	14.04	0.66	0.02	0.09	1.00	3.08	4.86	0.13	98.35
WH-PT	335	mi	73.85	0.50	14.99	0.54	0.06	0.11	1.24	3.46	5.14	0.15	99.80
WH-PT	335	mi	73.61	0.30	15.33	0.62	0.02	0.15	1.41	3.74	4.72	0.13	99.54
WH-PT	335	mi	70.59	0.44	17.32	1.03	0.04	0.24	3.32	4.36	2.55	0.13	100.22
WH-PT	335	mi	70.66	0.43	17.34	1.13	0.00	0.24	3.39	4.04	2.67	0.13	100.02
WH-TR	260	gm	73.32	1.36	11.92	3.56	0.29	0.13	1.06	3.30	5.04	0.09	99.40
WH-TR	260	gm	73.60	1.11	12.47	2.86	0.23	0.08	1.00	3.69	4.95	0.05	100.21
WH-TR	260	gm	73.25	0.95	12.50	3.32	0.31	0.11	0.94	3.44	5.21	0.04	100.33
WH-TR	260	gm	73.99	1.23	11.93	3.12	0.28	0.14	0.96	3.38	5.00	0.04	99.32
WH-TR	260	gm	73.97	1.10	12.42	2.93	0.18	0.08	1.11	4.09	4.12	0.04	100.34
WH-TR	260	gm	73.44	1.10	12.32	3.34	0.31	0.10	1.02	3.40	4.96	0.07	100.15
WH-TR	260	gm	74.69	1.05	11.84	2.77	0.25	0.09	0.85	3.27	5.18	0.06	100.06
WH-TR	260	gm	73.27	1.39	11.68	3.78	0.26	0.13	1.10	3.45	4.94	0.06	99.49
WH-TR	260	gm	74.14	1.19	12.11	2.94	0.26	0.08	0.95	3.23	5.09	0.07	98.76
WH-TR	260	gm	73.54	1.32	12.16	3.18	0.26	0.12	1.12	3.21	5.11	0.03	98.58
WH-TR	260	gm	73.91	1.20	12.31	2.94	0.26	0.06	0.79	3.43	5.11	0.06	100.31
WH-TR	260	gm	74.03	1.26	12.26	2.82	0.27	0.07	0.85	3.32	5.10	0.08	100.12
WH-TR	260	gm	73.53	1.32	12.39	2.95	0.26	0.11	0.98	3.35	5.13	0.04	99.61
WH-TR	260	gm	73.57	1.17	12.18	3.13	0.25	0.13	1.05	3.50	5.00	0.09	100.30
WH-TR	260	gm	75.13	1.01	12.20	2.45	0.25	0.03	0.66	3.26	5.06	0.01	99.34
WH-TR	260	gm	74.20	1.11	12.26	2.78	0.28	0.09	0.96	3.17	5.17	0.04	98.12

Values are in weight %, normalised to anhydrous 100 % totals. Abbreviations are on page 251.

Table A7.2. (cont.) Major element data for glass in Ruapehu lava samples.

F-P	Sam	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	Total
MA-TK	415	mi	73.94	0.96	12.59	2.33	0.03	0.28	0.99	3.03	5.76	0.13	99.77
MA-TK	415	mi	72.88	0.99	13.18	2.37	0.02	0.26	1.54	3.43	5.24	0.13	99.88
MA-TK	415	mi	73.53	1.09	12.51	2.65	0.04	0.30	0.99	3.01	5.78	0.14	100.52
MA-TK	415	mi	73.95	0.87	12.59	2.31	0.05	0.26	1.00	3.07	5.80	0.14	99.57
MA-TK	415	mi	73.89	0.90	12.52	2.22	0.04	0.33	1.00	3.15	5.84	0.14	100.43
MA-TK	415	mi	74.19	0.90	12.39	2.33	0.06	0.28	1.04	3.15	5.57	0.14	99.77
MA-TK	415	mi	71.38	0.43	16.03	2.16	0.03	0.23	0.74	3.56	5.36	0.10	99.84
MA-TK	415	mi	71.49	0.73	14.08	2.78	0.03	0.31	1.34	3.49	5.65	0.13	99.87
MA-TK	415	mi	74.63	0.85	14.52	2.05	0.05	0.19	1.25	1.03	5.33	0.14	99.74
MA-TK	415	mi	70.77	0.93	14.86	2.60	0.05	0.20	1.25	3.51	5.71	0.16	99.62
MA-TK	415	mi	74.68	1.14	12.43	2.29	0.05	0.19	0.92	2.91	5.31	0.12	98.77
MA-TK	415	mi	73.61	1.22	12.65	2.34	0.05	0.29	1.09	3.10	5.55	0.13	98.49
MA-TK	415	mi	73.45	1.19	12.60	2.50	0.02	0.27	1.20	3.20	5.47	0.14	99.32
MA-TK	415	mi	73.82	0.75	13.57	1.97	0.04	0.15	0.97	3.10	5.52	0.15	99.57
MA-TK	415	mi	74.35	1.00	12.46	2.26	0.02	0.20	0.87	3.10	5.62	0.14	99.42
MA-TK	415	mi	73.79	1.08	12.96	2.19	0.04	0.23	0.94	3.30	5.38	0.11	100.36
MA-TK	415	mi	73.16	0.95	13.60	2.15	0.07	0.16	1.01	3.33	5.48	0.11	99.47
MA-TK	415	mi	72.94	0.30	15.26	1.08	0.04	0.20	1.68	3.31	5.05	0.17	100.50
MA-TK	415	mi	70.28	0.38	16.15	2.03	0.00	0.28	2.42	3.47	4.85	0.17	100.44
MA-TK	415	mi	74.75	0.87	12.09	2.48	0.03	0.23	0.86	2.94	5.67	0.10	100.38
MA-TK	415	mi	74.40	0.92	12.42	2.23	0.04	0.24	0.94	3.03	5.70	0.11	100.58
MA-TK	415	mi	75.30	0.20	13.01	2.43	0.04	0.18	1.44	2.57	4.70	0.16	100.26
MA-TK	415	mi	71.18	0.63	15.15	2.08	0.04	0.38	2.28	3.60	4.56	0.12	99.87
MA-TK	415	mi	74.29	1.16	12.69	2.04	0.05	0.21	1.01	2.97	5.47	0.14	100.11
MA-TK	415	mi	71.43	0.77	14.49	2.57	0.00	0.33	1.26	3.76	5.27	0.14	100.34
MA-TK	415	mi	74.79	0.80	12.45	1.93	0.02	0.22	0.80	3.13	5.78	0.11	99.54
MA-TK	415	mi	75.06	0.69	12.38	2.31	0.00	0.19	0.77	3.12	5.40	0.11	99.74
MA-TK	415	mi	74.63	0.80	12.53	2.18	0.00	0.21	0.88	3.17	5.52	0.10	100.06
MA-TK	415	mi	73.59	0.96	12.90	2.47	0.00	0.28	1.04	3.21	5.44	0.13	99.74
MA-TK	415	mi	74.10	0.99	12.42	2.38	0.00	0.25	0.98	3.13	5.66	0.12	100.24
MA-TK	415	mi	74.75	0.74	12.47	2.11	0.00	0.21	0.91	3.18	5.57	0.09	99.61
MA-TK	415	mi	74.18	0.73	13.22	1.93	0.00	0.19	1.33	3.19	5.16	0.10	100.30
MA-TK	415	mi	74.21	0.99	12.35	2.38	0.00	0.26	0.95	3.14	5.62	0.13	99.86
MA-TK	415	mi	74.45	0.95	12.38	2.14	0.02	0.28	0.97	3.16	5.55	0.14	99.29
MA-TK	415	mi	71.27	0.78	15.18	2.06	0.07	0.14	1.12	3.69	5.57	0.15	100.33
MA-TK	415	mi	75.34	0.84	12.37	2.00	0.04	0.18	0.77	2.90	5.48	0.10	100.74
MA-TK	415	mi	72.44	0.51	14.52	1.81	0.04	0.27	2.53	3.72	4.02	0.18	100.27
MA-TK	415	mi	74.38	0.76	12.54	1.90	0.03	0.23	0.94	3.15	5.99	0.10	100.19
MA-TK	415	mi	69.95	0.41	14.33	2.85	0.07	1.47	2.35	4.06	4.40	0.15	99.67
MA-TK	415	mi	70.58	0.37	15.73	1.97	0.06	0.17	2.51	4.10	4.40	0.17	100.38
MA-TK	415	mi	70.92	0.40	15.13	2.16	0.02	0.20	2.37	3.87	4.79	0.18	100.81
MA-TK	415	mi	73.52	0.63	13.19	1.92	0.06	0.16	0.97	3.30	6.17	0.10	100.44
MA-TK	415	mi	71.77	0.36	14.60	2.10	0.06	0.17	2.08	3.60	5.14	0.13	100.19
MA-TK	415	mi	75.60	0.72	12.32	1.60	0.03	0.15	0.76	3.07	5.68	0.08	99.98
MA-TK	415	mi	72.65	0.55	14.92	1.17	0.02	0.32	1.63	3.76	4.88	0.14	100.25
MA-TK	415	mi	70.22	0.66	15.75	1.99	0.05	0.30	2.84	3.61	4.48	0.14	100.40
MA-TK	415	mi	71.04	0.89	15.11	1.55	0.00	0.28	1.43	3.70	5.87	0.16	98.71
MA-TK	415	mi	72.18	0.70	15.29	1.91	0.00	0.27	2.23	2.59	4.72	0.14	98.65
MA-TK	415	mi	72.62	0.55	15.05	0.95	0.06	0.33	1.70	3.74	4.89	0.14	98.65
MA-TK	415	mi	71.22	0.45	16.15	1.01	0.03	0.28	1.67	4.17	4.90	0.15	100.07
MA-TK	415	mi	73.24	0.65	14.92	1.11	0.05	0.23	1.78	3.74	4.16	0.15	100.43
MA-TK	415	mi	72.73	0.65	14.76	1.07	0.03	0.22	1.61	3.48	5.33	0.15	98.96
MA-TK	415	mi	72.77	0.52	15.22	1.01	0.06	0.27	1.76	3.78	4.49	0.15	99.70
MA-TK	415	mi	72.67	0.71	15.01	1.26	0.00	0.32	1.81	4.04	4.09	0.13	100.42
MA-TK	415	mi	72.00	0.82	14.26	1.78	0.02	0.15	1.31	3.42	6.12	0.16	99.93
MA-TK	415	ig	70.51	0.87	14.83	2.79	0.04	0.24	1.40	3.65	5.55	0.15	98.75
MA-TK	415	ig	73.41	0.97	12.66	2.57	0.05	0.22	0.99	3.24	5.80	0.12	98.69
MA-TK	415	ig	73.31	1.08	12.64	2.57	0.03	0.30	1.02	3.15	5.78	0.15	99.02
MA-TK	415	xg	74.53	1.25	12.11	2.47	0.05	0.20	0.93	2.74	5.62	0.13	97.35
MA-TK	415	xg	74.44	1.32	12.10	2.50	0.00	0.24	0.98	2.78	5.52	0.14	97.47
MA-TK	415	xg	73.98	1.24	12.11	2.45	0.05	0.23	1.09	2.90	5.85	0.14	97.14

Values are in in weight %, normalised to anhydrous 100 % totals. Abbreviations are on page 251.

Table A7.2. (cont.) Major element data for glass in Ruapehu lava samples.

F-P	Sam	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	Total
MA-TK	415	xg	73.76	1.15	12.38	2.48	0.05	0.26	1.00	3.04	5.75	0.16	97.71
MA-TK	415	xg	74.03	1.20	12.13	2.56	0.02	0.27	1.02	2.98	5.71	0.12	97.06
MA-TK	415	xg	73.80	1.14	12.31	2.48	0.07	0.28	1.04	3.13	5.66	0.12	97.60
MA-TK	415	xg	75.12	0.81	12.08	1.76	0.03	0.27	0.95	2.91	5.97	0.12	98.05
MA-TK	415	xg	75.18	0.77	12.07	1.75	0.05	0.23	0.92	3.09	5.84	0.12	98.35
MA-TK	415	xg	75.15	0.82	12.26	1.82	0.00	0.26	0.91	2.98	5.70	0.12	97.95
MA-TK	415	xg	74.92	0.83	12.15	1.84	0.04	0.27	0.96	2.92	5.97	0.13	97.96
MA-TK	415	gm	75.04	0.79	12.03	2.22	0.05	0.20	0.82	2.99	5.77	0.10	101.59
MA-TK	415	gm	71.72	0.62	15.10	1.75	0.00	0.15	2.34	3.82	4.44	0.06	101.81
MA-TK	415	gm	75.10	0.77	12.08	2.18	0.00	0.17	0.80	2.95	5.85	0.10	101.03
MA-TK	415	gm	75.00	0.79	12.32	2.19	0.00	0.17	0.97	2.93	5.54	0.10	100.66
MA-TK	479	mi	73.74	0.46	12.11	3.27	0.01	1.23	0.87	2.90	5.35	0.09	99.77
MA-TK	479	mi	70.50	0.78	15.04	2.05	0.04	0.40	1.79	3.40	5.88	0.15	100.16
MA-TK	479	mi	71.69	0.34	14.17	2.33	0.01	0.35	1.36	3.48	6.15	0.16	100.12
MA-TK	479	mi	73.44	0.93	12.80	2.27	0.03	0.34	1.15	3.15	5.80	0.13	100.08
MA-TK	479	mi	71.73	0.31	15.00	2.34	0.00	0.32	1.22	2.97	6.01	0.14	99.38
MA-TK	479	mi	74.99	0.84	12.61	2.28	0.02	0.32	0.95	2.42	5.51	0.10	98.69
MA-TK	479	mi	71.37	0.33	14.68	2.22	0.00	0.31	1.42	3.42	6.15	0.12	99.61
MA-TK	479	mi	72.80	1.08	13.96	2.07	0.02	0.29	1.07	2.77	5.86	0.13	99.64
MA-TK	479	mi	71.60	0.54	14.72	2.54	0.00	0.24	1.17	2.86	6.23	0.11	99.55
MA-TK	479	mi	74.82	0.68	12.38	2.01	0.00	0.21	0.88	3.04	5.90	0.10	100.17
MA-TK	479	mi	72.67	0.98	13.77	2.01	0.00	0.21	0.88	3.26	6.12	0.14	100.25
MA-TK	479	mi	72.93	1.06	13.71	1.90	0.03	0.18	1.94	3.04	5.13	0.10	99.72
MA-TK	479	ig	70.66	0.74	15.48	2.40	0.02	0.36	1.19	3.17	5.87	0.15	98.25
MA-TK	479	ig	72.85	0.91	13.12	2.37	0.02	0.30	1.08	2.96	6.28	0.15	98.33
MA-TK	479	ig	73.67	0.90	12.78	2.45	0.01	0.29	1.08	3.05	5.66	0.13	98.55
MA-TK	479	ig	74.55	0.91	12.34	2.18	0.00	0.26	0.90	2.80	5.96	0.12	98.29
MA-TK	479	gm	75.01	0.82	12.19	2.24	0.03	0.22	0.92	2.90	5.59	0.09	100.34
MA-TK	479	gm	74.95	0.81	12.22	2.23	0.03	0.23	0.95	2.84	5.68	0.08	101.11
MA-TK	479	gm	75.05	0.82	12.06	2.28	0.02	0.22	0.89	2.81	5.77	0.09	101.15
MA-TK	479	gm	74.67	0.82	12.40	2.13	0.04	0.21	1.15	2.95	5.56	0.07	100.83
MA-TK	479	gm	75.38	0.78	12.04	2.08	0.00	0.21	0.92	2.78	5.76	0.09	100.81
MA-TK	479	gm	75.00	0.76	12.31	2.13	0.00	0.22	0.97	2.75	5.79	0.10	100.80
MA-TK	479	gm	73.13	0.83	12.69	2.75	0.04	0.60	1.68	3.15	5.05	0.11	100.94
MA-TK	479	gm	73.42	0.80	13.25	2.24	0.03	0.25	1.46	3.28	5.20	0.09	100.58
MA-TK	479	gm	73.57	0.79	13.31	1.98	0.03	0.22	1.65	3.25	5.13	0.10	101.28
MA-ME	69	gm	69.38	1.83	13.18	4.87	0.11	0.52	2.55	4.52	2.98	0.08	99.66
MA-ME	69	gm	68.96	1.81	12.32	5.84	0.10	0.87	2.63	4.11	3.32	0.07	100.16
MA-ME	69	gm	70.10	1.71	13.26	4.33	0.09	0.46	2.38	4.55	3.09	0.06	99.95
MA-ME	69	gm	69.22	1.74	12.74	5.44	0.12	0.79	2.67	4.56	2.65	0.09	99.70
MA-ME	69	gm	69.79	1.77	12.52	5.19	0.13	0.64	2.41	4.37	3.12	0.10	99.99
MA-ME	69	gm	69.33	1.73	12.82	5.37	0.12	0.64	2.41	4.41	3.14	0.06	100.36
MA-ME	69	gm	69.04	1.64	13.23	5.15	0.12	0.66	2.49	5.03	2.56	0.10	99.77
MA-ME	69	gm	69.39	1.75	13.38	4.75	0.12	0.64	2.51	4.79	2.62	0.09	100.00
MA-ME	69	gm	69.33	1.59	13.83	4.45	0.11	0.50	2.73	4.36	3.05	0.08	99.84
MA-ME	69	gm	69.73	1.71	13.14	4.92	0.11	0.66	2.92	4.13	2.64	0.06	99.85
MA-ME	69	gm	68.97	1.79	12.70	5.48	0.13	0.68	2.39	4.41	3.42	0.07	100.08
MA-ME	69	gm	69.69	1.61	12.70	5.12	0.14	0.69	2.43	4.59	2.99	0.06	99.32
MA-ME	69	gm	69.10	1.66	13.11	5.19	0.12	0.65	2.56	4.60	2.96	0.08	99.87
MA-ME	69	mi	68.27	1.30	16.30	3.04	0.14	0.19	2.99	3.99	3.74	0.06	100.41
MA-ME	69	mi	67.81	1.23	17.11	2.74	0.14	0.20	3.60	3.99	3.17	0.05	99.11
MA-ME	69	mi	67.56	1.29	17.06	2.95	0.15	0.67	3.57	3.38	3.34	0.05	100.20
MA-ME	69	mi	71.16	0.78	14.88	2.86	0.14	0.18	2.60	3.46	3.91	0.05	100.20
MA-ME	77	mi	71.58	0.92	15.54	1.23	0.15	0.07	1.98	4.20	4.35	0.01	100.34
MA-ME	77	mi	72.65	0.60	15.40	0.69	0.12	0.16	1.71	3.43	5.23	0.03	99.55
MA-ME	77	mi	72.66	0.81	14.87	1.40	0.15	0.04	1.70	3.98	4.39	0.03	100.02
MA-ME	77	mi	72.54	0.84	15.02	1.35	0.16	0.07	1.51	4.01	4.53	0.02	100.55
MA-ME	77	mi	72.89	0.45	15.29	1.07	0.13	0.08	2.28	4.27	3.49	0.07	100.37
MA-ME	77	mi	74.32	1.86	12.96	1.44	0.15	0.12	0.56	3.03	5.60	0.00	99.35
MA-ME	77	mi	75.40	0.65	14.02	0.48	0.13	0.07	1.58	3.75	3.90	0.05	99.71
MA-ME	77	mi	76.62	0.59	13.28	0.44	0.14	0.07	1.12	3.73	3.98	0.05	99.84

Values are in weight %, normalised to anhydrous 100 % totals. Abbreviations are on page 251.

Table A7.2. (cont.) Major element data for glass in Ruapehu lava samples.

F-P	Sam	Type	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cl	Total
MA-ME	77	mi	69.36	0.77	17.49	1.10	0.16	0.15	3.12	4.56	3.30	0.02	100.41
MA-ME	77	mi	69.28	1.53	16.03	1.72	0.07	0.15	2.59	4.89	3.72	0.03	100.56
MA-ME	77	mi	69.50	0.83	16.12	1.50	0.03	0.14	0.66	7.15	4.07	0.01	100.24
MA-ME	77	mi	71.13	1.58	15.11	1.42	0.08	0.11	2.85	3.82	3.89	0.02	99.44
MA-ME	154	mi	73.85	0.13	15.08	1.02	0.12	0.04	1.53	3.84	4.38	0.02	99.56
MA-ME	154	mi	73.84	0.10	14.96	0.91	0.13	0.04	1.77	3.87	4.39	0.01	100.05
MA-ME	154	mi	73.60	0.14	15.24	1.01	0.14	0.06	1.50	3.92	4.40	0.02	100.22
MA-ME	154	mi	73.71	0.15	15.13	1.17	0.13	0.04	1.46	4.00	4.24	0.01	100.27
MA-ME	154	mi	74.21	0.19	14.56	0.71	0.15	0.05	1.68	3.76	4.70	0.01	99.02
MA-ME	154	mi	75.17	0.15	14.41	0.73	0.12	0.05	0.94	3.68	4.76	0.00	100.40
MA-ME	154	mi	74.98	0.12	14.47	0.66	0.12	0.04	1.28	3.64	4.66	0.05	99.85
MA-ME	154	mi	74.98	0.14	14.50	0.86	0.12	0.07	1.59	3.54	4.19	0.03	100.08
MA-ME	154	mi	75.24	0.13	14.21	1.00	0.14	0.04	1.51	3.48	4.26	0.04	99.77
MA-ME	154	mi	73.31	0.73	14.53	1.59	0.16	0.06	0.94	3.59	5.08	0.04	99.87
MA-ME	154	mi	74.24	0.13	14.79	0.81	0.17	0.05	1.12	3.61	5.12	0.01	100.10
MA-ME	154	mi	74.68	0.16	14.43	1.21	0.13	0.01	1.41	3.52	4.45	0.03	100.04
MA-ME	154	mi	75.71	0.11	14.54	0.53	0.13	0.06	0.86	4.11	3.96	0.02	99.65
MA-ME	154	mi	74.50	0.13	15.22	0.58	0.17	0.03	1.00	4.41	3.99	0.01	100.02
TH	348	mi	70.22	0.40	17.16	1.08	0.05	0.07	2.53	5.93	2.42	0.18	99.30
TH	326	mi	74.15	0.22	15.95	0.65	0.01	0.02	1.38	5.01	2.50	0.14	100.07
TH	326	mi	73.27	0.16	16.25	1.20	0.03	0.06	2.13	4.57	2.18	0.20	100.47
TH	326	mi	74.77	0.19	13.45	1.58	0.05	0.71	2.63	3.52	3.06	0.06	99.01
TH	326	mi	74.02	0.18	13.29	2.09	0.00	0.81	3.39	3.28	2.84	0.11	98.12
TH	326	mi	75.52	0.10	14.50	1.48	0.06	0.09	1.91	4.18	2.04	0.18	98.78
TH	326	mi	76.61	0.11	14.07	1.07	0.05	0.03	1.81	4.19	1.93	0.15	100.48
TH	326	mi	77.45	0.11	13.49	1.06	0.03	0.04	1.70	3.81	2.21	0.14	100.71
TH	326	mi	71.65	0.47	17.85	1.41	0.07	0.07	2.72	3.26	2.35	0.21	100.64
TH	326	mi	78.70	0.12	13.97	0.93	0.02	0.00	1.61	1.62	2.96	0.10	98.21
TH	326	mi	77.45	0.06	12.94	0.84	0.05	0.02	1.34	3.74	3.49	0.08	100.20
TH	308	mi	74.86	0.29	15.43	0.97	0.04	0.08	2.15	4.21	1.85	0.16	99.81
TH	308	mi	72.31	0.32	16.43	1.38	0.00	0.09	2.26	4.72	2.34	0.18	100.37
TH	308	mi	69.74	0.99	17.36	1.90	0.06	0.08	2.94	4.57	2.22	0.19	100.74
TH	308	mi	70.20	0.95	16.89	1.92	0.05	0.07	2.83	4.74	2.22	0.16	101.62
TH	308	mi	70.54	0.93	16.73	1.78	0.03	0.10	2.68	4.71	2.35	0.17	101.27
TH	308	mi	69.94	1.13	17.02	1.77	0.04	0.16	2.84	4.69	2.28	0.17	100.85
TH	308	mi	71.03	1.06	16.51	1.63	0.04	0.07	2.63	4.57	2.34	0.17	101.49
TH	308	mi	70.74	0.87	16.73	1.76	0.04	0.13	2.58	4.56	2.44	0.18	100.72
TH	308	mi	70.60	0.99	17.00	1.45	0.04	0.11	2.68	4.62	2.36	0.18	100.66
TH	308	mi	70.25	0.99	17.12	1.75	0.01	0.07	2.78	4.64	2.25	0.17	101.12
TH	308	mi	70.56	1.03	16.62	1.70	0.02	0.06	2.66	4.83	2.38	0.16	101.75
TH	308	mi	69.92	1.08	16.88	1.57	0.03	0.10	2.76	4.65	2.87	0.19	100.99
TH	308	mi	69.90	0.39	17.50	2.13	0.03	0.05	3.45	4.71	1.74	0.13	101.31

Values are in in weight %, normalised to anhydrous 100 % totals. Abbreviations are on page 251.

Appendix 8. EPMA: mineral major element standard data

Major element compositions for minerals in 15 lava samples were analysed by electron probe microanalysis (EPMA) using the JEOL JXA 8230 instrument at VUW. This instrument is equipped with 5 wavelength dispersive X-ray spectrometers (WDS), an energy dispersive X-ray spectrometer (EDS) and highly sensitive detectors for acquisition of back-scattered electron (BSE) images. Thin sections were prepared from lava samples and coated with a ~25 nm film of carbon before analysis. For quantitative measurements of pyroxene and plagioclase the instrument was calibrated using international mineral (Kakanui augite and labradorite plagioclase) standards of similar composition to the material being analysed for most elements and synthetic oxides for elements in low abundance (<1 wt. %). For each element, calibration was undertaken during a 30 seconds peak-search and a 15 seconds background measurement. Analysis of crystal phases were performed using a focussed electron beam (~1µm-wide) at a current of 12 nA and accelerating voltage of 15 kV. Element concentrations were calculated using the ZAF correction method (where Z is atomic number, A is absorption and F is fluorescence; Carpenter, 2008 and references therein). Calibration and secondary standards were analysed as unknowns to monitor instrumental drift and precision and accuracy of the measurements throughout analytical sessions. Approximate 2sd analytical precision from repeated analysis of mineral standards are generally 1–7 relative % for major element oxides with concentrations >0.5 wt. %. Analyses of the standards are accurate to within 5 % of the preferred values for those major element oxides. Full sample data are provided in the electronic appendix files.

Table A8.1. Precision and accuracy of pyroxene major element analysis by EPMA:
Kakanui augite n = 129

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	Cr ₂ O ₃	Total
Avg	50.4	0.8	8.5	6.2	0.1	16.7	15.8	1.2	0.2	100.0
Max	51.1	0.9	8.8	6.7	0.2	17.4	16.1	1.3	0.2	101.1
Min	48.5	0.7	8.2	5.3	0.1	16.2	15.4	1.1	0.1	97.8
2sd	0.8	0.1	0.2	0.4	0.0	0.4	0.3	0.1	0.0	1.2
2sd %	1.6	6.8	2.8	6.8	27.0	2.6	1.8	6.6	27.0	1.2
Ref	50.7	0.7	8.7	6.3	0.1	16.7	15.8	1.3	0.2	100.6
Off %	3.3	-11.2	0.5	2.2	-5.7	-0.2	0.1	4.2	-2.8	0.6

Reference values from Jarosewich et al. (1980) and Klügel et al. (2005)

Table A8.2. Precision and accuracy of plagioclase major element analysis by EPMA:
Labradorite plagioclase n = 107

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
Avg	51.1	0.0	30.8	0.4	0.0	0.1	13.4	3.4	0.2	99.5
Max	51.9	0.1	31.3	0.5	0.0	0.2	13.7	3.7	0.2	100.5
Min	50.0	0.0	30.2	0.3	0.0	0.1	13.0	3.1	0.1	97.7
2sd	0.9	0.0	0.6	0.1	0.0	0.0	0.4	0.2	0.1	1.2
2sd %	1.7	86.7	1.9	19.6	209.9	17.2	3.0	6.6	29.4	1.2
Ref	51.3	0.1	30.9	0.2	0.0	0.1	13.6	3.5	0.2	100.2
Off %	0.3	48.8	0.5	-177.8	15.9	-5.1	1.6	0.8	-0.7	0.7

Reference values from Jarosewich et al. (1980)

Appendix 9. LA-ICP-MS glass standard data

Laser ablation (LA) ICP-MS analyses of interstitial glass and xenolith-hosted glass in dacite lava sample CC415 were carried out at VUW using a Resonetics RESolution S155-SE laser ablation system equipped with an ATL ArF Excimer laser (wavelength 193 μm) and coupled to an Agilent 7500CS ICP-MS. Instrument set-up and data processing are described in Chapter 4.

BHVO-2G and BCR-2G were analysed as secondary standards. Because the analysis session was intended as a preliminary exercise for collecting trace element data for Ruapehu glasses, only 2 spots on each standard, and 11 spots on samples were analysed. Analyses of standards were generally accurate to within 15 % of reference values, and mostly <5 % for the light rare earth elements and elements of interest for the purposes of this study (Rb, Sr, Zr, Ba). Exceptions to these values were calculated for Tm and Hf in BCR-2G and Cs, Eu and Lu in BHVO-2G (Table A9.1).

Table A9.1. Accuracy of LA-ICP-MS trace element analyses of BCR-2G and BHVO-2G.

BCR-2G	Ref.	std 1	std 2	Avg	% off	BHVO-2G	Ref.	std 1	std 2	Avg	% off
Sc45	33	34.4	36.1	35.3	6.9	Sc45	33	30.5	32.0	31.3	-5.3
V51	425	456	444	450	5.9	V51	308	337	311	324	5.1
Zn66	125	177	161	169	35.2	Zn66	102	133.9	134.3	134.1	31.5
Rb85	47	47.5	43.8	45.7	-2.8	Rb85	9.2	10.4	8.5	9.4	2.6
Sr88	342	354	367	360	5.4	Sr88	396	383	374	379	-4.4
Y89	35	35.2	36.7	36.0	2.8	Y89	26	26.3	23.0	24.7	-5.2
Zr91	184	192	176	184	0.0	Zr91	170	180	144	162	-4.7
Nb93	12.5	10.5	12.0	11.2	-10.2	Nb93	18.3	16.7	15.6	16.2	-11.7
Cs133	1.16	1.4	1.1	1.2	7.1	Cs133	0.1	bdl	0.1	0.1	-25.0
Ba137	683	703	699	701	2.6	Ba137	131	110	123	116	-11.2
La139	24.7	27.0	25.6	26.3	6.5	La139	15.2	13.3	14.8	14.1	-7.5
Ce140	53.3	51.7	56.4	54.0	1.4	Ce140	37.6	37.9	34.9	36.4	-3.2
Pr141	6.7	6.6	6.3	6.5	-3.5	Pr141	5.35	5.2	4.9	5.1	-5.6
Nd146	28.9	26.3	27.5	26.9	-6.9	Nd146	24.5	24.0	21.9	22.9	-6.4
Sm147	6.59	8.7	6.2	7.5	13.1	Sm147	6.1	6.2	6.3	6.2	2.2
Eu151	1.97	2.4	2.1	2.2	13.6	Eu151	2.07	1.3	1.9	1.6	-20.6
Gd157	6.71	7.6	7.4	7.5	11.6	Gd157	6.16	5.4	6.0	5.7	-7.3
Tb159	1.02	0.7	1.2	1.0	-5.2	Tb159	0.92	0.8	0.9	0.8	-8.6
Dy163	6.44	7.7	7.1	7.4	15.3	Dy163	5.28	5.8	5.5	5.7	7.5
Ho165	1.27	1.0	1.1	1.1	-13.9	Ho165	0.98	0.7	0.9	0.8	-16.7
Er166	3.7	3.2	3.5	3.4	-8.5	Er166	2.56	4.1	1.9	3.0	17.0
Tm169	0.51	0.3	0.4	0.4	-26.1	Tm169	0.34	0.4	0.3	0.4	9.7
Yb172	3.39	2.0	3.9	3.0	-12.6	Yb172	2.01	1.9	2.4	2.1	6.1
Lu175	0.503	0.6	0.6	0.6	14.0	Lu175	0.279	0.2	0.1	0.2	-43.6
Hf178	4.84	6.2	5.8	6.0	24.1	Hf178	4.32	4.0	4.1	4.1	-6.1

Values are concentrations in ppm. Reference values from Georem.