MELT MIGRATION IN THE LOWER CRUST BY POROUS MELT FLOW

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Ehara taku toa, i te toa takitahi Engari, he toa takitini

Success is not the work of one, but the work of many

-Maori proverb

ABSTRACT

Migration of melt transfers heat, mass, and volatiles from depth towards the surface, driving differentiation of the Earth and playing a major role in generating its compositionally layered structure. Additionally, stress dissipation is strongly accommodated by strain partitioning into inherently weak melt-bearing rocks and particularly into the melt itself. Therefore, knowledge of the mechanisms of melt migration and their spatial distribution is fundamental to understanding the chemical and rheological evolution of the continental crust over time. The current understanding of crustal melt migration mechanisms is biased towards mechanisms that preserve large segregations of leucosome in outcrop, such as dyking or zones of stromatic migmatite. Therefore, existing knowledge is lacking about other melt migration mechanisms that preserve little to no melt along their pathways of migration, such as porous melt flow. Porous melt flow occurs at the grain scale and is defined as the migration of melt through an interconnected network of grain boundaries and triple junctions within a solid rock.

This thesis aims to fill this knowledge gap by identifying zones fluxed by porous melt flow and assessing its potential as a significant melt migration mechanism by studying relationships in the Pembroke Granulite, a low-strain outcrop of magmatic arc lower crust, Fiordland, New Zealand. Identification of zones fluxed by porous melt flow is based on i) field relationships, ii) microstructures, and iii) composition of the whole rock and mineral assemblage. This multidisciplinary approach provides insight into the chemical and rheological evolution of the lower continental crust during porous melt flow.

Four distinct episodes of partial to complete hydration of the host two-pyroxene–pargasite gneiss are identified in the Pembroke Granulite, each resulting in spatially and geologically distinct rocks. The development of these distinct rocks is largely due to different magnitudes of melt–rock reaction during porous melt flow. In this thesis, the difference in magnitude of melt–rock interaction ranges from a nearly isochemical reaction involving the addition of volatiles to the host rock, to the transformation of a gabbroic protolith to hornblendite. The spatial distribution of melt is inferred to localise strain, as high-strain zones are associated with melt-rich channels. Within the high-strain zones, a lack of deformation microstructures implies the dissipation of stress was accommodated by the fluxing melt. A lack of deformation microstructures indicates that deformation ceased when the melt crystallised, suggesting the timing and duration of deformation is controlled by the volume and spatial distribution of melt. The presence of microstructures indicative of the former presence of melt within partially to completely hydrated zones of the Pembroke Granulite indicate hydration occurred because of melt–rock interaction. In both low- and high-strain zones, interaction between the Pembroke Granulite and fluxing melt replaced the pre-existing, deformed assemblage with an undeformed, hydrated assemblage. Minerals in the hydrated assemblage have homogeneous compositions at an outcrop scale, and igneous-like rare earth element patterns.

Four distinct episodes of porous melt flow are identified within the 0.15 km² outcrop of Pembroke Granulite. The identification of multiple episodes within such a small, representative outcrop of magmatic arc lower crust strongly suggests that this melt migration mechanism may be more common in the lower crust than previously recognised. In general, recognition of porous melt flow in the lower crust is likely hampered by a combination of lack of exposure, overprinting during exhumation, and a lack of microstructural and geochemical tools to aid identification. This thesis characterises key microstructures indicative of the former presence of melt and igneous-like signatures within new, hydrated assemblages, which are proposed as tools for recognising rocks formed by melt–rock interaction during porous melt flow.

ACKNOWLEDGEMENTS

Sometimes someone else says it better than you can:

> *My favourite line from 'Lord of the Rings' comes when Frodo has all but given up his quest, and Samwise says to him, "Come Mr. Frodo ... I can't carry it for you, but I can carry you."*
>
> *Writing is a lonely quest at times. You lose the path. You take the mountain pass only to realize you've made a mistake and must double back through a more treacherous route. Often there's no wizard to guide you. No signposts except those you conjure. Everything is up to you, and that can be daunting, at least to me. But though my friends and family may not be able to guide the story, they carry me with their love and friendship, and I'm lucky for it.*
>
> *Pierce Brown, in 'Golden Son'*

AUTHOR'S DECLARATION OF ORIGINALITY

I, Catherine A. Stuart, declare that the material presented in this thesis is my own original research except where otherwise acknowledged, and that no part of this thesis has been submitted for a higher degree to any other university or institution.

24/07/2018

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CHAPTER ONE

INTRODUCTION

Melt migration is a fundamental process driving differentiation of the Earth's crust, forming its compositionally layered structure. Geochemical signatures in erupted arc lavas and exposed mid- to upper-crustal rocks indicate they were sourced from the mantle or lower crust, requiring significant migration of melt through the lower crust (Bourdon et al., 2002, Cashman et al., 2017, Davidson et al., 2007, Keay et al., 1997, Rapp et al., 2003). Melt–rock interaction during melt migration can impart a chemical signature on both the melt and the surrounding rock as a function of melt distribution, composition, temperature and pressure. The presence of melt is also known to significantly reduce the strength of a rock (Holyoke & Tullis, 2006, van der Molen & Paterson, 1979), localising strain in melt-present areas. Therefore, a thorough understanding of melt migration is vital when considering the chemical and rheological evolution of the continental crust over time, and yet, details of movement of melt in the deep crust remain obscure.

Melt ascent through the crust is driven by gradients in fluid pressure caused by differential stress, and buoyancy forces due density contrasts between the melt and the rock. The type of ascent mechanism is partly dependent whether the rock matrix deforms in a brittle or ductile regime. In the crust, the most commonly recognised mechanism of melt migration over large (m-km) scales is dyking (Brown, 1994, Petford, 1996, Weinberg, 1996). Dykes can be categorised as brittle-elastic (Pollard and Segall, 1987) or ductile (Weinberg and Regenauer-Lieb, 2010), depending on the temperature (Gandhi and Ashby, 1979). Brittle-elastic dykes form when buoyancy of an accumulation of melt overcomes the tensile strength of the surrounding rock, creating an open fracture which the melt can flux through (Sleep, 1988). Ductile dykes form under shear conditions through rock creep and growth of voids to form an interconnected, open channel (Weinberg and Regenauer-Lieb, 2010). Dykes are easily recognised in outcrop due to partial preservation of the migrating melt within the former fracture. However, there are an insufficient quantity of recognised dykes to accommodate the calculated volumes of melt fluxing through the lower crust to higher crustal levels (Rudnick, 1995). Therefore, some alternate melt migration mechanism must exist to facilitate mass melt ascent through the crust.

Melt ascent through mantle rocks in the ductile regime occurs via porous flow, where melt migrates through an interconnected network of melt-filled grain boundaries and triple junctions. In conditions of low differential stress, the melt-filled network is dispersed evenly throughout a rock, and buoyancy of the melt drives it upwards towards higher crustal levels (Jackson & Cheadle, 1998, Jackson et al., 2003, Jackson et al., 2005). In conditions of high differential stress, migration through the melt-filled network is localised within high-strain zones, or shear zones (Hall & Parmentier, 2000, Rosenberg & Handy, 2000, Rosenberg & Riller, 2000, Stevenson, 1989). Deformation drives melt migration along the principle finite elongation direction (Brown

& Solar, 1998), which may be oblique within the crust. Disequilibrium between the melt and the rock may drive a melt–rock interaction simultaneous with migration, which may act to increase porosity if some of the solid minerals are unstable in the presence of the melt (e.g. Aharonov et al. (1995), Chadam et al. (1991), Daines and Kohlstedt (1994)). The dispersal of melt into grain-scale structures during migration, combined with the variable effects of deformation and melt–rock interaction within an open system, can produce nuanced and complex microstructures and mineral compositions, making it difficult to identify rocks fluxed by porous melt flow, especially in circumstances where little to no melt crystallises in the melt pathway.

Porous melt flow is recognised in the crust as the process by which in situ partial melts segregate from melting sites to form larger accumulations, occurring on a scale of several centimetres (Brown, 1994, Brown et al., 1995, Sawyer, 2001, Vanderhaeghe, 2001, Vanderhaeghe, 2009). A range of numerical studies show that the process may be viable at larger scales within the crust (Fountain et al., 1989, Jackson et al., 2003, Jackson et al., 2005, Solano et al., 2012). Despite this, examples of porous melt flow at large spatial scales have been limited (Hasalová et al., 2008a, Hasalová et al., 2008b, Hasalová et al., 2008c), and its potential as a significant melt migration mechanism in the crust remains unknown.

AIMS:
The aims of this thesis are:

1. Identify areas in an exposure of the lower crust (Pembroke Granulite) that have been fluxed by porous melt flow, and characterise examples of porous melt flow during both low and high differential stress;

2. Assess the effect of porous melt flow on the chemical and rheological evolution of the lower crust; and

3. Develop a set of chemical and microstructural tools for the identification of porous melt flow in crustal rocks.

THESIS STRUCTURE:
This thesis comprises seven chapters: this introductory chapter (Chapter 1), five related studies, and a concluding chapter (Chapter 7). Chapters are arranged in chronological order following the metamorphic history of the study site, the Pembroke Granulite, Fiordland, New Zealand. The Pembroke Granulite records four distinct styles of porous melt flow within the roots of a Cordilleran arc system. Chapter 2 describes an example of porous melt flow that was diffuse throughout the entire Pembroke Granulite. Detailed trace element maps are used to reveal the grain boundary pathways of melt migration at the thin section-scale, and a model for porous melt flow in the lower crust is proposed. Chapter 3 characterises a second example of porous melt flow that is focused in

metre-scale channels. The chapter details thorough recrystallisation and hydration in the host rock leading to in situ partial melting. Chapter 4 characterises microstructures indicative of the former presence of melt along grain boundaries within metre-scale shear zones that were also fluxed by porous melt flow. Chapter 5 details the field and microstructural relationships of a fourth example of porous melt flow, which involved significant melt-rock reaction and metasomatism during melt flow forming channels of hornblendite. Chapter 6 examines mineral and whole rock chemistry of all four examples of porous melt flow detailed in the previous four papers, characterises the products of melt-rock reaction and provides a set of chemical tools for identifying former melt flux. The concluding chapter summarises findings from each preceding chapter and puts them into the context of the thesis aims, melt migration mechanisms and their effects in the lower crust.

PUBLISHED PARTS:

Chapter 2, Mass transfer in the lower crust: Evidence for incipient melt assisted flow along grain boundaries in the deep arc granulites of Fiordland, New Zealand, was published in Geochemistry, Geophysics, Geosystems 17, 3733–3753 in September 2016, and was co-authored by Sandra Piazolo and Nathan Daczko.

Chapter 3, Local partial melting of the lower crust triggered by hydration through melt-rock interaction: an example from Fiordland, New Zealand, was published in the Journal of Metamorphic Geology 35, 213–230 in February 2017, and was co-authored by Nathan Daczko and Sandra Piazolo.

Chapter 4, The recognition of former melt flux through high-strain zones, was submitted to the Journal of Metamorphic Geology in May 2017 and accepted in April 2018. Co-authors are Sandra Piazolo and Nathan Daczko.

Chapter 5, Hornblendite delineates zones of mass transfer through the lower crust, was published in Scientific Reports 6, 31369 in September 2016. Chapter 5 was written by Nathan Daczko and Sandra Piazolo, with co-authors Uvana Meek, Catherine Stuart (thesis author), and Victoria Elliott.

Chapter 6, Chemical signatures of melt–rock interaction in the root of a magmatic arc, was resubmitted to the Journal of Petrology in January 2018, and was accepted for publication in March 2018. Co-authors are Uvana Meek, Nathan Daczko, Sandra Piazolo, and Jin-Xiang Huang.

Chapters are formatted according to manuscript preparation requirements as set forward by journals, resulting in slight style changes between chapters. Each chapter includes an introduction tailored to the specific material presented, which includes a degree of similar background information as a matter of necessity. The adaptation of these manuscripts into thesis chapters results in unavoidable repetition of background material.

AUTHOR CONTRIBUTION:

The direction for each of the manuscripts was determined by the candidate in discussion with Sandra Piazolo (SP) and Nathan Daczko (ND). Initial directions were developed further by the candidate, SP, and ND during discussions of results and preparation of the manuscripts. Field work, data acquisition, analysis, interpretation, and manuscript preparation were undertaken by the candidate under supervision and reviews of SP and ND, unless explicitly stated otherwise below.

Certain parts of this thesis were developed in conjunction with or with contributions by other authors. The manuscripts, except for Chapter 5, were written by the candidate with reviews by SP, ND, other co-authors, reviewers and journal editors. The candidate was involved in idea development and preparation of Chapter 5, which was written by ND and SP, and 10% of this paper can be credited towards this thesis. Field work and sampling was conducted with assistance from SP, ND, Geoffrey Clarke, Liene Spruzeniece, and Robyn Gardner. Samples used in Chapters 2, 4, and 6 with numbers starting with 12 were collected by SP, ND, and James Smith in 2012. Samples used in Chapters 5 and 6 with numbers starting with 15 were collected by SP, ND, Uvana Meek (UM), and Victoria Elliott in 2015, and UM acquired chemical data for these samples used in Chapter 6. David Paterson and Daryl Howard provided technical assistance with Synchrotron trace element mapping used in Chapters 2 and 6. Jin-Xiang Huang provided microprobe data for samples of Style 3 melt flux used in Chapter 6.

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CHAPTER TWO

MASS TRANSFER IN THE LOWER CRUST: EVIDENCE FOR INCIPIENT MELT ASSISTED FLOW ALONG GRAIN BOUNDARIES IN THE DEEP ARC GRANULITES OF FIORDLAND, NEW ZEALAND

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Pages 9-29 of this thesis have been removed as they contain published material. Please refer to the following citation for details of the article contained in these pages.

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CHAPTER THREE

LOCAL PARTIAL MELTING OF THE LOWER CRUST TRIGGERED BY HYDRATION THROUGH MELT–ROCK INTERACTION: AN EXAMPLE FROM FIORDLAND, NEW ZEALAND

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Supplementary data provided in Appendix A.

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CHAPTER FOUR

THE RECOGNITION OF FORMER MELT FLUX THROUGH HIGH-STRAIN ZONES

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CHAPTER FIVE

HORNBLENDITE DELINEATES ZONES OF MASS TRANSFER THROUGH THE LOWER CRUST

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SCIENTIFIC REP⚙RTS

OPEN

Hornblendite delineates zones of mass transfer through the lower crust

Nathan R. Daczko, Sandra Piazolo, Uvana Meek, Catherine A. Stuart & Victoria Elliott

Geochemical signatures throughout the layered Earth require significant mass transfer through the lower crust, yet geological pathways are under-recognized. Elongate bodies of basic to ultrabasic rocks are ubiquitous in exposures of the lower crust. Ultrabasic hornblendite bodies hosted within granulite facies gabbroic gneiss of the Pembroke Valley, Fiordland, New Zealand, are typical occurrences usually reported as igneous cumulate hornblendite. Their igneous features contrast with the metamorphic character of their host gabbroic gneiss. Both rock types have a common parent; field relationships are consistent with modification of host gabbroic gneiss into hornblendite. This precludes any interpretation involving cumulate processes in forming the hornblendite; these bodies are imposter cumulates. Instead, replacement of the host gabbroic gneiss formed hornblendite as a result of channeled high melt flux through the lower crust. High melt/rock ratios and disequilibrium between the migrating magma (granodiorite) and its host gabbroic gneiss induced dissolution (grain-scale magmatic assimilation) of gneiss and crystallization of mainly hornblende from the migrating magma. The extent of this reaction-replacement mechanism indicates that such hornblendite bodies delineate significant melt conduits. Accordingly, many of the ubiquitous basic to ultrabasic elongate bodies of the lower crust likely map the 'missing' mass transfer zones.

Earth has a heterogeneous, layered crust that overlies a relatively homogeneous mantle. Geochemical signatures in middle to upper crustal rocks suggest that they are sourced from melting of lower crustal and mantle environments[1–3]. This requires mass transfer through the lower crust. Though some geological pathways of magma migration are recognized as dykes[4] and shear zones[5], dykes are relatively rare and shear zones documented to be associated with mass transfer are insufficient to facilitate the volume required for crustal differentiation throughout Earth's history[6]. Therefore, there must exist structures that are yet to be recognized as zones of substantial mass transfer. Elongate bodies of basic to ultrabasic rocks are ubiquitous in exposures of the lower crust. Hornblendite bodies of the Pembroke Valley, New Zealand, contain igneous features that contrast with the metamorphic character of their host gneiss. The field relationships are inconsistent with a cumulate origin for the hornblendite. In contrast, a model is presented in which melt flux and extreme melt-rock interaction results in modification of the host gneiss into hornblendite. We define our use of (i) 'hydrous silicate melt', hereafter referred to as melt, as a silicate magma with a H_2O content at or below water saturation for given P-T-X conditions; (ii) 'dissolution' as grain-scale magmatic assimilation, analogous to assimilation of a xenolith in a magma chamber and distinct to *in situ* partial melting; and (iii) 'flux' as the passage of melt through the rock, distinct to 'influx' which implies injection and stagnation of melt.

Results

Granulite facies two-pyroxene-hornblende gabbroic gneiss (pale rock, Fig. 1a), with ubiquitous garnet granulite reaction zones (Fig. 1b), is the main rock type exposed[7–9]. The gneissosity is defined by elongate clusters of pyroxene and hornblende within a plagioclase matrix. All minerals display evidence of dynamic recrystallisation including undulose extinction, presence of subgrains and a bimodal grain size distribution. Reaction zones are directly associated with felsic dykes which cut the gabbroic gneiss forming a distinct rectilinear grid pattern (Fig. 1b). In reaction zones, garnet grains partially to completely pseudomorph the gneissosity (Fig. 2a)[7,8]. This grid pattern of garnet granulite reaction zones provides unique markers. Reaction zones may be traced from the

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Figure 1. Relationships between the hornblendite and its host gneiss. (a) 30–40 m wide hornblendite body (dark rock outlined by dashed lines). Locations of detailed photographs in (**b–e**) shown by small squares. (**b**) Host gneiss with rectilinear grid pattern of garnet granulite reaction zones. Location of photomicrograph in 2a shown. (**c**) Sharp contact (dashed line) between hornblendite and a transition zone characterized by garnet surrounded by thin leucosome (yellow arrows) and garnet trains surrounded by plagioclase (red arrow) or hornblende (white arrow). (**d**) Grid pattern of garnetite stringers in hornblendite body. Location of photomicrograph in 2c shown. (**e**) Pegmatitic coarse euhedral garnet (yellow arrows), plagioclase (red arrows) and hornblende (white arrows) within hornblendite. Note finer-grained garnetite stringer (left to right, center) and clinozoisite-rich hornblendite matrix to coarser-grained pegmatitic minerals.

Figure 2. Petrographic relationships within the hornblendite and its host gneiss. (a) Two-pyroxene-hornblende gneiss (right) and garnet granulite reaction zone (left). (**b**) Hornblendite (right) and garnetite stringer (left). (**c**) Clinozoisite-rich hornblendite (right) and garnetite stringer (left). Note shape preferred orientation of elongate clinozoisite and hornblende grains. (**d–f**) Back-scattered electron images of low dihedral angles, films along grain boundaries and small pockets representing the crystallization of former melt, along with well-developed crystal faces at unlike mineral boundaries (e.g. plagioclase-hornblende boundaries in upper left of **f**). Mineral labels are plagioclase (p, yellow arrows), hornblende (h, white arrows), biotite (b) and garnet (g).

gabbroic gneiss (Fig. 1b) across a narrow (2–7 m wide) transition zone (Fig. 1c) into 30–40 m wide bodies of hornblendite (Fig. 1c,d) that are hosted by the gabbroic gneiss (Fig. 1a). The garnet granulite reaction zones change along strike into garnet trains variably surrounded by plagioclase (red arrow, Fig. 1c) or hornblende (white arrow, Fig. 1c) and are continuous with garnetite stringers (<5 cm wide) in the hornblendite (Fig. 1c,d).

Hornblendite bodies have highly irregular boundaries (dark rock, Fig. 1a), and may contain patches rich in clinozoisite (Fig. 1c,d) and/or large euhedral garnet (<10 cm across). Within the hornblendite, stringers of garnetite occur in a grid pattern (Fig. 1d) closely resembling the pattern made by garnet granulite reaction zones in the gabbroic gneiss. Garnetite stringers are locally folded and/or dismembered. Metre-scale areas of pegmatitic plagioclase-hornblende-garnet occur within the hornblendite with euhedral mineral grain sizes up to 10 cm (Fig. 1e).

The hornblendite (grains <5 mm; Fig. 2b) may contain up to 20 vol.% prismatic clinozoisite (<5 mm long; Fig. 2c). Both minerals exhibit unimodal grain size (Fig. 2b,c) and clinozoisite grains contain inclusions of hornblende. The unit contains minor interstitial plagioclase (~1 vol.%) with some dihedral angles <10° (Fig. 2d). Rare fine-grained biotite, hornblende, garnet and rutile occur in small plagioclase-rich domains (Fig. 2e). Grains in the hornblendite lack evidence of internal crystal plastic deformation, but may show a shape preferred orientation (Fig. 2c). Garnetite stringers in the hornblendite comprise >95 vol.% garnet (Fig. 2b,c,f). Within and directly adjacent to the garnetite stringers, minor interstitial plagioclase and hornblende may have dihedral angles <10° (Fig. 2f).

The narrow transition zone between the host gabbroic gneiss and hornblendite bodies is characterised by large garnet grains (<10 cm across) surrounded by thin plagioclase rims, i.e. leucosome consistent with limited *in situ* partial melting of the host gneiss (<0.5 cm across; yellow arrows, Fig. 1c). Across the transition zone, the gneissic foliation and garnet granulite reaction zones progressively change orientation to become subparallel to the boundary of the hornblendite bodies (Fig. 1c).

The continuity and progressive modification of the garnet granulite reaction zones in the host gabbroic gneiss, to garnetite stringers in the hornblendite, link the two contrasting rock types. In the following, the igneous character of the hornblendite bodies is contrasted with the metamorphic character of the host gabbroic gneiss.

Discussion

The igneous nature of the hornblendite unit is supported by the following features: (i) high mode of one or two minerals (hornblende ± clinozoisite or garnet) with unimodal grain size distribution and interlocking euhedral grain shapes; (ii) interstitial minor phases (plagioclase) with low dihedral angles, representing pseudomorphs of former melt[10,11]; (iii) presence of domains exhibiting a shape preferred orientation of hornblende and clinozoisite grains while lacking microstructures typical of crystal plastic deformation; (iv) presence of small pockets rich in plagioclase and biotite, of approximate granodioritic composition[12]; and (v) minor pegmatitic domains with very coarse, randomly oriented, interlocking euhedral grains. These characteristics are not only typical for an igneous ultrabasic rock but are also consistent with a cumulate origin. In contrast, the gabbroic gneiss that hosts the hornblendite (Fig. 1a) has tectono-metamorphic features such as a gneissic foliation, evidence of crystal plastic deformation at the grain scale, and well-studied metamorphic reaction textures[8,13–15].

The presence of a body with typical igneous character within a high-grade metamorphic gneiss, without a structural break, requires that the former is younger than its metamorphic host. The classic interpretation here would involve intrusion of the hornblendite into the metamorphic gneiss, for example as a dyke. However, this is inconsistent with the highly irregular boundaries of the hornblendite, and the mineral assemblage would require an unusual ultrabasic composition of the intruding body. Importantly, the physical continuity and progressive modification of metamorphic microstructures and assemblage of the garnet granulite reaction zones into the igneous microstructures and assemblage of the garnetite stringers precludes any interpretation involving dyke-like intrusion of the hornblendite bodies. Consequently, this focuses attention on the processes that can explain these intriguing relationships.

A viable option to explain both the field and petrographic relationships involves the modification (reaction replacement) of the host gabbroic gneiss to form hornblendite as a consequence of channeled high melt flux through the lower crust. In this case, the continuity of the pre-existing garnet granulite reaction zones and their modified counterparts (i.e. garnetite stringers) is explainable by extensive melt-rock interaction due to flux of an externally-derived hydrous silicate melt that is in disequilibrium with the gneiss it migrates through. Consequently, the hornblendite bodies represent "imposter cumulates" that delineate channels of mass transfer.

A model is proposed, in which the gabbroic gneiss and garnet granulite reaction zones in the host rock are progressively replaced during melt-rock interaction by hornblendite (±clinozoisite) and garnetite, respectively. The interaction involves (i) flux of an externally-derived hydrous silicate melt, (ii) dissolution (grain-scale magmatic assimilation) of host gneiss plagioclase and pyroxene, and (iii) crystallization of hornblende (±clinozoisite) and garnet from the migrating magma during channelized melt flow (Fig. 3). Two main stages in the development of hornblendite bodies can be distinguished, encompassing (i) melt flux of an externally-derived hydrous silicate melt in a high-strain zone, causing chemical and mineral assemblage modification of the host rock (metasomatism) due to extensive melt-rock interaction, and (ii) armored channelized melt flux with little further interaction (Fig. 3). The partial to complete reaction-replacement of host gneiss plagioclase and pyroxene in the first stage closely resembles the production of hornblendite from clinopyroxenite cumulate rocks documented in other arc settings[16], where clinopyroxene-melt reaction produces hornblende as later melts are inferred to have ascended through the cumulate pile. A similar dissolution mechanism is proposed here, whereby hydrous silicate melts capable of precipitating hornblende (±clinozoisite) and garnet are fluxed through 30–40 m wide zones of lower crust (Fig. 3, stage 1). A reactive infiltration instability process is invoked, where one or more phases (plagioclase and pyroxene in this case) dissolve to enhance porosity and permeability, which enhances flow of the externally-derived hydrous silicate melt, and focuses porous flow within the channel[17–19].

Chapter Five

(a) Stage 1: metasomatic flow
[grain-scale magmatic assimilation & hornblende crystallization]

(b) Stage 2: armored flow
[minimal melt-rock interaction]

gabbroic gneiss

flux of externally-derived melt

partial reaction to hornblendite

continued melt flux

hornblendite

Figure 3. Schematic diagram showing the two stages involved in the production of hornblendite as the result of channeled, externally-derived melt flux through the lower crust. (**a**) Stage 1: gabbroic gneiss (white) with grid pattern of garnet granulite reaction zones is progressively modified by melt-rock reactions to become successively depleted in plagioclase and pyroxene through dissolution (grain-scale magmatic assimilation) and enriched in hornblende and clinozoisite by crystallization (light grey, **a**) to become hornblendite (dark grey, **b**). (**b**) Stage 2: mass transfer within channelized melt flux zone delineated by hornblendite; the zone is armored from chemical interaction with the host rock during continued melt flux.

The localized strain observed within and at the margins of the hornblendite bodies suggest porous melt flow was facilitated and/or enhanced by localized deformation[20–23] which also increases the porosity and permeability of the melt flux zone. As the high melt flux event progresses, the minerals within the host rock that are in disequilibrium with the melt are completely dissolved via grain-scale magmatic assimilation. The crystallization of new phases (mainly hornblende) from the migrating melt locally produces an unreactive conduit. As a result, the channel becomes chemically armored and a large volume of melt can be transported through the channel without any further physical or chemical fingerprint (Fig. 3, Stage 2). Similar chemically isolated or armored conduits, where little to no reaction occurs between the migrating magma and surrounding rock, have been identified in a less hydrous and more mafic system in the mantle[17–19,24]. For this scenario, migration processes are well documented in experiments[25,26] and numerical models[27–29]. As our system wanes and the conduit cools, final crystallization produces minerals with small dihedral angles (Fig. 2d,f) and pockets of melt crystallize to form fine-grained biotite, hornblende, garnet and rutile in small plagioclase-rich domains (Fig. 2e), similar to the 'nanogranite' inclusions of Cesare *et al.*[30]. The mineral assemblage and modes in these domains are consistent with the fluxing melt being of intermediate (granodiorite) composition. In the final stages, pegmatitic garnet, plagioclase and hornblende crystallize (Fig. 1e).

Experimental research[31] shows that hornblende, clinozoisite, biotite, plagioclase and granodioritic magma are stable between T = ~675–720 °C and 8–11 wt.% H_2O at 8 kbar. These conditions correspond to temperature estimates of metamorphism in high-P shear zones in the valley[14], suggesting the lower crust was at appropriate P-T conditions for a migrating granodioritic melt to dissolve plagioclase and pyroxene of the host rock via grain-scale magmatic assimilation and crystallize the observed mineral assemblage of the hornblendite bodies. The migration of intermediate composition magma through the lower crust of a magmatic arc is likely to be common.

Our model indicates the protolith to an ultrabasic rock, ubiquitous in the lower crust, does not necessarily have to form by cumulate processes or intrusion of unusually basic to ultrabasic magmas. These rocks may in fact be the geological expression of localized channels of melt flux in the lower crust. While initially reactive, these channels soon armor melt migration from chemical modification during global redistribution of matter through the crust and are likely to be important for transport of metals to sites of economic concentration.

The conclusion that an ultrabasic body can form by flux of an externally-derived melt and melt-rock interaction, rather than cumulate processes, invites a reevaluation of the significance of basic to ultrabasic bodies in exposures of lower crust, emphasizes their importance in delineating zones of mass transfer, and therefore may help resolve the cryptic pathways of melt migration at depth.

Methods
Petrographic analysis of polished thin sections used a petrographic microscope in combination with the Virtual Petrographic Microscope[32] and ImageJ v1.48a, along with back-scatter electron (BSE) imaging performed on a Carl Zeiss IVO scanning electron microscope (SEM; high vacuum, 30 kV accelerating voltage; Geochemical Analysis Unit, Macquarie University).

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Author Contributions

N.R.D. and S.P. initiated this project, lead the field work and interpretation of field relationships, and wrote the majority of the paper on the basis of Masters and PhD research currently underway by U.M., C.A.S. and V.E. The three research student co-authors assisted in field work, interpretation and rewriting of the manuscript. All authors reviewed and approved this paper.

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CHAPTER SIX

CHEMICAL SIGNATURES OF MELT–ROCK INTERACTION IN THE ROOT OF A MAGMATIC ARC

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Supplementary data provided in Electronic
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CHAPTER SEVEN

SUMMARY AND CONCLUSIONS

In this thesis, porous melt flow in the lower crust is investigated to address the paucity of observed melt migration pathways in the lower crust, and to provide a set of microstructural and compositional tools to allow further identification of rocks fluxed by porous melt flow.

Achievement of thesis aims:

1) Identify areas in the lower crust that have been fluxed by porous melt flow, and characterise examples of both intertectonic and deformation-assisted porous melt flow

Due to limited identification of porous melt flow in the crust, this thesis takes a ground-up approach that focuses primarily on identifying and characterising examples of melt flux from natural samples. Four distinct examples of porous melt flow are identified within the Pembroke Granulite, including two apparently intertectonic melt flux events and two melt flux events through shear zones. Each example of porous melt flow is characterised from outcrop- to grain-scale, focusing on mineralogy, microstructures, mineral compositions and whole rock compositions resulting from melt–rock interaction. Chapters 2 to 5 characterise field relationships, assemblage changes, and microstructures indicative of melt–rock interaction.

In the Pembroke Granulite, melt–rock reaction during porous melt flow results in hydration of the host rock, observed at an outcrop scale as a darker coloured rock with increasing modes of amphibole in the assemblage. The spatial distribution of hydrated rocks in outcrop depends on the stress field at the time of melt flux – under deviatoric stress conditions and while the rock is deforming during melt flux, hydration is focused in high strain zones or shear zones (Chapters 4 and 5), whereas under isotropic stress conditions, the intertectonic examples of melt flux are diffuse over a wider area (Chapters 2 and 3).

At a thin section scale, melt–rock interaction during porous melt flow is characterised by: i) increased modes of amphibole, observed forming replacement microstructures around pyroxene grains (see Chapters 2 and 3); ii) microstructures indicative of the former presence of melt (pseudomorphs of former melt, including: small dihedral angles; grain boundary films; felsic dykelets; multiphase aggregates at triple junctions; pseudomorphing of phyllosilicates by plagioclase; and three mineral assemblages of K-feldspar, quartz, and plagioclase), observed in rocks that do not necessarily have outcrop features indicating the former presence of melt (see Chapters 2–5); and iii) replacement of the pre-existing, coarse-grained, deformed assemblage with an undeformed, hydrated assemblage (see Chapters 2–4, observed even in examples of porous melt flow during deformation (see Chapter 4). The assemblage and microstructure formed by melt–rock interaction is not unusual for lower crustal rocks, and so identification of melt–rock interaction in

this study is only possible because a progression of rocks is preserved in outcrop from those not fluxed by melt to rocks pervasively fluxed and reacted with the melt.

Chapter 6 explores the factors controlling major and rare earth element compositions of minerals forming via melt–rock reaction during porous melt flow. Despite significant recrystallisation during open system melt–rock reaction, whole rock compositional changes during melt–rock reaction are subtle and masked by natural variations in the protolith. The exception to this is presented in Chapter 5, where significant melt–rock reaction altered the whole rock composition to form hornblendite. Minerals formed by melt–rock reaction have relatively homogeneous major element compositions at an outcrop scale. The degree of homogeneity in major element compositions is interpreted to be dependent on the time-integrated melt flux, where rocks fluxed by large volumes of melt have increasingly homogeneous mineral major element compositions. Rare earth element patterns show more heterogeneity and complexity, interpreted to be a factor of distribution and composition of the fluxing melt. In diffuse examples of porous melt flow, mineral rare earth element patterns are homogeneous, recording the flux of one distinct melt composition. In contrast, examples of porous melt flow through shear zones form less homogeneous mineral rare earth element patterns, recording the flux of several melts of varying composition distributed within discrete bands during deformation.

2) Assess the effect of porous melt flux on the chemical and rheological evolution of the lower crust
Movement of melt represents a transfer of heat, mass, and volatiles from depth towards the Earth's surface. As melt migrates to higher crustal levels, evolving P–T conditions may result in the melt being out of equilibrium with its host, driving a melt–rock reaction. Distribution of melt along a pervasive grain boundary network facilitates equilibration of the fluxing melt with the solid host, which has the potential to involve significant chemical exchange and metasomatism of both the melt and host rock.

Chapter 6 explores changing whole rock compositions resulting from melt–rock reaction during porous melt flow in the Pembroke Granulite. Three out of four examples of melt flux form rocks consistent with nearly isochemical melt–rock reaction, aside from the addition of volatiles. The addition of volatiles lowers the solidus and can trigger in situ melting, as seen in Chapter 3, driving migmatisation of the crust. The fourth example of melt flux forming hornblendite involved significant metasomatism, as detailed in Chapters 5 and 6. The formation of hornblendite by melt–rock reaction and the ubiquity of the presence of hornblendite in lower crustal exposures invites further investigation into the role of melt–rock interaction in the generation of a heterogeneous and banded lower crust.

As melt–rock reaction has the capacity to change the composition of the rock experiencing melt flux, so too does it have the capacity to change the composition of the fluxing melt. Although the melt that fluxed through the Pembroke Granulite is not preserved, and the open-system nature of melt flux makes it impossible to constrain the melt composition, pervasive melt–rock

interaction during melt flux is proposed as a mechanism to alter melt composition during migration (Chapter 2). Chemical signatures in mid- to upper-crustal rocks and erupted lavas are commonly used to infer evolving assemblages at depth. These inferences are based on assumptions of cryptic fractionation in "mush" zones, requiring extremely high temperatures and local accumulations of melt. In contrast, porous melt flow may generate the same geochemical signatures without requiring the presence of magma chambers and/or a crystal mush.

In the Pembroke Granulite, the spatial and temporal distribution of melt is found to be intimately related to deformation and strain localisation. Melt flux described in Chapter 3 is focused into 10–20 m wide channels forming domains of migmatite. Small high-strain zones formed in D_3 and described in Chapter 4 are spatially associated with migmatites, nucleating within or at the boundary of the melt-rich channels. Stress was dissipated by partitioning of deformation into the fluxing melt, and deformation ceased once the rock crossed the solidus and melt crystallised. As a result, the solid components of the rock experienced little to no deformation and a corresponding paucity of deformation microstructures is observed, even in domains of the highest strain where up to 60% horizontal shortening has been identified. Melt flux by porous melt flow through the lower crust may therefore play an important role in strain localisation and rheological evolution of the continental crust.

3) Develop a set of chemical and microstructural tools for the identification of porous melt flow in crustal rocks

Due to the inherent complexity of crustal rocks and the wide variety of melt compositions present within the lower crust, the style of melt–rock reaction is expected to differ widely and rocks fluxed by porous melt flow may be overlooked. The third aim of this thesis was to provide a set of microstructural and chemical tools that may be applied in other exposures of the lower crust to aid identification of former porous melt flow.

Chapters 2 to 5 take great care to detail specific microstructures that indicate melt was present within the studied samples. Microstructural evidence for melt–rock reaction during porous melt flow takes the form of: i) asymmetric development of undeformed reaction microstructures (Chapter 2); ii) the presence of an undeformed, equilibrated microstructure in a deformed rock (Chapters 2, 3, 4, 5); and iii) microstructures indicative of the former presence of melt, particularly those pseudomorphing melt distributed along grain boundaries and at triple point junctions (Chapters 2, 3, 4, 5).

Chapter 6 characterises the geochemical signatures recorded in rocks fluxed by porous melt flow. Common to all observed examples of porous melt flow is a new mineral assemblage and broadly homogeneous mineral compositions at an outcrop scale. The degree of homogeneity is related to the time-integrated volume of melt flux, where rocks fluxed by large volumes of melt have more homogeneous mineral compositions. Mineral major element composition is determined by P-T-X conditions, as in subsolidus metamorphic rocks. Minerals formed in the presence of the

grain boundary network of melt have igneous-like REE patterns, and the degree of homogeneity in REE patterns is related to the localisation of melt flux.

Implications for porous melt flow in the lower continental crust

This thesis identified four distinct examples of porous melt flow within a 0.15 km^2 outcrop of the Pembroke Granulite, showing that porous melt flow is a viable melt migration mechanism in the lower crust. What remains unknown is whether the number and volume of exceptionally preserved melt migration pathways in the Pembroke Granulite are representative of conditions throughout the magmatic arc lower crust. If it is a true representation of lower crustal conditions, then this work provides a solution to the apparent lack of observed melt migration pathways. Rheological consequences of widespread melt migration by porous flow would be considerable due to the dissipation of stress within the melt. Multiple episodes of porous melt flow would significantly weaken the lower crust, and over time may prove to be the most critical factor in the rheological evolution of the lower crust. The outcome of this thesis emphasises the possibility of significant melt migration by porous melt flow in the lower crust, suggesting that rocks fluxed by porous melt flow have been previously overlooked. In future, the dynamic interplay of melt–rock interaction and deformation during porous melt flow should be considered when interpreting lower crustal rocks, taking into consideration its effect in rheological models and global chemical cycles.

ADDITIONAL RESEARCH SUGGESTIONS:

The identification of rock fluxed by porous melt flow, and the microstructural and chemical tools developed in this thesis are true for examples in the Pembroke Granulite, but should be applied to other settings and tested against different rock compositions and mineral assemblages. Because this is a relatively newly discovered phenomenon in the crust, there are a multitude of possible future research directions. Suggested areas for further research include:

- Exploration for rocks fluxed by porous melt flow in other low-strain exposures of lower crustal rocks in the Fiordland arc as well as within the roots of other magmatic arcs, such as the Kohistan Arc (Pakistan), the North American Cordilleran arc (USA), and collisional orogens such as the Variscan Belt, Europe. The Kohistan Arc is of particular interest, as it is composed of similar rock types and records significant melt migration in an exposed section of the mantle-crust boundary.

- Porous melt flow is a well-known phenomenon in the mantle. Future studies should consider adapting numerical models built for porous flow in the mantle to crustal examples.

- Further research into the effect of melt–rock interaction on the fluxing melt would be invaluable when interpreting geochemical signatures in arc lavas. Does migration by porous melt flow result in a measurable effect on the composition of the fluxing melt? And is the effect systematic? This may be tested using natural samples if outcrops favourably

preserve both fluxing melt and fluxed rocks, or through experimental techniques using natural samples.

- One analytical option not explored in this text is isotopic studies. Can porous melt flow be identified using in situ and/or whole rock isotope ratios?

- Similar to the hornblendite, are there other common lower crustal rock types that may be formed by porous melt flow? Hornblendites are typically interpreted as forming by cumulate processes – how many of these can be re-interpreted to be formed by porous melt flow?

- An association with large volumes of melt and large scale shear zones has been noted in many locations, as outlined in Chapter 4. Do these shear zones show evidence for porous melt flow? Is porous melt flow a common factor in strain localisation in the high-T crust? Can the observed microstructures indicative of the former presence of melt be replicated in experimental deformation studies using natural samples?

- Grain size, mineral assemblage, and the presence of melt are all known to influence the viscosity of a rock. Melt–rock reaction in the Pembroke Granulite formed a variety of grain sizes and assemblages, and the combined effect of these on the viscosity of the lower crust has not been assessed. Further investigation into the influence of melt–rock reaction on strain localisation, especially where time-integrated melt flux is high, would provide important constraints for numerical models of deformation in the crust.

- This thesis only examines porous melt flow through the plutonic roots of a magmatic arc. Can porous melt flow also be identified within the surrounding meta-sedimentary basement rocks? What are the differences between porous melt flow through a meta-sedimentary rock compared to examples studied in this thesis? The melt–rock reaction is likely to be significantly different, since the composition of the Pembroke Granulite is itself that of an arc magma.

- What is the vertical extent of porous melt flow in the crust? Porous melt flow is commonly observed in exposures of mantle wedges; can melts flow via porous melt flow across the crust-mantle boundary and move significant distances through the lower crust? Is porous melt flow a viable melt migration mechanism only in the lower crust, or could it extend upwards into the middle crust as well? Is the vertical extent of porous melt flow expanded when deformation is driving melt flow? Crustal-scale shear zones may be important target sites for answering these questions. Experimental studies at a range of temperatures and pressures would be invaluable in answering these questions.

APPENDIX A

SUPPLEMENTARY DATA FOR CHAPTER THREE

SUPPORTING INFORMATION

Local partial melting of the lower crust triggered by hydration through melt–rock interaction: An example from Fiordland, New Zealand

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Figure S1. Harker diagrams of major element oxides and trace element ratios for the three rock types.

Figure S2. Mineral rare earth element (REE) chemistry. All measured REE patterns are plotted for minerals from both the host and GRZ in the three rock types.

Table S1. Whole rock compositions of representative samples of the three rock types. Major elements obtained by XRF analyses; trace and rare earth elements obtained by ICP-MS analyses.

Table S2. Representative electron microprobe analyses.

Figure S1. Harker diagrams of major element oxides and trace element ratios for the three rock types.

Figure S2. Mineral rare earth element (REE) chemistry. All measured REE patterns are plotted for minerals from both the host and GRZ in the three rock types.

Table S1: Whole rock compositions obtained by XRF (major elements) and solution ICP-MS (trace and rare earth elements)

Rock Type	Two-pyroxene–pargasite gneiss				Tschermakite–clinozoisite gneiss					Migmatite		
Sample name	PV1453	PV1456	PV1460	PV1461	PV1449	PV1457	PV1462	PV1463	PV1452	PV1454	PV1455	PV1459
Major elements, wt% oxide												
SiO_2	51.93	52.76	51.89	52.00	51.66	53.26	51.76	51.64	51.71	51.69	51.90	51.43
TiO_2	0.65	0.70	0.67	0.59	0.61	0.42	0.66	0.64	0.74	0.74	0.78	0.79
Al_2O_3	20.16	19.98	19.88	19.94	19.79	20.40	19.87	19.69	19.38	20.03	19.91	19.90
Fe_2O_3*	8.03	8.31	8.13	7.98	7.92	6.90	7.65	7.75	8.58	8.13	8.22	7.63
MgO	4.91	4.55	4.78	5.07	4.93	4.43	4.99	4.99	4.89	4.51	4.70	4.71
CaO	8.92	8.72	8.97	9.09	9.05	8.44	9.20	9.09	8.69	8.56	9.04	9.29
Na_2O	4.73	5.06	4.59	4.52	4.88	5.22	4.48	4.50	4.77	5.09	4.25	4.50
K_2O	0.37	0.42	0.37	0.35	0.42	0.34	0.42	0.40	0.36	0.28	0.54	0.46
P_2O_5	0.08	0.08	0.08	0.10	0.09	0.08	0.09	0.06	0.08	0.08	0.04	0.04
S	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01
LOI (loss on ignition)	0.35	0.13	0.21	0.25	1.24	0.85	1.00	1.04	0.95	0.63	1.22	0.99
Total	100.12	100.70	99.57	99.89	100.60	100.35	100.10	99.79	100.15	99.74	100.60	99.74
Trace elements, ppm												
Li	7.23		7.67		13.03		10.90			10.60		13.37
Be	0.67		0.63		0.63		0.62			0.59		0.59
Sc	22.43		22.97		22.72		21.43			22.03		25.21
Ti	4019		4110		3631		3545			4459		4834
V	217.0		242.8		180.0		162.5			250.4		265.4
Cr	28		25		27		43			23		26
Mn	973		960		953		690			1049		545
Co	51.53		56.40		67.00		40.24			47.86		46.85
Ni	25.1		20.7		25.5		22.1			18.8		19.5
Cu	29.0		41.5		21.8		76.3			10.7		43.8
Zn	67.1		65.0		66.4		59.0			60.3		72.9
Ga	20.32		20.90		19.80		17.80			19.63		23.19
Br	0.04		0.05		0.05		0.04			0.04		0.04
Rb	1.60		1.54		2.49		2.60			2.49		6.03
Sr	889.3		898.6		916.6		827.9			885.0		935.0
Y	6.23		6.23		6.47		6.21			5.61		5.81
Zr	8.7		8.3		5.3		4.1			5.8		6.9
Nb	0.42		0.42		0.45		0.53			0.54		0.52
Mo	0.15		0.18		0.22		0.30			0.18		0.20
Cs	0.129		0.095		0.140		0.134			0.582		1.025
Ba	207.0		199.7		203.4		220.1			96.3		296.7
Hf	0.29		0.27		0.22		0.21			0.25		0.28
Ta	0.411		0.762		0.533		0.398			0.533		0.584
Th	0.112		0.121		0.125		0.110			0.101		0.111
U	0.030		0.035		0.036		0.033			0.030		0.036
Ba/La	62.8		63.3		60.6		65.8			32.2		103.0
Sr/Y	142.7		144.3		141.6		133.3			157.8		160.9
Rare earth elements, ppm												
La	3.30		3.15		3.36		3.34			2.99		2.88
Ce	7.08		6.82		7.56		7.36			6.54		6.22
Pr	0.95		0.92		0.98		1.03			0.89		0.85
Nd	4.29		4.24		4.52		4.59			4.10		3.91
Sm	1.05		1.05		1.10		1.13			1.00		0.99
Eu	0.696		0.671		0.717		0.735			0.656		0.766
Gd	1.08		1.09		1.11		1.17			1.03		1.03
Tb	0.167		0.169		0.170		0.179			0.159		0.160
Dy	1.00		1.01		1.01		1.05			0.95		0.95
Ho	0.216		0.210		0.214		0.226			0.199		0.201
Er	0.615		0.600		0.610		0.624			0.564		0.563
Yb	0.593		0.555		0.594		0.600			0.531		0.511
Lu	0.094		0.088		0.090		0.093			0.082		0.077

* Total Fe as Fe^{3+}

Table S2: Representative electron microprobe analyses.

	PP gneiss					PP gneiss GRZ					TC gneiss			TC gneiss GRZ						Migmatite					Migmatite GRZ			
	Di_{1a}	En_{1a}	$PrBk_{1a}$	Pl_{1b}	Czo_{1a}	Di_{1a}	Di_{1b}	En_{1a}	Grt_{1b}	Pl_{1b}	Ts_{2a}	Pl_{2a}	Czo_{2a}	Ts_{2b}	Pl_{2b}	Czo_{2b}	Grt_{1b}	Grt_{2b} rim	Grt_{2b} core	Ts_{3a}	Pl_{3a}	Czo_{3a}	Grt_{3a} core	Grt_{3a} rim	Ts_{3b}	Pl_{3b}	Czo_{3b}	Grt_{3b}
SiO_2	51.22	50.95	39.71	56.38	37.82	52.17	53.45	51.65	37.71	59.81	41.46	61.70	37.71	41.59	61.70	37.47	36.81	37.34	37.96	40.98	61.51	38.12	38.12	38.29	41.03	62.01	37.89	37.09
TiO_2	0.24		1.72		0.03	0.20	0.35	0.04	0.03		0.29		0.05	0.49		0.05	0.04	0.03	0.06	0.59		0.08	0.14	0.00	0.60		0.09	
Al_2O_3	4.50	2.78	14.54	26.75	27.32	4.43	6.63	1.89	21.87	25.55	15.13	24.16	27.32	14.70	23.99	27.12	20.60	21.54	21.94	15.54	23.86	28.12	21.74	22.09	15.35	23.63	27.87	21.46
FeO (tot)	8.79	24.56	14.48	0.08	8.21	8.39	4.90	22.80	23.23	0.05	13.72	0.11	7.66	14.12	0.10	7.87	26.28	23.95	20.30	13.33	0.12	6.74	26.20	27.10	13.59	0.12	6.86	27.88
MnO	0.18	0.62	0.22		0.10	0.19	0.00	0.57	0.75		0.22		0.14	0.20		0.11	5.33	1.20	0.45	0.11		0.09	1.86	1.35	0.11		0.06	1.77
MgO	11.37	19.87	10.26		0.15	11.83	11.74	21.72	7.82		11.58		0.11	11.10		0.10	3.78	7.93	10.83	11.10		0.15	5.78	6.50	10.98		0.11	5.91
CaO	20.75	0.40	11.03	9.39	23.38	20.35	18.88	0.50	8.84	7.48	10.71	5.66	23.46	10.80	5.60	23.58	6.93	7.10	7.37	10.64	5.68	23.53	7.25	6.01	10.78	5.27	23.82	5.44
Na_2O	1.99		1.77	6.51	0.02	2.10	2.92	0.07	0.02	7.56	2.03	8.95		1.98	8.75				0.03	2.07	8.76	0.15	0.03		2.14	9.06	0.11	
K_2O			1.60	0.15						0.27	0.32	0.06		0.41	0.05					0.51					0.49	0.07		
Cl											0.06			0.04														
F		0.00	0.05			0.00		0.00					0.09									0.08					0.07	
P_2O_5					0.10																							
SrO					0.53																							
Total	99.04	99.18	95.38	99.26	97.66	99.66	98.87	99.24	100.27	100.72	95.52	100.64	96.54	95.43	100.19	96.30	99.77	99.09	98.94	94.87	99.93	96.91	101.12	101.34	95.07	100.16	96.77	99.55
Oxygens	6	6	23	8	25	6	6	6	12	8	23	8	25	23	8	25	12	12	12	23	8	25	12	12	23	8	25	12
Si	1.91	1.93	6.07	2.55	5.92	1.93	1.96	1.94	2.88	2.65	6.21	2.73	5.94	6.25	2.74	5.92	2.92	2.89	2.88	6.18	2.74	5.96	2.94	2.94	6.19	2.75	5.94	2.91
Ti	0.01	0.00	0.20		0.00	0.01	0.01	0.00	0.00		0.03		0.01	0.06		0.01	0.00	0.00	0.00	0.07		0.01	0.01	0.00	0.07		0.01	0.00
Al	0.20	0.12	2.62	1.43	5.04	0.19	0.29	0.08	1.97	1.34	2.67	1.26	5.07	2.61	1.25	5.05	1.93	1.97	1.96	2.76	1.25	5.18	1.98	2.00	2.73	1.24	5.15	1.99
Fe^{3+}	0.11	0.01	0.12	0.00	1.08	0.09	0.00	0.04	0.28	0.00	0.25	0.00	1.01	0.21	0.00	1.04	0.23	0.26	0.27	0.20	0.00	0.88	0.14	0.14	0.19	0.00	0.90	0.20
Fe^{2+}	0.16	0.77	1.74			0.17	0.15	0.68	1.21		1.47			1.57			1.52	1.30	1.02	1.48			1.55	1.60	1.53			1.63
Mn^{2+}	0.01	0.02	0.03		0.00	0.01	0.00	0.02	0.05		0.03		0.01	0.03		0.00	0.36	0.08	0.03	0.01		0.00	0.12	0.09	0.01		0.00	0.12
Mg	0.63	1.12	2.34		0.04	0.65	0.64	1.22	0.89		2.58		0.03	2.49		0.02	0.45	0.92	1.23	2.49		0.03	0.66	0.74	2.47		0.03	0.69
Ca	0.83	0.02	1.81	0.46	3.92	0.81	0.74	0.02	0.72	0.36	1.72	0.27	3.96	1.74	0.27	3.99	0.59	0.59	0.60	1.72	0.27	3.94	0.60	0.49	1.74	0.25	3.94	0.46
Na	0.14	0.00	0.52	0.57	0.01	0.15	0.21	0.01		0.65	0.59	0.77	0.00	0.58	0.75	0.00				0.61	0.76	0.00			0.63	0.78	0.00	
K			0.31	0.01						0.02	0.06	0.00		0.08	0.00					0.10	0.00				0.09	0.00		
P			0.02																									
F			0.00					0.00			0.00			0.00						0.00					0.00			
Cl											0.02			0.01						0.00					0.00			
Sum	4.00	4.00	15.78	5.02	16.01	4.00	4.00	4.00	8.00	5.01	15.63	5.03	16.01	15.61	5.01	16.03	8.00	8.00	8.00	15.62	5.02	16.00	8.00	8.00	15.65	5.02	16.03	8.00
Enstatite	0.36	0.58				0.38		0.62																				
Ferrosillite	0.16	0.41				0.15		0.37																				
Wollastonite	0.48	0.01				0.47		0.01																				
Jadeite							0.21																					
Aegrine							0.00																					
Quad							0.79																					
X_{An}				0.55						0.64		0.74			0.74						0.74					0.75		
X_{Ab}				0.44						0.35		0.26			0.26						0.26					0.24		
X_{Or}				0.01						0.01		0.00			0.00						0.00					0.00		
X_{Alm}									0.42								0.52	0.45	0.36				0.53	0.55				0.56
X_{Sps}									0.31								0.15	0.32	0.42				0.23	0.25				0.24
X_{Prp}									0.22								0.18	0.18	0.18				0.19	0.16				0.14
X_{Grs}									0.02								0.12	0.03	0.01				0.04	0.03				0.04

ELECTRONIC APPENDICES

SUPPLEMENTARY DATA FOR CHAPTER SIX

Chemical signatures of melt–rock interaction in the root of a magmatic arc

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Electronic Appendix A: Whole rock compositions for S_1 and melt flux styles 1 to 4.

Electronic Appendix B: Mineral major and trace element compositions for S_1 and melt flux styles 1 to 4.