Ascent of ultrahigh-pressure rocks in southeastern
Papua New Guinea, as revealed by Ti-in-quartz
thermometry and Rb-Sr dating

Megan S. Korchinski

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Frontispiece: Jumbled gneiss boulders in the Gulawata gorge, looking northwest towards the highest peak of Goodenough Island with a fisherman from Maligalima Village in the foreground. This trek was to be the most difficult of our 2010 field season, as the boulders in this river were rumored to be extremely slippery. Two weeks of clear skies made the walking easy.

Thesis abstract

Debate concerns the timing of ultra-high pressure (UHP) metamorphism and the kinematics of exhumation of the world's youngest known eclogite-facies rocks (U-Pb ages of 4 – 8 Ma) in the Woodlark Rift of southeastern Papua New Guinea. End-member kinematic models that have been proposed for the crustal exhumation of metamorphic gneiss domes that host these young eclogites include detachment-related (asymmetric) gneiss doming (metamorphic core complexes), and pure shear-dominated (symmetric or diapiric) gneiss doming. The former is predicted to exhume the deepest structural levels of the domes adjacent to a major normal fault. The latter is predicted to yield a concentric pattern of exhumation levels with the deepest rocks located near the center of the domes. As far as can be determined, there are no mappable field gradients with respect to either the high-pressure metamorphism or the later pervasive amphibolite-facies overprint in the lower crust. This apparent uniformity contributes to uncertainty regarding the distribution of vertical strain in the body, and thus to the mode of dome emplacement.

To delineate spatial differences in exhumation and cooling rates, I measured Ti content in quartz for 90 samples of quartzofeldspathic gneiss and eclogite distributed across four migmatitic gneiss domes using laser ablation inductively coupled plasma mass spectrometry. I calculated paleo-temperatures from these data using the Ti-in-quartz geothermometer (Thomas et al., 2010; Wark and Watson, 2006). The Ti concentration in quartz in these samples ranges from 10 to 20 ppm, corresponding to an apparent temperature range of 500°C to 600°C (calculated using the Wark and Watson, 2006 calibration). As the apparent temperatures do not have a clear correlation with lithology and the quartz grains exhibit amoeboid grain boundaries, I infer that the Ti content in the quartz grains is capturing information related to quartz recrystallization and grain growth during the final stages of dynamic recrystallization by high-temperature grain-boundary migration (GBM). The presence of pervasive partial melt in the rocks and of chessboard microstructures in the quartz grains implies that the rocks in the D'Entrecasteaux Islands once attained temperatures of >630°C; however the 93% of the apparent temperatures calculated here are <630°C. Based on the pervasive GBM and the Ti-in-quartz apparent temperatures, I infer that the mean Ti content in these quartz grains was chiefly dependent on the relative rates of cooling and recrystallization as the body ascended through the crust. If the recrystallization rate was less spatially variable relative to the cooling rates across the gneiss domes, more quickly exhumed rocks would retain a larger relict fraction of unrecrystallized, high-temperature quartz grains. Ti content in quartz can therefore be used to map spatial changes

in mean exhumation rate. As a rule, Ti concentrations in quartz in the D'Entrecasteaux Islands increase concentrically inward from 2.5 – 25 ppm at the dome margins to 20 – >100 ppm in the core of the domes. Based on this apparent increase in Ti content in quartz, I interpret the most rapidly cooled and exhumed rocks to occur today near the center of the gneiss domes. Thus, the Ti content in quartz data presented here indicate that the gneiss domes were emplaced in the crust by predominantly pure-shear symmetric doming.

The timing of *rock fabric* development at the (U)HP conditions and during the main amphibolite-facies retrogression at lower crustal depths in the D'Entrecasteaux Islands has not been dated. To that end, I present nine Rb-Sr internal mineral isochrons for samples of eclogite, quartzofeldspathic gneiss, and granitic rock from four gneiss domes. Rb-Sr internal mineral isochrons for two samples of eclogites from the core zone of the Mailolo gneiss dome (Fergusson Island) date the timing of the (U)HP eclogite-facies metamorphism at mantle depths to 5.7 ± 2.0 Ma and 5.6 ± 1.6 Ma (2σ), respectively. One sample preserves coesite and the other contains radial fractures around quartz inclusions in garnet, implying that coesite was once been present in this rock. From this data, I infer that the eclogites in the Mailolo dome were metamorphosed at UHP depths of >90 km at 5.6 ± 1.2 Ma (approximate 95% confidence interval for the weighted mean of the two samples). The Rb-Sr isochron ages of amphibolite-facies rock fabric development in a granodioritic orthogneiss and quartzofeldspathic gneiss from the Mailolo and Goodenough dome are 2.4 ± 1.4 Ma (2σ) and 2.38 ± 0.3 Ma (2σ) respectively. This similarity in these Rb-Sr ages implies that deformation at amphibolite-facies conditions took place nearly simultaneously in these gneiss domes. A granodiorite >40 km to the south of the Mailolo granodioritic orthogneiss yielded a Rb-Sr age of 3.90 ± 0.44 Ma. This latter age is 1.5 ± 1.1 Ma (approximate 95% confidence interval) older than the Mailolo and Goodenough samples, indicating an apparent westward younging in the age of the amphibolite-facies metamorphism in the northwestern D'Entrecasteaux Islands.

Five samples of quartzofeldspathic gneiss and quartzose rock were analyzed for pressure and temperature estimates using the garnet-plagioclase-muscovite-quartz barometer, the garnet- Al_2SiO_5 -plagioclase-quartz barometer, and the garnet-phengite exchange thermometer. These data indicate a temperature range of 640 – 720 °C and a corresponding pressure range of 10 – 17 kbar for the amphibolite-facies metamorphic overprint in the D'Entrecasteaux Islands. This pressure estimate is higher than previous estimates (7 – 11 kbar) by ~3 – 6 kbar, which implies the HP body was thicker than previously inferred when it ponded at the lower crust.

Combining these new Rb-Sr ages with U-Pb zircon ages by Gordon et al. (*in review*), I calculate a time lag of 2.2 ± 1.2 Ma (approximate 95% confidence interval) between eclogite-facies deformation in the mantle and amphibolite-facies foliation development in the lower crust for rocks in the Mailolo dome. This time lag, when combined with the amphibolite-facies pressure estimates presented here and pressure estimates consistent with the preservation of coesite in one sample, implies a minimum unroofing rate of 19 ± 11 mm yr⁻¹ (approximate 95% confidence interval) for the (U)HP body from the mantle to the lower crust. This minimum unroofing rate strongly supports previous inferences that the exhumation from the mantle to the surface of the gneiss domes in the D'Entrecasteaux Islands took place at plate tectonic rates.

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1. Introduction

The recognition of coesite-bearing rocks in eclogite-facies metamorphic terranes has been an exciting discovery in the field of continental dynamics (Chopin, 1984; Smith, 1984). Coesite-bearing rocks may have once been generated in the majority of global exhumed collisional orogen, even if they are no longer preserved or are not currently exposed at the surface (Beltrando et al., 2010; Chopin, 1984; Chopin, 2003; Ernst, 2001; Liou et al. 2004; Liou et al., 2009). The exposure of these ultrahigh-pressure (UHP) rocks at the Earth's surface implies subduction of low-density crustal material through dense mantle rocks to depths of >90 km at subduction zones (Chopin, 1984; Chopin, 2003; Lapen et al., 2003; Leech, 2001; Liou et al. 2009; Little et al., 2007; Little et al., 2011; Smith, 1984). In some cases this subduction has been followed by exhumation at plate tectonic rates (cm yr^{-1}), resulting in the rapid translation of UHP rocks into the crust or even to the Earth's surface (Baldwin et al., 2004; Baldwin et al., 2008; Glodny et al., 2005b; Parrish et al., 2006; Rubatto and Hermann, 2001). The exhumation of UHP rocks may be the result of buoyancy-driven transport of material, when buoyancy of the crustal material overrides the subduction or slab-pull forces and results in detachment of material from the subducting slab (Ernst, 2001; Hacker, 2007; Jolivet et al., 2005; Kurz, 2005). This exhumation can occur in two stages: (1) rapid and nearly isothermal decompression from the mantle to the lower crust, and (2) cooling and emplacement in the crust (Baldwin et al., 2004; Baldwin et al., 2008; Ernst, 2001; Gordon et al., *in review*). For example, the UHP slab of the Western Gneiss Region, Norway, underwent isothermal decompression as a coherent body (>20 – 30 km thick) from UHP conditions at 410 – 400 Ma to the lower crust in ~5 Ma, and was exhumed through the crust between 400 – 390 Ma (Glodny et al., 2008b; Hacker, 2007; Hacker and Gans, 2005; Terry et al., 2000; Young et al., 2007). The subduction of crustal material to depths in excess of >90 km does not fit with the conventional plate tectonic theory, which includes classic metamorphic recycling of continental crust to 30 – 40 km (Beaumont et al., 2009; Chopin, 2003; Lapen et al., 2003; Smith, 1984).

The D'Entrecasteaux Islands of southeastern Papua New Guinea (PNG) are domal culminations of quartzofeldspathic gneiss, which host the youngest known (U)HP

eclogite-facies rocks on Earth (U-Pb zircon ages of 8 – 4 Ma; Baldwin et al., 2004; Gordon et al., *in review*; Monteleone et al., 2007). Previous geochronological studies in the D'Entrecasteaux Islands have focused on dating the timing of zircon crystallization during (U)HP and amphibolite-facies metamorphism, and magmatic crystallization of zircons in granitic dikes that intrude the migmatitic gneiss domes (Baldwin and Ireland, 1995; Baldwin et al., 2004; Gordon et al., *in review*; Monteleone et al., 2007). A recent study by Zirakparvar et al. (2011) carried out Lu-Hf dating on garnets in a sample of coesite-bearing eclogite, determined an age of 7.1 ± 0.7 Ma (2σ) for the timing of garnet crystallization at UHP conditions. In addition, the timing of final cooling in the upper crust ($<400^\circ\text{C}$) has been constrained by $^{40}\text{Ar}/^{39}\text{Ar}$ techniques on white mica and biotite (3.0 – 1.4 Ma) and apatite fission track analysis (0.4 – 0.1 Ma; Baldwin et al., 1993; Fitzgerald et al., 2008). As of yet, the timing of *deformation* during the (U)HP and subsequent amphibolite-facies metamorphism has not been well constrained. In addition, the exhumation of these gneiss domes through the crust is controversial, as a lack of metamorphic isograds makes tectonic reconstruction of post-metamorphic ductile strain patterns difficult. Two possible models that have been proposed for the mode of crustal emplacement of the gneiss in the D'Entrecasteaux Islands include detachment-bounded metamorphic core complexes, and symmetrical (diapiric) gneiss domes (Davies and Warren, 1988; Hill, 1994; Hill and Baldwin, 1993; Hill et al., 1995; Little et al., 2011; Martinez et al., 2001; Webb et al., 2008).

1.1 Thesis organization and outline

This thesis contains two chapters designed and organized as self-contained papers intended for publication in a scientific journal, and as such each chapter necessarily contains repetition of some introductory material, context setting, and certain figures. Chapter 2, entitled “Evaluation of gneiss dome emplacement mechanisms in southeastern Papua New Guinea using Ti content in quartz”, examines the significance of variations of Ti content in quartz in high-grade metamorphic rock, particularly in rapidly exhuming and high-temperature bodies. I present Ti content in quartz data and Ti-in-quartz apparent temperatures for 90 samples of

quartzofeldspathic gneiss, granitic rock, and eclogites from the northwestern D'Entrecasteaux Islands. The physical processes of Ti mobility and homogenization in ductilely deforming metamorphic rock are constrained here by optical microscopy and cathodoluminescence analysis. Spatial gradients in Ti content in quartz across the gneiss domes are used as a proxy for relative cooling and exhumation rates within the dome, which refines the current understanding of kinematics of gneiss dome exhumation in the D'Entrecasteaux Islands.

Contributions to Chapter 2 include supervision, guidance, and editing of the manuscript by Timothy Little. He also offered guidance during two field seasons (2009, 2011), and provided thin-sections and hand samples for my analysis from previous field seasons in the D'Entrecasteaux Islands. Marc-Alban Millet provided technical assistance with analysis of samples on the LA-ICP-MS, and proofread Chapter 2 and the associated appendices. Euan Smith wrote a MATLAB™ script that calculated background-corrected counts per second or signal for ICP-MS analysis. He also advised on data processing and error calculations, and proofread a copy of this Chapter.

In Chapter 3, entitled “Rb-Sr dating of eclogite- and amphibolite-facies metamorphism in the D'Entrecasteaux Islands, southeastern Papua New Guinea”, I present Rb-Sr internal mineral isochrons for nine samples of mafic and quartzofeldspathic composition collected from four gneiss domes in the D'Entrecasteaux Islands. These ages are inferred to date rock fabric development during: (1) the peak eclogite-facies metamorphism, and (2) the later amphibolite-facies retrogression. Moreover, these ages constrain the duration of time between the peak UHP metamorphism in the mantle and the later retrogressive amphibolite-facies metamorphism in the lower crust, and thus the exhumation rate of the (U)HP body. I also contribute to a revision in the estimate of the age of the UHP metamorphic event from 8 – 7 Ma down to ~5 Ma (Baldwin et al., 2004; Baldwin et al., 2008; Gordon et al., *in review*; Monteleone et al., 2007; Zirakparvar et al., 2011). Pressure and temperature estimates for five samples of quartzofeldspathic gneiss and quartzose rocks retrogressed during the amphibolite-facies metamorphic event are presented here, along with an estimate of the unroofing rate for the (U)HP body from the mantle to the surface.

Contributions to Chapter 3 include scientific guidance and editing from Timothy Little. Marc-Alban Millet provided technical assistance with chemical purification of samples and analysis of sample aliquots on the multi-collector ICP-MS and ICP-MS. In addition, Marc-Alban Millet advised on data processing and interpretation of Rb-Sr ages, and proofread Section 2.4.2 (Sampling and Analytical Method for Rb-Sr dating and thermobarometry) and Appendix E (Rb-Sr dating and thermobarometry methods). Julie Vry assisted with preparation of mineral separates and electron probe microanalyzer lab work for Chapter 3, and wrote the Microsoft Excel (Microsoft, Redmond, WA, USA) spread sheets used in major element data processing.

Appendix A contains all cathodoluminescence images of quartz grains collected during this study on a compact disk. Images are organized first by rock type and then by sample number. Images are labeled according to the wavelength that was isolated during data processing: “blue” is the 415 nm wavelength inferred by Spear and Wark (2009) to be associated with the Ti concentration within quartz, “green” is the 650 nm wavelength which may be related to the oxygen vacancy in quartz, “bluegreen” is a combination of both the 450 nm and 650 nm wavelengths, and “onlySi” is a specific wavelength dispersive spectrometry map showing the location of quartz grains. Appendix B presents Ti-in-quartz analytical and statistical methods not included in Chapter 2, along with machine settings and conditions used during LA-ICP-MS analysis. Appendix C presents the MATLAB™ script written by Euan Smith and instructions for its use. Appendix D contains a complete petrologic description of each sample analyzed for Rb-Sr isotopic composition and thermobarometry in Chapter 3, along with representative major element analysis for white mica, garnet, and plagioclase. Appendix E details the analytical technique used for chemical purification of mineral separates and standards, and the machine settings and conditions used during LA-ICP-MS analysis and quantitative major element analysis on the electron probe microanalyzer.

2. Evaluation of gneiss dome emplacement mechanisms in southeastern Papua New Guinea using Ti content in quartz

2.1 Introduction

Previous petrological and geochronological work on four young metamorphic gneiss domes that host the world's youngest eclogite-facies rocks in the Woodlark Rift of southeastern Papua New Guinea (PNG; Fig. 2.1) has focused on the timing of high-pressure (HP) and the ultrahigh-pressure (UHP) metamorphism, and the pressure/temperature conditions of this crystallization (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008; Davies and Warren, 1988; Hill et al., 1992; Hill et al., 1995; Gordon et al., *in review*; Monteleone et al., 2007; Zirakparvar et al., 2011). The D'Entrecasteaux Islands do not exhibit mappable metamorphic isograds or preserved metamorphic field gradients, for example between (U)HP eclogite-facies rocks and lower grade rocks (Little et al., 2011). The homogeneity between the UHP and HP rocks within the D'Entrecasteaux Islands makes determining spatial differences in exhumation level within the gneiss domes difficult. The kinematics of the metamorphic terrane's deformation and crustal exhumation and emplacement is thus relatively uncertain; for example, it is controversial to what degree the gneiss domes are detachment-bounded metamorphic core complexes or symmetrical gneiss domes (Baldwin et al., 2004; Davies and Warren, 1988; Hill et al., 1995; Little et al., 2011; Martinez et al., 2001; Webb et al., 2008).

Application of the Ti-in-quartz geothermometer (TitaniQ) as a potential tool to constrain the deformational and temperature history of ductilely deformed metamorphic rocks is an exciting prospect, but is currently in its infancy (Grujic et al., 2011; Kohn and Northrup, 2009; Pennacchioni et al., 2010; Spear and Wark, 2009). Aspects of the TitaniQ under scrutiny include uncertainties in the Ti activity coefficient in quartz (Grujic et al., 2011). More generally, the validity of the thermodynamics on which the original calibrations were based has been questioned (Wilson et al., *in review*). Another major uncertainty related to the application of the TitaniQ to deformed metamorphic rocks is identifying which grain-scale process or

Figure 2.1 (a) Plate tectonic map of eastern Papua New Guinea. Adapted from Wallace et al. (2004), Webb et al. (2008), and Little et al. (2011): PAC, Pacific Plate; AUS, Australian Plate; WLK, Woodlark Plate; NBP; North Bismark Plate, SBP; South Bismark Plate. Direction of movement of the Pacific Plate relative to the Australian Plate shown by the bold red arrow. Pole of WLK-AUS relative rotation (with error ellipse) for the present-day (after Wallace et al., 2004). Pole of WLK-AUS relative rotation (with error ellipse) for 3.6–0.5 Ma (after Taylor et al., 1999). The small red arrows depict the current velocities of the Woodlark Plate relative to the Australian Plate (after Wallace et al., 2004). (b) Simplified tectonic map of southeastern Papua New Guinea. Background is a Digital Elevation Model from GeoMapApp (<http://www.GeoMapApp.org>). Location for figures 2.3, 2.4, and 2.13 shown in the dashed box. Location of Woodlark Rift zone after Baldwin and Ireland (1995).

processes may be responsible for Ti transport and equilibration within plastically deforming and dynamically recrystallizing grains of metamorphic quartz (Spear and Wark, 2009). For these reasons it is now timely to test the TitaniQ in sequences of metamorphic tectonites that span a wide crustal range of exposure levels and metamorphic grades (paleo-temperatures), in order to better clarify the technique's potential applicability to tectonic studies of ductilely deformed quartzose rocks. Potential problems in the application of the TitaniQ to metamorphic quartz include: incomplete Ti homogenization within quartz grains (zoning), heterogeneous Ti concentrations between quartz grains, and the possibility of post-recrystallization volume diffusion of Ti in quartz grains (Spear and Wark, 2004).

The D'Entrecasteaux Islands are domal culminations of quartzofeldspathic gneiss with minor mafic units (5 – 10% volume), the latter of which has been exposed to eclogite-facies metamorphic conditions at 8 – 4 Ma (Baldwin et al., 2004; Gordon et al., *in review*; Monteleone et al., 2007; Zirakparvar et al., 2011). Rocks that comprise the D'Entrecasteaux Islands underwent rapid (cm yr^{-1}) and nearly isothermal decompression from the mantle to the lower crust at 4 – 2 Ma, followed by extremely rapid cooling at <2 Ma (>100 $^{\circ}\text{C Ma}^{-1}$; Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008). The young, almost neotectonic, age of the exhumation in the D'Entrecasteaux Island region provides several advantages towards the study of (U)HP exhumation processes, including the active and well-constrained geodynamic context that surrounds the terrane and the lack of tectonic overprinting unrelated to the exhumation from the mantle to the surface.

This study is an attempt to map spatial differences in exhumation rates within the gneiss domes of the D'Entrecasteaux Islands. In particular, I will test which of the following end-member kinematic models is more applicable for crustal exhumation of (U)HP-bearing gneiss domes in the Woodlark Rift: a) pure-shear dominated symmetric domes, or b) detachment-style asymmetric metamorphic core complexes (Fig. 2.2; Yin, 2004). Each model predicts a unique spatial pattern of exhumation rates, and I will argue that gradients in Ti content and apparent TitaniQ deformational temperatures help to distinguish between these models. In particular, these spatial patterns may be used to better understand processes that have led to the exhumation of gneiss domes that host the world's youngest (U)HP rocks in

a) pure-shear dominated symmetric doming

b) detachment-style asymmetric metamorphic core complex development

Figure 2.2 Schematic cartoons of end-member kinematic models for crustal exhumation of gneiss domes in the D'Entrecasteaux Islands. Bold text shows predicted spatial pattern of Ti concentration. (a) Pure-shear dominated symmetric doming after Little et al. (2011). (b) Detachment-style asymmetric metamorphic core complex development after Davis et al. (1986).

southeastern PNG. In this study, I report on new data set of Ti content in quartz determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for 90 quartz-bearing samples from the D'Entrecasteaux Islands, including both quartzofeldspathic and mafic protoliths. I calculate TitaniQ apparent paleotemperatures, and address the effects of pressure, uncertainties in Ti activities, and alternate calibrations for the TitaniQ geothermometer. This paper is particularly focused on the application of Ti-in-quartz data to a body of high-grade metamorphic rocks that was rapidly exhumed into the upper crust, and continued to deform ductilely until it cooled rapidly at shallow crustal levels.

2.2 Geologic and tectonic setting

2.2.1 Regional tectonics

Eastern PNG is situated in a mosaic of microplates between the Pacific and Australian plates, which includes the Woodlark microplate (Fig. 2.1; Wallace et al., 2004). This boundary accommodates $\sim 110 \text{ mm yr}^{-1}$ of north-northwest to south-southeast horizontal motion (Wallace et al., 2004). The continental Woodlark Rift separates the Woodlark microplate to the north from the Australian plate to the south, and transitions along strike to the east into the Woodlark Basin oceanic spreading center (Fig. 2.1; Taylor et al., 1999; Wallace et al., 2004). Since $\sim 6 \text{ Ma}$, the Woodlark Basin spreading center has been actively spreading and has propagated westward through orogenic continental crust of the Papuan Orogen at a rate of $\sim 150 \text{ km Ma}^{-1}$ (Taylor et al., 1999). This orogen developed in the early to middle Eocene as the result of an arc-continent collision that emplaced the Cenozoic Papuan Ultramafic Body over Australian crustal material along the Owen Stanley fault zone (Davies and Jaques, 1984; Lus et al., 2004). The D'Entrecasteaux Islands are situated $\sim 100 \text{ km}$ to the west of the tip of the Woodlark Basin spreading center (Fig. 2.1). The shedding of metamorphic debris as conglomerate in the offshore region to the north of the D'Entrecasteaux Islands indicates that the gneiss domes became emergent in the Pliocene (Baldwin et al., 1993; Davies and Warren, 1988). Elevated coral platforms of probable Holocene age on the southeast coast of Goodenough

Island, and incised flights of river terraces on the northeastern coastal plains of Goodenough Island, indicate that uplift of the D'Entrecasteaux Islands has persisted, if only slowly, into the Late Quaternary (Little et al., 2011). In addition, apatite fission track ages of $\sim 0.8 \pm 0.1$ Ma indicates unroofing of the domes in the Late Quaternary (Baldwin et al., 1993).

2.2.2 Structural geology of the D'Entrecasteaux Islands

The Goodenough, Mailolo, and Oiatabu gneiss domes are bounded by active north or northeast-dipping normal faults on their northeast margins (Fig. 2.3, 2.4). The Morima dome is bounded to the southwest by an active southwest-dipping normal fault (Fig. 2.3, 2.4). Where exposed on Goodenough Island, the Wakonai normal fault dips $35 - 40^\circ$ (Fig. 2.3; Little et al., 2011). These faults separate unmetamorphosed late Quaternary alluvium sediments and volcanic rock in their hangingwall, from erosional remnants of the Cenozoic Papuan Ultramafic Body and underlying amphibolite-facies gneisses in their footwall (Fig. 2.3; Hill, 1994; Little et al., 2011). Structural data suggest that Goodenough and Mailolo Domes have been back-tilted $\sim 20^\circ$ to the southwest as a result of slip on the dome-bounding faults, implying an original dip for the faults of $\sim 55 - 60^\circ$ (Little et al., 2011).

The footwalls of these normal faults consist of a high-grade gneissic terrane with an outwardly dipping domal foliation. The dome-defining foliation post-dates the (U)HP metamorphic event, and developed during a widespread syn-exhumational upper amphibolite-facies overprint that affected the gneiss terrane after it had risen from the mantle to the lower crust (Little et al., 2011). At the crest of the domes the foliation is generally sub-horizontal but elsewhere it dips outward at $30 - 70^\circ$, with the steepest dips typically being found on the southwest flanks of the domes as a result of their back-tilting (Little et al., 2011). These gneiss domes are 2 – 2.5 km high at their crests, and are rounded or elongate in map view. They have been eroded sufficiently so that a once continuous sheet of overlying ultramafic rock of the Cenozoic Papuan Ultramafic Body has largely been stripped away from their uplifted centers, leaving only a scatter of small erosional remnants that are exposed in structural lows (Fig. 2.3; Little et al., 2011). Each dome is separated from its neighboring domes by tight synforms (Fig. 2.3). The gneiss domes can be divided

Figure 2.4 Digital Elevation Model of the northwest D'Entrecasteaux Islands from GeoMapApp (<http://www.GeoMapApp.org>). Note locations of main dome-bounding normal faults (solid black lines) and faults zones (dashed black lines). See Figure 2.1b for location. Note locations of gneiss domes described in text.

into two structural zones: a structurally higher carapace zone (up to ~ 1.5 km thick), and a structurally deeper core zone (Fig. 2.3; Hill, 1994; Little et al., 2011). The carapace zone strongly resembles the core zone in protolith compositions and the presence of meter-scale eclogite boudins, and both share the same domal foliation that is outwardly dipping and defines the gneiss dome culminations (Little et al., 2011). The carapace differs from the core in that it is characterized by a more planar, thinly laminated, and strongly lineated solid-state tectonic fabric relative to the subjacent core rocks (Little et al., 2011).

The gneiss domes are composed primarily (~90%) of quartzofeldspathic gneiss, much of it orthogneiss (Fig. 2.5; Little et al., 2011 *and ref. therein*). It has been inferred that the gneisses are derived from Cretaceous or older Australian continental margin protoliths, and probably represent a once deeply subducted part of the collisional Papuan Orogeny (Davies and Jaques, 1984; Davies and Warren, 1988; Little et al., 2011; Zirakparvar et al., 2010). Marbles and pelites are rare (<1%), and eclogite constitutes 5 – 10% of the terrane (Fig. 2.5d; Little et al., 2011 *and ref. therein*).

The eclogite blocks in the D'Entrecasteaux Islands originate from meter-thick basaltic dikes that intrusively crosscut the quartzofeldspathic host gneiss (Baldwin et al., 2008). These mafic dikes were later metamorphosed under eclogite-facies conditions prior to final boudinage and retrogression in upper amphibolite-facies conditions (Baldwin et al., 2008). The verification of coesite in one sample of mafic eclogite (08-010a) from the west of the Mailolo dome implies that certain portions, or perhaps all, of the metamorphic terrane was subducted to depths of >90 km (Baldwin et al., 2008; Monteleone et al., 2007). In the cores of the mafic boudins the unretrogressed (U)HP eclogite-facies metamorphic assemblage consists of garnet, omphacite, phengite, quartz, and rutile (Brownlee et al., *in prep.*). The rinds of the boudins have typically been retrogressed to amphibolite-facies metamorphic assemblage (hornblende and plagioclase symplectite, garnet, quartz, and ilmenite) together with the quartzofeldspathic gneiss that wraps around the relict (U)HP boudins. The degree of amphibolite-facies retrogression is variable, with some mafic blocks preserving the unretrogressed UHP eclogite-facies assemblage, and others

Figure 2.5 Photographs of typical lithologies in the D'Entrecasteaux Islands. Foliations have been rotated to the horizontal in the photographs. (a) Strongly foliated and lineated carapace zone quartzofeldspathic gneiss (lower Gulawata River gorge, Goodenough Island). (b) Quartzofeldspathic core zone gneiss (southeast Mailolo dome). Note patch of leucosome within the 0.25m x 0.25m grid. (c) Strongly deformed dm-thick granodiorite foliation-parallel sheets (upper left) with zircon U-Pb age of 3.00 ± 0.02 Ma (2σ ; Gordon et al., *in review*). Relatively less deformed (younger) granodiorite intrusion with zircon U-Pb ages of ~ 2.4 Ma (single zircon ages range from 2.418 ± 0.004 Ma to 2.482 ± 0.007 Ma; 2σ ; Gordon et al., *in review*). Lower Mwadeia River gorge, Mailolo dome. (d) Core zone quartzofeldspathic gneiss with mafic eclogite boudins (southwest Goodenough Island).

being thoroughly retrogressed to an amphibolite-facies assemblage (Baldwin and Ireland, 1995).

The timing of the main phase of amphibolite-facies metamorphism and ductile deformation in the lower crust in the Goodenough and Mailolo domes has been constrained to 3.5 – 2.4 Ma. Baldwin and Ireland (1995) dated zircons from two samples of felsic gneiss in the Goodenough dome by the U-Pb method using a sensitive high-resolution ion microprobe, and determined ages of 2.63 ± 0.16 Ma (2σ) and 2.72 ± 0.28 Ma (2σ) respectively. These ages are interpreted to represent the timing of metamorphic zircon growth subsequent to the eclogite-facies metamorphism (Baldwin and Ireland, 1995). Gordon et al. (*in review*) dated zircons from pre- to syn-kinematic granodioritic gneiss from the Mailolo dome by U-Pb chemical-abrasion thermal ionization mass spectrometry, thereby bracketing the timing of the main phase of the amphibolite-facies deformation. A strongly deformed granodioritic orthogneiss from the core zone of the Mailolo dome yielded a U-Pb age range of 3.41 ± 0.02 Ma to 3.50 ± 0.01 Ma (2σ). A deformed granodioritic orthogneiss (expressed in foliation-parallel sheets) from the carapace zone of the Mailolo dome yielded a weighted mean U-Pb zircon age of 3.082 ± 0.007 Ma (2σ ; MSWD = 0.56; five zircons), and a nearby granodioritic dike yielded a U-Pb zircon age of 3.00 ± 0.02 Ma (2σ ; two zircons). A relatively undeformed granodioritic dike from the same location yielded a U-Pb zircon age range of 2.418 ± 0.004 Ma to 2.482 ± 0.007 Ma (2σ). The latter ages are interpreted to date the timing of the final stages of the amphibolite-facies foliation development in the gneiss domes (Gordon et al., *in review*).

These domes were intruded by granodiorite and leucogranodiorite dikes and plutons of Pliocene age during the main deformation event in the lower crust (Fig. 2.5b,c; Hill et al., 1995; Little et al., 2011 *and ref. therein*). Outcrop and microscale observations indicate that partial melting and granitic dike intrusion took place at the same time as amphibolite-facies deformation, and continued as the rocks were emplaced in the upper crust as gneiss domes (Little et al., 2011). The host gneisses preserve segregated partial melt as leucosomes, which are more abundant in the core region of the domes relative to the carapace zone (Fig. 2.5b). I have quantitatively estimated the amount of crystallized melt in leucosomes exposed in outcrop using a

0.25m × 0.25m grid after Solar (2008; Fig. 2.5b). The percentage of total leucosome content in outcrop was determined for 11 outcrops of quartzofeldspathic gneiss in the Goodenough and Mailolo gneiss domes. The ImageJ image analysis software package was used to calculate the area of crystallized partial melt in images of two outcrops of core zone rock from the Goodenough dome, one outcrop of carapace zone rock from the Goodenough dome, and eight outcrops of core zone rock from the Mailolo dome (Abramoff et al., 2004). I assume that the 2-D amount of partial melt at outcrop is an accurate representation of the 3-D volume percent of the migmatite component at each outcrop. If this assumption is valid, the calculated area of crystallized partial melt represents the percentage that the bulk rock was affected by partial melting (Solar, 2008). These percentages are biased by the location of rock exposure throughout the Goodenough and Mailolo dome that was free of plant material and available for imaging. The Goodenough dome contains ~2% in-situ crystallized melt content in the carapace zone, increasing to >20% in the dome's central core zone. The carapace and core zone in the Mailolo dome contains 5 – 15% in-situ crystallized melt; these data do not allow me to differentiate between the percentage of in-situ crystallized melt between the core and carapace zones of that dome. The widespread presence of a melt phase (leucosomes) in the migmatitic rocks in the D'Entrecasteaux Islands suggests that rocks with a granodioritic composition (gneiss protolith) were once heated to temperatures of >650 °C, based on the solidi for H₂O-saturated crustal rocks (Hacker, 2006 *and ref. therein*), and thermal and petrological modeling (Fig. 2.6; Brown, 2008; White, 2008). Crustal rocks will melt at ~700 °C if an aqueous phase is present, and at ~800 °C if the crustal rock is 'dry' (Fig. 2.6; Brown, 2008; Clemens and Watkins, 2001; England and Thompson, 1986; White, 2008). Little et al., (2011) interpret the crystallized partial melt to have been the result of decompression melting of the rocks during their rapid ascent. The last stage of granodioritic dike intrusion may have occurred at ~2 Ma, when large (km-scale) granitic plutons such as the Omara pluton in Fergusson Island were intruded (U-Pb ion microprobe zircon ages of 1.98 ± 0.08 Ma; 2σ ; Baldwin and Ireland, 1995). These plutons are mostly undeformed.

⁴⁰Ar/³⁹Ar ages calculated by Baldwin et al. (1993) on white mica and biotite imply rapid cooling of the lower plate gneisses through 400 – 300 °C, after they arrived in the upper crust and became emergent in the Plio-Pleistocene (Little et al., 2011).

Figure 2.6 Grey shaded area shows pressure-temperature (P-T) path from the mantle to the surface of the ultrahigh-pressure gneisses in the Mailolo dome in the D'Entrecasteaux: GS, greenschist; AM, amphibolite; BS, blueschist; EC, eclogite; GR, granulite. Adapted from Baldwin et al. (2004, 2008) and Little et al. (2011). Timing of eclogite-facies (~5 Ma) and amphibolite-facies metamorphism (2.5 – 3.0 Ma) after Chapter 3 this thesis and Gordon et al. (*in review*). Exhumation path after P-T data from Hill and Baldwin (1993). P-T data of high-temperature grain boundary migration (>500 – 550°C) and chessboard subgrains structure ($630 \pm 30^\circ\text{C}$) after Stipp et al. (2002). P-T data for the solidus for H_2O -saturated crustal rocks after Hacker (2006) and Little et al. (2011). Note that this study is specifically concerned with the last stage of cooling through the crust, above the thick black dashed line.

White mica and biotite typically yield $^{40}\text{Ar}/^{39}\text{Ar}$ plateau and isochron ages of 3.0 – 1.5 Ma and 1.9 – 1.4 Ma respectively, a near concordance that indicates rapid cooling of the granodiorites and basement rock after 3.0 – 2.0 Ma (Baldwin et al., 1993). The similarity between the white mica and phengite $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages and the biotite $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages indicates that this final cooling was rapid ($>100\text{ }^{\circ}\text{C Ma}^{-1}$; Baldwin et al., 1993). Apatite fission track analysis yields ages of 0.4 – 0.1 Ma, suggesting a late deceleration in cooling rates such that final cooling of the rocks to below $130\text{ }^{\circ}\text{C}$ was at $<0.4\text{ Ma}$.

Quartz in the gneisses has abundant deformation bands or sweeping undulose extinction structures, and typically exhibits strongly interlobate to amoeboid grain-boundary microstructures. These microstructures imply recovery via high-temperature grain-boundary migration recrystallization (GBM), followed by rapid textural quenching and little or no subsequent static recrystallization (Fig. 2.7a; Little et al., 2011). Quartz grains are typically inequigranular and range in diameter from 75 to $>1000\text{ }\mu\text{m}$, with an average grain size range of 200 – 500 μm . Chessboard subgrain structures are common. The latter microstructure is thought to form at deformational temperatures of $630 \pm 30\text{ }^{\circ}\text{C}$ (Fig. 2.6, 2.7b; Blumenfeld et al., 1986; Kruhl, 1996; Stipp et al., 2002). Quartz in the quartzofeldspathic gneiss commonly occurs as aggregates. In contrast, quartz grains in the eclogites are isolated by eclogite-facies minerals and are therefore sparse and generally isolated from one another.

2.3 Models for gneiss dome emplacement

Gneiss domes, including metamorphic core complexes, can be defined as domal structures cored by metamorphic rocks that exhibit an outwardly dipping foliation or gneissic layering (Whitney et al., 2004; Yin, 2004). A high-grade core mantled by a carapace typically characterizes such structures, the latter of which may be lower-grade (Tirel et al., 2004; Whitney et al., 2004). Gneiss domes and metamorphic core complexes are common in exhumed orogenic belts dating back to the Archean, and

Figure 2.7 (a) Photomicrograph of quartz grains showing strongly interlobate to amoeboid grain boundary microstructures, suggesting recovery via high-temperature grain boundary migration recrystallisation (09-022a; quartz band from the core zone of the Mailolo dome, northern Fergusson Island). (b) Photomicrograph of quartz grains showing chessboard subgrain structure (09-062c; granodioritic dike from the core zone of the northwest Normanby dome, northwest Normanby Island).

reflect the flow of mobile lower crustal rocks as a result of buoyant and isostatic stresses (Teyssier and Whitney, 2002; Tírel et al., 2004; Whitney et al., 2004).

Previous workers have proposed differing models for how the UHP-bearing gneiss domes in the D'Entrecasteaux Islands were emplaced from the lower crust to shallow crustal depths. Hill et al. (1992, 1994, 1995) and Baldwin et al. (2005) argue that normal slip on long-lived and deeply penetrating detachment faults has translated the (U)HP rocks from the mantle to the surface to form Cordillera-style asymmetric metamorphic core complexes (Fig. 2.2b). These authors suggest that the juxtaposition of the nearly un-metamorphosed Cenozoic Papuan Ultramafic Body in the hanging wall of these detachments structures against the complexly deformed metamorphic rocks in the footwall implies huge displacement along the detachment surface (enough to exhume the UHP eclogites). Assuming a fault dip of 40° and an original depth of 90 km from the presence of coesite in one sample, the displacement could be >100 km (Baldwin et al., 2008). More recently, Webb et al. (2008) suggest that counterclockwise rotation of the Woodlark microplate relative to the Australian plate has caused Neogene subduction inversion and exhumation of the (U)HP rocks along the inactive Papuan suture (Owen Stanley fault zone). By contrast, pure-shear dominated symmetric doming was first suggested for crustal emplacement by Davies and Warren (1988; Fig. 2.2a), and was modeled by Martinez et al. (2001). A recent field-based structural and microstructural study by Little et al. (2011) suggests that the exhumation of the gneiss domes through the crust was accomplished by pure-shear symmetric doming in conjunction with diapirism. These latter workers interpret the normal faults that currently bound sections of the D'Entrecasteaux Islands as relatively late-stage, normal faults that are related to the Woodlark Rift and post-date most of the (U)HP exhumation and dome formation. This interpretation implies that these faults are not long-lived, high-displacement detachment faults, and were not responsible for exhumation of rocks from mantle depths in the D'Entrecasteaux Islands.

The key difference between these two end-member models is the ratio of vertical to horizontal flow within the domes and the asymmetry of the expected crustal exhumation patterns (Whitney et al., 2004). Pure-shear symmetric doming (including diapirism) is the result of largely upward flow that results from buoyancy and

isostatic stresses of the upwardly emplaced, partially molten gneisses (Teyssier and Whitney, 2002; Whitney et al., 2004; Yin, 2004). By contrast, detachment-style asymmetric metamorphic core complexes are thought to result largely from lateral movement of the lower plate along a dipping major detachment fault (Tirel et al., 2004; Yin, 2004). This motion may result in tectonic unloading of the footwall, causing a corresponding isostatic uplift of the footwall relative to the hangingwall (Tirel et al., 2004). This uplift can potentially lead to a ‘rolling hinge’ evolution of a back-tilted detachment surface, which becomes inactive (Tirel et al., 2004; Tirel et al., 2008). This latter model therefore has a high component of horizontal flow. Where the degree of partial melting and/or magmatism is high or where exhumation rates are rapid, thermomechanical modeling suggests that pure-shear doming is dominant (Rey et al., 2009; Teyssier and Whitney, 2002; Tirel et al., 2008; Whitney et al., 2004).

The previously discussed kinematic models predict contrasting patterns of relative exhumation and cooling rates in gneiss domes. In pure-shear dominated symmetric doming the rates of exhumation are predicted to be fastest near the center of the dome where the deepest exhumation levels will occur and to decrease outwardly in all directions away from this central exhumational locus (Fig. 2.2a; Burg et al., 2004; Whitney et al., 2004). Pure-shear doming may therefore lead to a concentric or “bulls-eye” pattern of relative exhumation levels in map view (Burg et al., 2004). By contrast, gneiss domes that have been exhumed asymmetrically through the crust in the footwall of a Cordillera-style metamorphic core complex are predicted to expose the deepest and most recently exhumed structural levels adjacent to the major detachment that bounds the dome on one side (Burg et al., 2004; Tirel et al., 2004). Shallower exhumation levels within metamorphic core complexes will crop out in the footwall with increasing distance away from the dome-bounding fault in the direction of fault transport (Fig. 2.2b; Tirel et al., 2004).

2.4 Theory of the Ti-in-quartz geothermometer and analytical technique

2.4.1 The Ti-in-quartz geothermometer (TitaniQ)

The chemical potential of Ti and the extent of Ti substitution into the tetrahedral site within quartz are predicted to vary systematically with temperature and pressure (Thomas et al., 2010; Wark and Watson, 2006). The Wark and Watson (2006) experimentally calibrated geothermometer predicts that an increase in Ti content in quartz corresponds to an increase in temperature, based on the exchange reaction $Si^{4+} \Leftrightarrow Ti^{4+}$ for quartz and rutile. Based on comparison of TitaniQ results with other data sets such as Zr-in-sphene thermometer, Wark and Watson (2006) inferred that there was no pressure dependency for the temperature range over which they synthesized quartz (600 – 1000 °C). The TitaniQ was therefore calibrated at a uniform pressure of 10 kbar. Later, Thomas et al. (2010) argued that an increase in pressure would result in volumetric changes affecting the tetrahedral sites within quartz, and therefore in reduced substitution of Ti for Si within quartz. This decrease in the solubility of Ti in quartz with increasing pressure implies that the TitaniQ is both temperature- and pressure-dependent (Thomas et al., 2010). Depending on the geothermal gradient, the decrease in solubility for the pressure-sensitive calibration of the TitaniQ would result in reduced substitution of Ti for Si in quartz as a function of temperature, relative to the earlier pressure invariant (10 kbar) experimental calibration (Thomas et al., 2010). Both calibrations predict that an increase in Ti content in quartz will result in an increase in TitaniQ apparent temperatures. In order to ascertain whether the two TitaniQ calibrations would lead to different spatial gradients in apparent temperatures, I calculated TitaniQ apparent temperatures for the dense suite of samples from the Goodenough gneiss dome using both the Wark and Watson (2006) and the Thomas et al. (2010) calibrations. In this comparison I include an incremental pressure correction to account for the difference in structural depth of the foliation, which is assumed to have once been horizontal (Little et al., 2011).

There are two main assumptions that must be met if an apparent temperature calculated by the TitaniQ can be interpreted as the temperature associated with the

cessation of Ti mobility in the sampled quartz grains. First, the TitaniQ assumes that there was no diffusion of Ti after equilibration of Ti within quartz at the temperature of interest (Wark and Watson, 2006). Secondly, the Ti activity coefficient within quartz must be known (Wark and Watson, 2006). If the Ti activity is poorly constrained in rocks that lack rutile, then the TitaniQ will only yield a minimum temperature estimate (Wark and Watson, 2006). It is possible that the rutile and quartz present in a given rock did not equilibrate at the same time or metamorphic conditions, leading to potential ambiguity in the Ti activity coefficient (Thomas et al., 2010). It is therefore prudent to ensure that the reaction history is fully understood before interpreting spatial gradients in TitaniQ apparent paleotemperatures.

2.4.2 Analytical procedure and apparent temperature calculation

Grain-scale physical processes that may have lead to Ti mobility and/or equilibration in quartz grains includes volume diffusion, recrystallization, or quartz grain growth (Kohn and Northrup, 2009; Spear and Wark, 2009; Wark and Watson, 2006). Constraining the microstructural context of any Ti content variation within or between quartz grains is an important step towards understanding which of these grain-scale processes is dominant in the quartz grains of samples in the D'Entrecasteaux Islands (Spear and Wark, 2009). Cathodoluminescence (CL) imaging was therefore carried out on 20 of the 90 samples analyzed for Ti content here, using the JEOL JXA-8230 electron probe microanalyzer with an XCLent Combined Cathodoluminescence and X-ray microanalyzer at Victoria University of Wellington, New Zealand. Variation in intensity of the CL at the 415 nm wavelength has been predicted to be proportional to the concentration of Ti within quartz (Spear and Wark, 2009). Thus, this wavelength was used for imaging in order to evaluate the degree of homogeneity and microstructural context of Ti variation within the quartz grains (intra-granular variation or zoning) and between one grain and another (inter-granular variation). Sharp boundaries between zones of relatively higher and lower Ti content in a single quartz grain may suggest that some partial diffusion of Ti has taken place inside the crystal, or that primary growth zonation is preserved. Insignificant zoning implies homogenization of Ti content during either growth or recrystallization of the grain at near constant temperatures, or at a later time as a

result of pervasive diffusion subsequent to that growth (Spear and Wark, 2009). Five representative rock types were analyzed with CL: quartzofeldspathic gneiss, migmatitic quartzofeldspathic gneiss, eclogite, retrogressed eclogite, and metamorphosed granodiorite or leucogranodiorite. Four representative samples of each of these rock types were chosen for CL analysis from localities throughout the Goodenough, Mailolo, and northwest Normanby dome (Fig. 2.3). In order to target variations in Ti content in quartz, CL images were processed by isolating the best peak near 415 nm (Appendix A; Spear and Wark, 2009). CL imaging used an accelerating voltage of 20 kV, a probe current of 50 nA, and a dwell time of 40 seconds.

Ti-in-quartz analyses were carried out on an Agilent 7500 CS inductively coupled plasma mass spectrometer with a New Wave 193 μm solid-state Nd-YAG laser at Victoria University of Wellington, New Zealand. This study analyzed 68 samples of metamorphic granitic rock and quartzofeldspathic gneiss, 14 samples of strongly deformed foliation-parallel quartz veins that are embedded within such gneisses, and seven samples of quartz grains in eclogite boudins (Fig. 2.3). Samples were chosen to ensure a complete spread across both the carapace and core structural zones of Goodenough, Mailolo, Morima, and northwest Normanby dome. Samples were cut into <5 mm squares and mounted into polished epoxy briquettes (25 mm; Appendix B.1). The mounts were then carbon-coated and imaged using back-scattered electrons on the JEOL JXA-8230 electron probe microanalyzer at Victoria University of Wellington, New Zealand, to select locations for LA-ICP-MS. Back-scattered electron imaging was carried out with an accelerating voltage of 15 kV and a current of 12 nA. The quartz grains analyzed by this study were >75 μm in diameter, which is the resolution of the LA-ICP-MS. Analytical spots were scattered as far apart as possible in the mount, in an attempt to obtain a spatially-averaged mean Ti concentration for the sample as a whole.

Mean Ti concentrations were calculated by averaging up to eight spot analyses per sample (Table 2.1). In 54% of the samples, less than the full suite of eight spot analyses was included in the mean Ti concentrations because inclusion of extraneous mineral phases sometimes led to the rejection of one or more of the spot analyses. On average, seven spots were analyzed per sample. Wherever possible, spot analyses

Table 2.1 Mean Ti content of quartz grains in analyzed samples and the derived TitaniQ apparent temperatures with 95% confidence intervals

Sample No.	Easting (m) ^a	Northing (m) ^a	Lithology	Mean Ti (ppm) ^b	$\pm 2\sigma^c$ (ppm)	n ^d	No. grains analyzed	Wark and Watson (2006) calibration		Thomas et al., (2010) calibration	
								Mean T(°C) ^e	95% confidence interval (°C) ^f	Mean T(°C) ^g	95% confidence interval (°C) ^h
03-072a	261716	8917085	gneiss	3.62	0.32	8	7	475	18	496	36
03-074	261172	8917084	gneiss	5.03	0.38	8	7	497	18	518	37
03-076	247634	8930787	gneiss	4.34	0.36	4	4	487	18	511	37
03-082a	253182	8932355	gneiss	6.56	0.94	8	8	515	21	535	42
03-083	253037	8932439	granite	6.72	1.31	4	4	517	23	537	48
03-086a	237442	8933486	gneiss	3.98	1.36	5	5	467*	23	488*	59
03-086b	237442	8933486	orthogneiss	4.01	2.57	4	4	467	45	502	99
03-087b	237310	8934181	gneiss	3.76	0.24	3	3	465*	7	487*	38
03-090b	221229	8950648	granite	8.15	0.63	8	4	531	20	505	38
03-102a	221453	8954081	orthogneiss	15.73	1.00	8	8	583	22	550	41
03-107d	221511	8954396	orthogneiss	22.05	4.32	7	7	613	29	577	53
03-118a	198070	8950738	orthogneiss	10.40	1.77	7	5	533	24	-	-
06-002a	184025	8960783	granodiorite	32.11	1.88	6	5	648	26	662	45
06-002b	184025	8960783	mafic eclogite	22.95	9.52	4	4	597*	38	613*	82
06-005a	183899	8961496	granodiorite	29.07	4.11	5	4	639	28	653	50
06-008b	182478	8962719	gneiss	18.54	2.01	8	8	598	24	614	45
06-010a	187075	8975518	granite	9.76	3.53	3	2	545	34	564	65
06-012a	186887	8975066	granitic schist	8.14	0.99	4	4	531	21	552	41
06-018a	187060	8975466	gneiss	9.51	0.76	8	6	526	21	562	40
06-019a	202474	8969360	gneiss	18.94	3.23	7	5	599	27	616	50
06-020e	202427	8969319	gneiss	14.45	3.12	7	6	576	28	594	52
06-024a	201779	8969078	gneiss	12.65	10.02	4	3	565	66	586	127
06-029a	200607	8968644	gneiss	27.97	19.36	3	2	614	69	658	131
06-033a	200055	8967953	gneiss	70.43	13.98	8	8	707*	24	754*	65
06-034a	199663	8967706	gneiss	37.73	7.42	7	7	664	32	691	58
06-039a	198635	8967405	granitic sheet	10.71	0.69	4	4	535	21	582	40
06-039b	198635	8967405	gneiss	17.80	3.86	8	8	594	29	623	54
06-044b	192686	8973978	gneiss	9.20	1.04	7	7	540	21	560	41
06-045d	192765	8973812	gneiss	10.56	0.93	8	7	551	21	571	41
06-048b	228014	8964182	orthogneiss	7.78	0.71	8	8	528	20	547	40

Table 2.1 Mean Ti content of quartz grains in analyzed samples and the derived TitaniQ apparent temperatures with associated 95% confidence intervals (cont.)

Sample No.	Easting (m) ^a	Northing (m) ^a	Lithology	Mean Ti (ppm) ^b	$\pm 2\sigma^c$ (ppm)	n ^d	No. grains analyzed	Wark and Watson (2006) calibration		Thomas et al., (2010) calibration	
								Mean T(°C) ^e	95% confidence interval (°C) ^f	Mean T(°C) ^g	95% confidence interval (°C) ^h
06-049c	227960	8963957	granitic sheet	8.74	0.72	8	6	536	20	556	40
08-001a	198232	8951141	orthogneiss	13.29	1.45	8	8	551*	11	-	-
08-002b	197370	8950409	orthogneiss	10.29	0.88	7	6	532*	9	-	-
08-003c	197774	8950143	quartz	11.11	0.44	8	8	538*	7	-	-
08-003d	197774	8950143	orthogneiss	9.40	0.81	8	7	542	21	-	-
08-007c	227210	8940378	gneiss	6.44	0.94	8	8	514	21	536	42
08-010a	221437	8950193	mafic eclogite	16.06	3.93	6	5	654*	22	535*	61
08-010c	221423	8950218	granodiorite	8.32	0.84	4	4	533	21	507	40
08-011a	221369	8950119	quartz	10.41	0.58	8	4	533	21	522	39
08-011b	221369	8950119	granodiorite	6.62	0.31	8	7	516	19	491	37
08-013b	219361	8961756	gneiss	9.75	0.90	5	5	545	21	-	-
08-016b	219795	8961245	granitic sheet	6.83	0.74	7	6	518	20	-	-
08-020a	200431	8971290	quartz vein	11.55	0.86	8	6	541*	9	577*	40
08-021a	200008	8970737	gneiss	11.05	1.52	7	7	555	23	576	44
08-028a	199012	8970881	orthogneiss	8.02	0.43	7	7	530	20	554	38
08-028c	199012	8970881	quartz sheet	10.50	1.48	6	6	551	23	574	44
08-032a	199613	8971406	gneiss	10.72	1.37	7	7	535*	12	572*	43
08-033d	219596	8953857	granodiorite	9.61	1.40	3	3	544	23	515	45
08-036a	220378	8954539	ret. eclogite	7.85	0.74	4	4	512*	9	486*	39
08-037a	220353	8954686	gneiss	13.85	0.46	8	8	555*	7	525*	39
08-037c	220353	8954686	ret. eclogite	14.03	0.48	7	6	574	21	542	39
08-039b	220408	8954854	quartz vein	11.42	0.81	8	7	557	21	526	40
08-043L	256055	8959614	gneiss	8.93	0.64	7	7	538	20	-	-
08-071a	257635	8923363	quartz band	8.55	0.77	8	8	535	21	568	40
08-077a	257171	8922145	granite sheet	14.27	1.02	7	7	557	22	606	42
09-002d	227854	8963870	granodiorite	11.02	3.77	7	5	554	33	573	67
09-004c	227897	8960669	quartz layer	18.16	7.06	7	5	596	40	615	80
09-007a	227792	8959455	granite sheet	8.75	0.81	8	7	536	21	559	40
09-008a	227845	8959248	quartz sheet	16.76	1.33	8	3	589	23	609	43
09-014a	227915	8960382	orthogneiss	20.23	2.11	7	5	605	25	625	45

Table 2.1 Mean Ti content of quartz grains in analyzed samples and the derived TitaniQ apparent temperatures with associated 95% confidence intervals (cont.)

Sample No.	Easting (m) ^a	Northing (m) ^a	Lithology	Mean Ti (ppm) ^a	$\pm 2\sigma$ (ppm)	n ^d	No. grains analyzed	Wark and Watson (2006) calibration		Thomas et al. (2010) calibration	
								Mean T(°C) ^e	95% confidence interval (°C) ^f	Mean T(°C) ^g	95% confidence interval (°C) ^h
09-022a	227528	8963353	quartz vein	15.55	3.10	8	4	582	27	601	52
09-024b	225566	8961469	quartz band	17.70	2.71	8	7	593	26	614	49
09-032b	231170	8962783	gneiss	22.33	8.74	8	7	614	42	632	82
09-035a	229698	8953526	gneiss	10.52	2.10	8	8	534	25	519	48
09-038b	229864	8954022	mafic eclogite	19.72	5.03	8	8	603	32	566	59
09-044a	232011	8952642	granodiorite	14.83	0.24	8	7	560	22	544	39
09-048a	230960	8952806	gneiss	10.21	0.59	7	6	531	21	517	39
09-052b	260867	8917841	orthogneiss	11.41	2.68	8	7	557	27	581	54
09-062c	260279	8918662	granite sheet	10.32	1.89	7	4	549	24	578	48
09-065a	260087	8918420	orthogneiss	10.00	2.67	6	6	547	28	574	58
10-008a	254641	8922685	pelite	8.93	0.27	8	6	521	20	560	38
10-019a	254724	8920799	gneiss	12.14	9.86	3	3	544*	64	563*	156
10-021a	253335	8921798	mafic dike	20.76	7.88	7	7	608	40	623	80
10-021f	253335	8921798	quartz band	12.46	5.54	3	1	564	41	582	91
10-027a	202196	8969337	gneiss	28.25	11.80	3	3	615	54	652	86
10-031a	201780	8969055	gneiss	25.58	11.94	8	7	627	49	644	92
10-035a	200566	8968671	mafic eclogite	10.22	2.35	8	5	531*	19	574*	51
10-042a	197575	8967725	granodiorite	24.82	4.28	8	5	624	28	652	52
10-047a	196395	8968380	granodiorite	116.94	27.24	8	8	795	45	813	77
10-048a	195560	8968139	quartz sheet	79.01	17.00	8	7	746	40	754	68
10-051a	195277	8967862	quartz band	15.90	2.68	7	6	584	26	614	49
10-053a	197649	8967350	orthogneiss	32.49	5.08	8	7	628*	17	657*	53
10-056a	190904	8974483	mafic eclogite	20.71	2.16	8	6	588*	11	625*	45
10-058a	191132	8972160	granite sheet	11.96	2.36	8	7	561	26	587	49
10-062a	189638	8969431	orthogneiss	16.04	3.84	8	8	585	30	602	55
10-065a	191489	8967618	granodiorite	20.97	3.75	8	8	608	28	637	52
10-067a	192893	8967055	orthogneiss	24.89	9.13	7	5	622	41	653	78
10-070a	231117	8962751	quartz band	14.62	7.54	7	5	559*	43	597*	96
10-071a	231087	8962728	gneiss	10.61	1.48	8	5	551	23	572	44

^a Australia Map Grid 66 (UTM zone 55L).

^b Weighted mean of Ti concentration for all spot analyses in the sample (weight equal to $(\text{std dev})^{-2}$).

^c Analytical error calculated as a weighted standard deviation (weight equal to $(\text{std dev})^{-2}$) of all spot analysis within a sample. Error is a 95% confidence interval of the mean Ti concentration (2σ denotes t statistic multiplied by σ).

^d Number of spot analysis per sample.

^e Apparent temperatures are calculated using the Wark and Watson calibration (2006) and a Ti activity of 0.8 with the exception of the apparent temperatures noted with an asterisks, which are calculated using the Wark and Watson calibration (2006) and a Ti activity of 1.0.

^f The uncertainty is derived from the analytical, calibration, and α_{TiO_2} uncertainties and is calculated as a 95% confidence of a quotient (Appendix B.2).

^g Apparent temperatures are calculated using the Thomas et al. (2010) and a Ti activity of 0.8 with the exception of the apparent temperatures noted with an asterisks, which are calculated using the Thomas et al. (2010) and a Ti activity of 1.0.

^h The uncertainty is derived from the analytical, calibration, and α_{TiO_2} uncertainties and is calculated as a 95% confidence of a quotient (Appendix B.2).

were taken from both the rim and core of up to four different quartz grains to yield eight spot analyses. This was successfully undertaken on 22% of the samples analyzed here. On average six quartz grains were analyzed per sample (Table 2.1). The high number of quartz grains that do not include separate core and rim spot analyses resulted from several analytical limitations: (1) rejection of contaminated signal (~42%), (2) fracturing during ablation destroying the rim or core of the grain analyzed (~32%), and (3) small grain size (<125 μm) allowing only one ablation pit per grain (~26%).

The mean concentration of Ti, Al, Si, and Ca in quartz was calculated relative to the National Institute of Standards and Technology standard reference material 612 (NIST 612), which was analyzed under near-identical conditions to the quartz grains (Appendix B.1). The LA-ICP-MS was tuned before every analytical run to ensure a high stability and sensitivity of the NIST 612 standard, and a good interaction of the laser with the target (Appendix B.1). Each analytical run was arranged using standard-sample bracketing; four unknown analyses were bracketed by two NIST 612 standard analyses. Consistency of $^{47}\text{Ti}/^{29}\text{Si}$ and $^{43}\text{Ca}/^{29}\text{Si}$ were monitored during data processing as variations in these ratios suggest there was ablation of an undesirable mineral phase.

For each spot analysis, an average signal and (two) standard deviation of the ^{47}Ti , ^{27}Al , ^{29}Si , and ^{43}Ca beam were calculated using an unpublished MATLAB™ script written by Euan Smith (Victoria University of Wellington). Background for all beams were measured and subtracted from the signal of each spot analysis prior to

calculation of the Ti concentration. The background-corrected signal for every spot analysis was converted into a Ti concentration using the equation:

$$\text{Sample [i]} = (\text{Sample CPS} / \text{average bracketing STD CPS}) \times \text{ref. [element]} \quad (2.1)$$

where [i] is the concentration in ppm by weight of the element of interest, Sample CPS is the counts per second or signal of the element of interest, average bracketing STD CPS is the average of the counts per second or signal of the NIST 612 analyses that bracket the unknown, and the ref. [element] is the GeoReM (<http://georem.mpch-mainz.gwdg.de/>) preferred concentration of the element of interest. The mean Ti concentration in quartz for each sample quoted in Table 2.1 was calculated as the weighted mean of all analyses (up to eight) of the sample (weight equal to std dev^{-2}). The uncertainty of the mean Ti concentration (standard error) was calculated by pooling the weighted residuals. The 95% confidence interval of the mean Ti concentration (quoted as 2σ in Table 2.1) is given by: $\pm t \times (\text{weighted standard error})$, where t is the Student's t statistic for 95% with $(n-1)$ degrees of freedom (n is the number of data).

Determining the Ti activity (α_{TiO_2}) is a prerequisite to the use of the TitaniQ to measure paleo-temperatures of Ti equilibration in quartz. Thin-sections for each sample (90 in total) were examined optically to determine the Ti-bearing phase that co-exists with quartz. Typically, these include rutile, ilmenite, or titanite. If rutile is present, the sample was assigned a α_{TiO_2} of 1.0 ($n = 17$, 19% of the samples analyzed). Previous studies have determined that crustal rocks with have a $\alpha_{\text{TiO}_2} \geq 0.6$, and felsic rocks with an amphibolite-facies mineral assemblage that includes ilmenite or rutile will have a $\alpha_{\text{TiO}_2} \geq 0.8$ (Ghent and Stout, 1984; Wark and Watson, 2006). I assigned titanite- and ilmenite-bearing samples a α_{TiO_2} of 0.8 with an uncertainty ± 0.2 (inferred as 2σ) to account for possible heterogeneities in Ti activity within and between samples (Ghent and Stout, 1984; Kohn and Northrup, 2009). Even if the Ti activity values chosen here are not accurate, this study is chiefly concerned with determining spatial gradients in apparent temperatures and does not rely on accurate absolute temperatures. As long as all similar mineral assemblages were assigned the same activity, any inaccuracies in the assigned activity should not adversely affect the spatial trends presented here.

Ti concentration was internally corrected during data reduction with respect to Si. The equations used for this correction can be written as:

$$[Si]_{Smpl} = [Si]_{Std} \times \frac{CPS_{Smpl}}{CPS_{Std}} \quad (2.2)$$

and

$$[Ti]_{Smpl} = [Ti]_{Std} \times \frac{CPS_{Smpl}}{CPS_{Std}} \quad (2.3)$$

where $[i]_{Smpl}$ is the concentration of the element of interest in the sample or unknown, $[i]_{Std}$ is the concentration of the element of interest in the standard, and CPS_i is the counts per second or signal of the sample or standard. SiO_2 is by far the major oxide in quartz and therefore has an assumed value of 100% for a pure quartz grain. If the measured Si concentration is less than 100% during analysis, this secondary internal correction for Si increases the Ti concentration of the unknown by a proportional amount.

After measuring Ti concentrations, TitaniQ apparent temperatures were calculated using the Wark and Watson (2006) calibration:

$$T(^{\circ}C) = \frac{-3765}{\log \left[\frac{X_{Ti}^{Qtz}}{\alpha_{TiO_2}} \right] - 5.69} - 273 \quad (2.4)$$

where X_{Ti}^{Qtz} is the Ti concentration in quartz in ppm by weight and α_{TiO_2} is the activity of TiO_2 in the system ($\alpha_{TiO_2} = 1$ for rutile; $\alpha_{TiO_2} = 0.8 \pm 0.2$ for other Ti phases as above). TitaniQ apparent temperatures were also calculated using the Thomas et al., (2010) calibration:

$$T(^{\circ}C) = \frac{60952 + 1741P}{1.52 - R \ln X_{TiO_2}^{Qtz} + R \ln \alpha_{TiO_2}} - 273.15 \quad (2.5)$$

where P is the inferred pressure in kbar, R is the gas constant 8.3145 J K^{-1} , $X_{TiO_2}^{Qtz}$ is the mole fraction of TiO_2 -in-quartz (calculated using the equation given in Thomas et al., 2010), and α_{TiO_2} is the activity of TiO_2 in the system (as per above). For the quartzofeldspathic host gneiss, the pressure value input into equation 2.5 was 7-11 kbar in accordance with existing pressure estimates for the amphibolite-facies

retrogression in the D'Entrecasteaux Islands, after Hill and Baldwin (1993). Moreover, a further incremental pressure correction between samples collected at different relative structural depths in the domes was made by assuming: (1) prior to doming the foliation was originally horizontal (Little et al., 2011), and (2) that the bulk density of the gneiss sequence is 2700 kg m^{-3} (Harkness, 1891; Hinze, 2003 *and ref. therein*). This pressure correction takes account of the pressure effect on the Ti equilibration in quartz inferred to exist by Thomas et al. (2010), in order to compare TitaniQ apparent temperatures for samples collected at different structural levels in the domes. The pressure correction was no more than 0.76 kbar between the deepest and shallowest samples, and was thus minor compared to other variances of Ti content in these quartz grains.

The 95% confidence interval for each TitaniQ apparent temperature presented here (Table 2.1) represents a combination of three independent sources of uncertainty. First, there is an uncertainty in least-squares regression analysis carried out during calibration of the Wark and Watson (2006) and the Thomas et al., (2010) TitaniQ on the Ti-in-quartz experimental data (calibration uncertainty; Appendix B.2). Second, there is the LA-ICP-MS analytical precision in the measured Ti concentration, which is quoted at the 95% confidence level (Appendix B.2). Third, there is the ± 0.2 uncertainty in α_{TiO_2} that I have assigned to those samples that lack rutile. The uncertainty values shown in Table 2.1 were calculated as a 95% confidence interval of the quotient:

$$\text{var}\left(\frac{A}{B}\right) = \frac{1}{B^2} \text{var } A + \frac{A^2}{B^4} \text{var } B \quad (2.6)$$

where A is the numerator of equation 2.4 and 2.5, and B is the denominator of equation 2.4 and 2.5. See Appendix B.2 for full explanation of this uncertainty calculation.

Over 600 Ti-in-Quartz LA-ICP-MS spot analyses were performed on 90 samples collected from four gneiss domes in the D'Entrecasteaux Islands (Fig. 2.3). The analytical precision for a single spot analysis collected during tuning of the LA-ICP-MS was <15%. Fig. 2.8 illustrates the internal and external precision, and accuracy of all analyses of the National Institute of Standards and Technology standard

Figure 2.8 Reproducibility of the National Institute of Standards and Technology standard reference material 612 (NIST 612) for all analytical sessions. The internal precision is the 2σ of the individual measurements of NIST 612 (error bar for each black diamond), each of which is a repeated measure of ~ 400 Si-corrected Ti integrations. The external precision or reproducibility of analysis is the 2σ of all measurement of the NIST 612 titanium concentration ($2\sigma = 3.10$ ppm). The accuracy of the NIST 612 measurement is the average of all measurements of the NIST 612 Ti concentration (44.16 ppm), and is shown by the solid red line. Reference value and 1σ (red dotted line) of the NIST 612 Ti concentration shown here are GeoReM preferred values (<http://georem.mpch-mainz.gwdg.de/>).

reference material 612 (NIST 612) standard during the LA-ICP-MS sessions. All measured values of the NIST 612 standard are within the 1σ error of the GeoReM preferred value for the Ti concentration in the NIST 612 (44 ± 5 ppm), and the data exhibit an excellent accuracy of 44.16 ppm (average value of all NIST 612 measurements). Total variation in Ti ppm across all the quartz grains analyzed in this study was 3.76 to 116.94 ppm. Analytical results are summarized by sample in Table 2.1, which also lists the calculated TitaniQ apparent temperatures and their associated 95% confidence intervals.

2.5 Results of CL Imaging and LA-ICP-MS Ti-in-quartz analysis

2.5.1 CL images

CL images are an efficient way to qualitatively assess any grain-scale variations in Ti content within and between quartz grains. By analyzing Ti concentrations in selected spots that fall on a given CL image using LA-ICP-MS, I was able to assign a Ti concentration to the CL image intensity scale. The LA-ICP-MS calibrated CL images are used here to estimate the scale of the differences in Ti content, which are implied by the differences in brightness between specific microstructural sites in the CL images. In general, there is no obvious correlation between the microstructural pattern of CL intensity variations and rock type. All five rock types analyzed (quartzofeldspathic gneiss, migmatitic gneiss, eclogite, retrogressed eclogite, leucocratic granodiorite) yielded similar microstructural patterns of CL variation as discussed below.

The CL images imply that the magnitude of intra-granular Ti variation within quartz grains in the D'Entrecasteaux Islands is slight (<5 ppm; Fig. 2.9a,b). In general, the intra-granular CL patterns are typically flat or quasi-homogeneous, with areas of slight higher and lower relative Ti content that I will refer to as “patches” (<1 ppm; Fig. 2.9b). Based on optical microscopy, the patches do not appear to be (sub)grain boundaries. Approximately 35% of the CL images exhibit resolvable differences of relative Ti content within individual quartz grains. These internal differences in CL

Figure 2.9 Selected wavelength-dispersive spectrometry (WDS; greyscale) and cathodoluminescence (CL; color) images showing intra-granular variation in Ti concentration: Fld, feldspar; Qtz, quartz; WM, white mica; Ilm, ilmenite. Warm red colors denote relatively high Ti content and cool blue colors denote relatively low Ti content. Black circles denote locations of LA-ICP-MS analysis sites with Ti concentration indicated in ppm by weight. (a) WDS Si map for a retrogressed mafic eclogite (08-036aviii). (b) CL Ti image for a retrogressed mafic eclogite (08-036aviii). Note patches of slight (<1 ppm) Ti variation described in text. The LA-ICP-MS analyses indicated variations in Ti concentration between spot analyses that are within error of each other. This is the most common pattern in quartz from the D'Entrecasteaux Islands. (c) WDS Si map for a quartzofeldspathic orthogneiss (09-014aiii). (d) CL Ti image for a quartzofeldspathic orthogneiss (09-014aiii), case a described in text (Section 2.5.1). Note thin rim of lower Ti content possibly caused by minor fluid-driven or volume diffusion of Ti at grain edges. This pattern is seen only in granitic rocks. (e) WDS Si map for a quartzofeldspathic orthogneiss (09-014aiii). (f) CL Ti image for a quartzofeldspathic orthogneiss (09-014aiii), case b described in text (Section 2.5.1). Note the uni-directional increase in Ti content across the four quartz grains separated by high-angle grain boundaries. The LA-ICP-MS analyses corroborate the uni-directional increase, and indicate this variation between spot analyses is not within the 95% confidence uncertainty in the mean Ti concentration. Also note the white mica near the high Ti content area of the quartz grains, suggesting pinned grain boundaries. (g) WDS Si map for a retrogressed mafic eclogite (06-002bv). (h) CL Ti image for a retrogressed mafic eclogite (06-002bv), case c described in text (Section 2.5.1). Low Ti cores and relatively high Ti rims, across three quartz grains separated by high-angle grain boundaries. This pattern is seen only in retrogressed mafic eclogites and appears to reflect prograde growth at HP conditions.

brightness correspond to relative variations in Ti concentration of 5 – 40 ppm at a spatial scale of <500 μm . The intra-grain domains with variable Ti concentrations suggest some zonation of Ti content as the result of either diffusion or growth. Examples of intra-granular variation in Ti content include: (a) grains with high Ti cores and thin low Ti rims (Fig. 2.9c,d), (b) large ($\sim 300 \mu\text{m}$) quartz grains with a uni-directional increase in Ti content in grains (found in six samples of migmatitic gneiss and metamorphic granodiorite; Fig. 2.9e,f), and (c) quartz grains (100 – 250 μm) with low Ti cores and high Ti rims (found in four samples of retrogressed eclogite; Fig. 2.9g,h).

As the boundaries between the high and low zones of Ti content (case a – c above) are diffuse on the CL images, it is difficult to determine if growth zonation or diffusion caused the less common intra-granular variation in Ti content. I measured the distances between these zones as an approximation of potential diffusion lengths, and compared these distances to diffusion lengths for Ti in quartz predicted by Cherniak et al. (2007). If the maximum duration for volume diffusion of Ti through the quartz lattice I allow is $\sim 2.5 - 3.0 \text{ Ma}$ (age of amphibolite-facies metamorphism), and the maximum estimate of temperature of the amphibolite-facies retrogression is taken to be $\sim 730^\circ\text{C}$, then the maximum possible diffusion distance of Ti through the quartz lattice at the temperature of interest would be $\sim 140 \mu\text{m}$ (*Chapter 3 this thesis*; Baldwin et al., 1993; Gordon et al., *in review*). This is an overestimate of diffusion distance as the rocks did not remain at $\sim 730^\circ\text{C}$ during the entire crustal exhumation, nor did they ascend to the surface instantaneously in the present-day. The high Ti cores and thin low Ti rims (case a above) occur on length scales of $\sim 10 \mu\text{m}$ in 20 samples across all five rock types analyzed here. Based on the length scale of case a, it is possible that volume diffusion of Ti may account for some of the narrower zonation exhibited by the CL images. The low Ti cores and high Ti rims present in samples of retrogressed eclogite occur on a length scale of $\sim 200 \mu\text{m}$ and the uni-directional increases in Ti content occur over distances of $300 \mu\text{m}$ (Fig. 2.9f,h). These latter patterns (case b and c above) cannot be the result of post-growth diffusion and were probably inherited from metamorphic grain growth (relict quartz from previous high-temperature crystallization events). The presence of mica near the edges of one of the quartz grains imaged by CL that exhibits a uni-directional increase in CL brightness (e.g. Fig. 2.9e,f) may suggest that mica grains have pinned

certain quartz grain boundaries. These grain boundaries may have been sheltered from the otherwise pervasive dynamic recrystallization, resulting in the preservation of growth zonation in some of the relict quartz.

Inter-granular variation in Ti content is typically much larger relative to the intra-granular variation in Ti content shown in the CL images (Fig. 2.10). Approximately 65% of the CL images exhibit relative differences in Ti content of $\sim 2 - 20$ ppm between quartz grains (Fig. 2.10). These inter-granular Ti variations imply that the quartz grain assemblage in samples analyzed here consists of mainly internally homogenous quartz grains of variable mean Ti content. The internal homogeneity in Ti content in the quartz grains implied by the LA-ICP-MS calibrated CL images suggests the quartz grains underwent either recrystallization or growth at near constant temperatures, or homogenization as a result of diffusion (Spear and Wark, 2009). The characteristic transport distance for Ti-in-quartz for a time lapse of 2.5 – 3.0 Ma between the amphibolite-facies metamorphism and emplacement in the upper crust is ~ 40 μm at 600 °C and 1,300 μm at 800 °C, as determined by Cherniak et al., (2007; *Chapter 3 this thesis*; Gordon et al., *in review*). Eighty percent of TitaniQ apparent temperatures calculated by this study are ≤ 600 °C (Table 2.1), suggesting that volume diffusion would only have affected a few tens of microns of the quartz grains. It is therefore unlikely that volume diffusion was the primary factor in the distribution of Ti within the 200 – 500 μm diameter quartz grains in the D’Entrecasteaux Islands. It is also unlikely that growth at near constant temperatures would cause the homogeneity within the quartz grains, as GBM recrystallization has pervasively affected quartz grains. I therefore suggest that the inter-granular variation in Ti concentration (typically 2 – 20 ppm) and the relatively flat or homogeneous intra-granular variation in Ti concentration (< 5 ppm) records Ti resetting during this GBM recrystallization. The inter-granular differences in Ti content may suggest that the quartz grain population is a mixture of older, Ti-rich and more recently recrystallized, Ti-poor quartz grains as a result of ongoing dynamic recrystallization during exhumation of the rocks.

a) 06-005aii, quartzofeldspathic granodiorite, Goodenough core (WDS silica map)

b) 06-005aii, quartzofeldspathic granodiorite, Goodenough core (CL titanium map)

c) 06-020eii, quartzofeldspathic gneiss, Goodenough carapace (WDS silica map)

d) 06-020eiii, quartzofeldspathic gneiss, Goodenough carapace (CL titanium map)

Figure 2.10 Selected wavelength-dispersive spectrometry (WDS; on the left-hand side) and cathodoluminescence (CL; on the right-hand side) images showing inter-granular variation in Ti content: Fld, feldspar; Qtz, quartz; WM, white mica. Warm red colors denote relatively high Ti content and cool blue colors denote relatively low Ti content. Black circles denote locations of LA-ICP-MS analysis sites with titanium concentration in ppm by weight. (a) WDS Si map for a quartzofeldspathic granodiorite (06-005aii). (b) CL Ti image for a quartzofeldspathic granodiorite (06-005aii). The differences in Ti content are much more significant between quartz grains than within them. The patches of slight (<1 ppm) Ti variation as described in text occur, and are much less significant than the difference in CL brightness between the grains. (c) WDS Si map for a quartzofeldspathic gneiss (06-020eii). (d) CL Ti image for a quartzofeldspathic gneiss (06-020eii). Again, note that the differences in CL brightness is much more significant between quartz grains than within grains.

2.5.2 Ti content in the quartz grains and TitaniQ apparent temperatures

Fig. 2.11 illustrates a linear relationship (correlation coefficient = 0.82) between the mean Ti concentration of each sample in ppm and the variance of the Ti concentration (95% confidence interval) in that sample. This relationship implies that a sample with a high apparent temperature will have a high variability of Ti content between quartz grains, relative to samples with low apparent temperatures. The mean Ti concentration for a sample calculated by this study is an average of up to eight analyses, each of which may have a different Ti content. Older quartz grains may preserve a high Ti content inherited from a higher-temperature stage in the history of ultra high pressure-bearing gneisses. The mixture of such Ti-rich relict quartz grains with more newly recrystallized (lower temperature) quartz grains may lead to a high variability of Ti content in the most rapidly exhumed rocks.

To determine if there are obvious first-order effects on the variations in Ti content within the D'Entrecasteaux Islands, I have compared mean Ti concentrations and TitaniQ apparent temperatures averaged by lithology, structural zone, and location (Fig. 2.12). For the entire data set, the averaged Ti concentrations generally vary from 10 – 20 ppm, corresponding to a calculated range of TitaniQ apparent temperatures of 500 – 600 °C (Fig. 2.12). As high-temperature grain-boundary migration recrystallization is thought to require temperatures of >500 – 550 °C, the average TitaniQ apparent temperatures calculated here correlate well with deformational temperatures predicted for the final stages of quartz recrystallization (Fig. 2.6; Stipp et al., 2002). Fig. 2.12a and 2.12d illustrate Ti concentrations averaged in categories corresponding to the four main rock types analyzed here (quartz veins, metamorphic granitic rock, eclogite, quartzofeldspathic gneiss). There is no statistical difference in mean Ti concentration between the four different rock types, implying that lithological variation is not the main control on Ti content in quartz. Fig. 2.12c and 2.12f show a comparison of average Ti concentration for samples in the core and carapace zone of the individual gneiss domes. These data reveal that only the Goodenough dome shows a statistically significant difference in the mean Ti concentration between the core and carapace zones as averaged across all samples. The northwest Normanby dome has minimal difference in the Ti

Figure 2.11 95% confidence interval of each sample's mean Ti concentration measurement as a function of that sample's mean Ti concentration in ppm by weight (correlation coefficient of 0.82). Each mean Ti concentration represents up to eight LA-ICP-MS spot analyses at both core and rim positions of the quartz grain.

Figure 2.12 (a) and (d) show the averaged Ti concentration in quartz and the averaged TitaniQ apparent temperatures calculated by the Wark and Watson (2006) calibration compared to lithology respectively (error bars represent the two standard errors). Note that averaged Ti concentrations in quartz include both rutile and non-rutile bearing samples and that there is no difference in Ti concentration between lithologies. (b) and (e) show the averaged Ti concentration in quartz and the averaged TitaniQ apparent temperatures calculated by the Wark and Watson (2006) calibration respectively compared to structural zone (error bars represent the two standard errors). (c) and (f) show the averaged Ti concentration in quartz and the averaged TitaniQ apparent temperatures calculated by the Wark and Watson (2006) calibration respectively, compared to the structural zone within each gneiss dome (error bars represent the two standard errors). Note that averaged Ti concentrations include both rutile and non-rutile bearing samples. The northwest Normanby dome has a negligible slope because of the inclusion of several samples with relatively high Ti concentrations (e.g. 10-021a; Fig. 2.13, 2.14) into the average Ti concentrations for the core and carapace of this dome.

concentration or apparent temperature between the core and carapace zones. These similar temperatures in the core and carapace zone of the northwest Normanby dome may result from the proximity of a large body of leucogranodiorite, resulting in several samples of carapace rock with high Ti concentrations (e.g. 10-021a) relative to the majority of samples situated near the dome margins. I note that the high average Ti concentration of samples from the core of the Goodenough dome and the low average Ti concentration of the samples from the carapace of the Morima dome strongly influence the bulk core and carapace zone Ti content in quartz in Fig. 2.12b and 2.12e.

Ti concentrations in quartz are plotted on a map of the northwest D'Entrecasteaux Islands in Fig. 2.13 with warm colors denoting high Ti concentrations. Ti concentrations in the northwest Normanby dome are lower (2.5 – 7.5 ppm) near the coast and higher (10.0 – 15.0 ppm) in the interior of the dome; however the pattern at the northwest end of the dome is complex with several coastal samples adjacent to the leucogranodiorite body in conflict with the aforementioned trend. The Morima dome shows lower Ti concentrations (2.5 – 5.0 ppm) near the south-central coast of Fergusson Island close to the bounding normal fault, and higher Ti concentrations (5.0 – 7.5 ppm) in a sample located closer to the dome's interior. In the Mailolo dome there are low Ti concentrations (5.0 – 10.0 ppm) near the south and northwest coasts, and higher Ti concentrations (10.0 – 20.0 ppm) in the interior of the dome. A few samples with relatively high Ti concentrations (20.0 – 25.0 ppm) appear scattered throughout this dome. The Goodenough dome has, in general, lower Ti concentrations (7.5 – 12.5 ppm) near the dome-bounding fault on its northeast margin and higher Ti concentrations (20.0 - >100 ppm) in the interior of the dome. Ti concentrations on the southwest margin of the Goodenough dome are higher on the outer southwest margin of the Goodenough dome (>20 ppm) relative to those near the northeast dome-bounding fault, and are generally lower than Ti concentrations in the interior of this dome. These results have also been projected onto a series of schematic structural cross-sections (Fig. 2.14a-d).

Fig. 2.15a-e illustrates regression analyses of the sample-averaged Ti concentrations as a function of their distance from five of the major dome-bounding normal faults in

Figure 2.13 Simplified structural map of the northwest D'Entrecasteaux Islands showing spatial pattern of mean Ti concentration as averaged per sample (adapted from Little et al., 2011). See Fig. 2.3 for sample numbers and Fig. 2.1b for figure location. Cross-section lines are shown for Fig. 2.14 and 2.15. Colors are coded by relative Ti concentration, with warmer colors denoting higher Ti.

Figure 2.14 Schematic structural cross-sections (no vertical exaggeration) across four gneiss domes in the D'Entrecasteaux Islands after Little et al. (2011): PUB, Papua Ultramafic Belt; Volc., volcanics.. Structural data is from the unpublished GIS database of Tim Little (Victoria University of Wellington). These cross-sections show horizontal pattern of Ti concentrations as averaged per sample. Line orientations shown in Fig. 2.13. Colors are coded by relative Ti concentration, with warmer colors denoting higher Ti concentrations. (a) A-A', northeast-southwest structural cross-section across Goodenough dome. (b) B-B', northeast-southwest structural cross-section across Mailolo dome. (c) B''-B''', northeast-southwest structural cross-section across Morima dome. (d) C-C', northwest-southeast structural cross-section across northern Normanby dome. Note that only samples that are within ~5km of the cross-section line are included in the horizontal pattern of Ti concentrations portrayed here.

the D'Entrecasteaux Islands. These analyses were carried out on Ti content in quartz for samples that are within ~5 km of the five normal faults examined here. All of linear regressions in Fig. 2.15 show an inward increase in Ti concentration away from the dome margins. Linear regressions presented here with high R^2 values may in part be an artifact of a low sample density or a bias in the sample set toward the carapace (i.e. $R^2 = 0.97$ for the southwest coast of Morima dome near the Morima Fault; Fig. 2.15c). R^2 values for samples on the northeast coast of Goodenough dome near Wakonai Fault ($R^2 = 0.31$; Fig. 2.15a), northeast coast of Mailolo dome near Mwadeia Fault ($R^2 = 0.16$; Fig. 2.15b), and the southeast coast of northwest Normanby dome near the northwest Normanby fault zone ($R^2 = 0.06$; Fig. 2.15d) show a weak fit of the inwardly-increasing regression line to the data points.

As the Goodenough dome has the densest concentration of samples, Ti concentrations measured in this dome were used to calculate TitaniQ apparent temperatures with three different Ti activity coefficients (0.4, 0.6, 0.8) for both the Wark and Watson (2006) calibration and the Thomas et al., (2010) calibrations (Fig. 2.16). All linear regressions of the data in Fig. 2.16b and 2.16c have a positive slope with an apparent horizontal (inward) temperature gradient of $26 - 34\text{ }^{\circ}\text{C km}^{-1}$. A comparison between the two calibrations indicates that the Wark and Watson (2006) calibration yields cooler apparent temperatures and produces a lower degree per kilometer gradient. Important here, however, is that the positive slope in apparent temperatures derived from each calibration and activity appears to be a robust feature of both calibrations, as quartz in the interior of each dome has a high Ti content on average relative to quartz grains on the margins of the domes. The Wark and Watson (2006) calibration was established at a pressure of 10 kbar, which is within error of the suggested 7 – 11 kbar pressure for the main amphibolite facies overprint that was

Figure 2.15 Mean Ti concentration as a function of structural depth in the D'Entrecasteaux Islands. Locations of plots a-e are shown in Fig. 2.13 along the cross-section profiles, however samples from further afield (along the coasts of the islands within ~5000 m of the dome-bounding faults) are included in the data set. Errors are 95% confidence intervals for the mean Ti concentration (Appendix B.2). (a) Northeast coast of Goodenough dome near Wakonai Fault (A-A'; Fig. 2.13). (b) Northeast coast of Mailolo dome near Mwadeia Fault (B, Fig. 2.13). (c) Southwest coast of Morima dome near Morima Fault (B'''-B'', Fig. 2.13). (d) Northwest coast of northwest Normanby dome near the northwest Normanby fault zone (C', Fig. 2.13). (e) Southeast coast of northwest Normanby dome near the southeast Normanby fault zone (C, Fig. 2.13).

Figure 2.16 Comparison of TitaniQ apparent paleo-temperatures calculated for a Ti concentration data set from the Wakonai Fault, Goodenough dome as a function of assigned activities and calibrations. (a) Mean Ti concentration (in ppm by weight) for each sample within 4000 m for the Wakonai fault, Goodenough dome. Errors are 95% confidence intervals. (b) and (c) show linear regression of TitaniQ apparent temperatures calculated using the Ti concentrations in (a) and the Wark and Watson (2006) and Thomas et al. (2010) calibrations respectively. Three different titanium activities were assigned to determine the effect of variations in Ti activity on the gradient in TitaniQ apparent temperatures. Average two standard errors for all data points used for the linear regression is quoted in the legend. The preferred titanium activity for non rutile-bearing quartz grains in the D'Entrecasteaux Islands is 0.8 (see text). Not that the gradient in TitaniQ apparent temperatures does not significantly change for either the two different calibrations or the three different activities assigned here, suggesting that the slope of the regression fit is always positive.

input into the pressure-sensitive Thomas et al., (2010) calibration (Section 2.4.2). Although I attempted to include the incremental effect of additional structural burial in the direction orthogonal to the main foliation in the Goodenough dome, the change in pressure between the shallowest and deepest samples is small (0.70 kbar) and does not yield an appreciable difference in the overall gradient in apparent temperatures.

2.6 Discussion

2.6.1 Fluid control on the uptake of Ti into the quartz tetrahedral

Wilson et al., (*in review*) undertook a review of the Thomas et al. (2010) calibration of the TitaniQ. These authors argue that the exchange reaction of Ti between quartz and rutile is mediated by a fluid phase that includes dissolved Ti complexes with partition coefficients of Ti between quartz and rutile not allowed for in the original calibrations. The chemistry of this fluid may therefore exert a first-order control on the uptake of Ti into the quartz grains (Wilson et al., *in review*). Such equilibrium reactions between quartz and aqueous Ti complexes are outside the original experimental conditions used in the Wark and Watson (2006) and the Thomas et al., (2010) experimental calibration studies. Wilson et al., (*in review*) argue that fluid control on the Ti uptake into quartz would adversely affect the applicability of the TitaniQ, as both calibrations are based on a simple three component system of quartz, rutile, and water, and assume that fluid phase for the $Si^{4+} \Leftrightarrow Ti^{4+}$ exchange between quartz and rutile is unimportant. Wilson et al., (*in review*) suggest that the TitaniQ geothermobarometer is therefore only valid in the pure SiO_2 (quartz) - TiO_2 (rutile) - H_2O system and cannot be extrapolated to natural systems, as they are relatively complex with a variable fluid composition.

A possible analogy for the chemical behavior of Ti-in-quartz solubility is the Al-in-quartz geothermometer, which was first proposed by Dennen et al. (1970; Wilson et al., *in review*). Like the TitaniQ, the Al-in-quartz geothermometer assumes that the equilibrium between solid phases defines the solubility of Al within quartz (Dennen et al., 1970). A later study by Scotfeld (1975) found that there is no linear

relationship between Al concentration in quartz and a range of apparent temperatures of crystallization determined by geological and mineralogical criteria. Based on this lack of a collinear variation, the uptake of Al into quartz may not be a simple function of the temperature of crystallization and instead may be controlled by physical conditions such as melt and fluid chemistry (Botis and Pan, 2009 *and ref. therein*; Scotfeld, 1975). Thus, the composition and chemistry of the fluid may control the uptake of Al into the Si tetrahedral site in quartz. Wilson et al., (*in review*) and Huang and Audétat (2011) observe a clear linear relationship between Al and Ti in volcanic and hydrothermally grown quartz crystals. Wilson et al., (*in review*) argue that this covariance implies that the uptake of Ti into quartz is controlled by fluid composition, similar to the affect of fluid chemistry on the uptake of Al into quartz. Thus, the fluid or melt composition exerts a control over both elements, and a direct proportionality between Al and Ti content in quartz crystals may imply that the uptake of Ti into quartz is primarily controlled by fluid chemistry of the system and is not strictly temperature-dependent (Huang and Audétat, 2011; Wilson et al., *in review*).

Fig. 2.17 illustrates the relationship between the mean Al concentration and the Ti concentration for all samples analyzed by this study. Fig. 2.17 does not show a clear collinear trend between the mean Al and Ti concentration for each sample (correlation coefficient = 0.20). This lack of direct proportionality implies the uptake of Ti into the quartz structure in these dynamically recrystallized quartz grains was not primarily dependent on the solubility of Ti in a host fluid. In addition, this study is focused on interpreting spatial gradients in Ti content and TitaniQ apparent temperatures, and the debate of the thermodynamic validity of the TitaniQ may be less crucial here relative to studies concerned with absolute TitaniQ temperatures.

2.6.2 Testing the activity model of the calculated apparent temperatures for rutile-bearing and non rutile-bearing samples

To test the appropriateness of the assigned activity coefficients (Section 2.4.2), I undertook a comparison of TitaniQ apparent temperatures calculated for rutile- and non rutile-bearing samples within 1 km of each other in the D'Entrecasteaux Islands. This comparison is important as the single variable with the most effect on the 95%

Figure 2.17 Mean Al concentration (in ppm by weight) versus mean Ti concentration (in ppm by weight) for each sample analyzed for Ti content in this study. Note the lack of an obvious co-linear trend (correlation coefficient of 0.20). Errors are the analytical error, which is a weighted two standard deviation of the LA-ICP-MS Ti and Al analytical precision.

confidence interval of the TitaniQ apparent temperatures is the assigned uncertainty in the α_{TiO_2} (± 0.2 ; Section 2.4.2). The linear regression in Fig. 2.18a has a slope of 0.94 and a correlation coefficient of 0.74, which suggests that there is a one-to-one linear relationship, or a proportionally, between the adjacent samples that contain rutile and non-rutile assemblages. Fig. 2.18b compares apparent temperatures calculated from adjacent samples with rutile-bearing assemblages and non-rutile bearing assemblages. All of the rutile-bearing apparent temperatures are within the 95% confidence interval of the non-rutile bearing apparent temperatures. In addition, the rutile-bearing samples do not exhibit a systematic relationship (i.e. higher or lower apparent temperatures) relative to the non rutile-bearing samples. Thus, the TitaniQ apparent temperatures calculated for the rutile-bearing samples accord well with the apparent temperatures for the non-rutile bearing samples, implying that the assigned activity coefficients are accurate.

2.6.3 Application of the TitaniQ to metamorphic rocks

The TitaniQ thermometer was originally calibrated for igneous quartz (600 – 1000 °C), whereas quartz grains analyzed in this study occur in a ductilely deforming metamorphic context. Ti content in metamorphic quartz can be affected by several different processes: solid-state volume diffusion of Ti within or between quartz grains and other adjacent minerals, introduction of aqueous Ti-rich fluids along quartz grain boundaries, and static or dynamic recrystallization which may completely reform the quartz grain causing Ti re-equilibration (Spear and Wark, 2009). Mean Ti concentrations and TitaniQ apparent temperatures averaged for different bulk composition are compared in Fig. 2.12a. From this data, I infer that bulk composition does not exert a first-order control on Ti content, nor do the eclogite samples return Ti concentrations that are significantly higher than other lithologies that were retrogressed in amphibolite-facies conditions. The Ti concentrations measured in this study are recording Ti equilibration occurring during the final stages of the exhumation history of the migmatitic rocks, presumably in the mid to upper crust at the time of final gneiss dome emplacement (Fig. 2.6; Baldwin et al., 1993).

Figure 2.18 (a) TitaniQ apparent temperatures calculated for samples with a non-rutile bearing assemblage as a function of TitaniQ apparent temperatures calculated for samples with a rutile-bearing assemblage. Samples are from the same or immediately adjacted localities. All apparent temperatures are calculated by the Wark and Watson (2006) calibration. Note the the slope of the regression line is 0.94; this relationship implies a near 1:1 correlation between TitaniQ apparent temperatures calculated for rutile and non-rutile assemblages (correlation coefficient of 0.74). Errors are a 95% confidence interval of the quotient and include analytical, calibration, and Ti activity uncertainty (Section 2.5.2, Table 2.1). (b) TitaniQ apparent temperatures calculated by the Wark and Watson (2006) calibration as a function of location and Ti phase present in the assemblage. Rutile-bearing samples are outlined in black. Errors are a 95% confidence interval of the quotient and include analytical, calibration, and Ti activity uncertainty (Section 2.5.2, Table 2.1). Note that all apparent temperatures that we calculated for rutile and non-rutile bearing adjacent samples are within 95% confidence interval.

Recrystallized quartz grains analyzed in this study exhibit highly interlobate to amoeboid grain boundaries. These microstructures, along with the typically homogeneous within-grain Ti variation (Section 2.5.1), imply that the chief mechanism responsible for Ti distribution within the quartz grains was dynamic recrystallization via high-temperature GBM. Based on this extensive crystallization, and the lack of any clear lithological control on the Ti content in quartz, I infer that the chief physical or chemical process responsible for the equilibration of Ti in quartz grains was recrystallization by GBM. This GBM may have included diffusion of Ti into grain-boundary fluids during the rapid migration of grain boundaries that accompanied continuing deformation (Grujic et al., 2011). This inference is similar to that of Grujic et al. (2011), who used the TitaniQ to elucidate how Ti equilibrated in quartz grains in the exhumationally static situation of a metamorphic aureole around the Adamello pluton near the Tonale Fault Zone in northern Italy. These authors argue that GBM was the chief process causing re-equilibration of Ti within and between quartz grains, with a possible subordinate contribution by pipe diffusion along dislocation pathways in the deformed quartz grains.

The mean Ti content in quartz and its variance may have been chiefly influenced by the ratio of the rock's rate of cooling and recrystallization during the rapid exhumation of the gneisses. As previously discussed, the widespread presence of a melt phase (leucosomes) in the migmatitic rocks in the D'Entrecasteaux Islands implies that rocks with a granodioritic composition (gneiss protoliths) were once heated to temperatures of $>650\text{ }^{\circ}\text{C}$ (Fig. 2.6; Brown, 2008; Hacker, 2006; White, 2008). In addition, the common presence of chessboard subgrains structure in quartz implies temperatures of at least $630 \pm 30^{\circ}\text{C}$ during the exhumation history of the rocks (Fig. 2.6; Stipp et al., 2002); however, 93% of the measured TitaniQ apparent temperatures are $<630\text{ }^{\circ}\text{C}$ (Table 2.1). Based on these temperature constraints, and the pervasive evidence of GBM in these quartz grains, I suggest that the observed Ti content in quartz in the exhumed rocks reflects a competition between two processes: a) the rate by which the rocks cooled during their exhumation, leading to a progressively lower Ti concentration being present in subsequent generations of quartz grains, and b) the rate of dynamic recrystallization, which controls the time scale of Ti-resetting in the deforming aggregate of quartz grains. This relationship may be visualized in newly recrystallized grains as:

$$[Ti_{qtz}] \propto \frac{\text{cooling rate}}{\text{recrystallisation rate}} \quad (2.7)$$

where $[Ti_{qtz}]$ is the mean Ti concentration in a sample of dynamically recrystallized quartz grains (in ppm by weight). As previously discussed, dynamic recrystallization together with diffusion into grain-boundary fluids along merging grains boundaries may have controlled the re-distribution of Ti within and between the assemblage of relict and new quartz grains that compose a sample. Thus, either a fast cooling rate or a low rate of recrystallization would result in the preservation of a large fraction of relict high-temperature grains in a sample. On the other hand, if the rate of cooling is low or the rate of dynamic recrystallization is fast, then few such relict high-temperature grains will be preserved in a rock that has been exhumed from high-temperature conditions at depth. Recrystallization would have terminated abruptly after the rocks were exhumed into the upper crust at <2 Ma, after which the rocks are known to have cooled rapidly below temperatures of 300 °C at rates of >100 °C Ma⁻¹ (Baldwin et al., 1993; Little et al., 2011). After dynamic recrystallization ceased, the amoeboid grain structure would have been frozen in together with the observed Ti contents of these grains.

My hypothesis that the mean Ti content in quartz grains is controlled by the ratio of the rate of cooling versus the rate of recrystallization is supported by Fig. 2.11, which illustrates a linear relationship between the mean Ti concentration of each sample in ppm and the 95% confidence interval of the mean Ti concentration for each sample (correlation coefficient = 0.82). Assuming a constant rate of recrystallization, a sample with a relatively fast cooling rate would contain not only a sub-population of newly formed low-temperature grains, but also a relict population of grains with high Ti content. As recrystallization is continuous, the quartz assemblage in this fast-cooling sample would include quartz grains with relatively lower Ti content, resulting in a diverse quartz assemblage and a high standard deviation of Ti concentration within this sample. By contrast, a population of quartz grains with a more uniform Ti content might dominate a thoroughly recrystallized sample that has experienced a slow cooling rate. The recent study by Grujic et al. (2011) suggests that there is a wider within-sample spread of Ti in zones with GBM, relative to zones with low-temperature deformation regimes (bulging recrystallization and subgrain rotation recrystallization). This relationship supports

my conclusion that a shorter equilibration period (and/or a fast cooling rate) results in large scatter of Ti content between individual quartz grains in a single sample.

2.6.4 Interpretation of the spatial pattern of TitaniQ apparent temperatures

If equation 2.7 is approximately correct, and if I assume the rate of recrystallization varies less than the rate of cooling across the gneiss domes in the D'Entrecasteaux Islands, then gradients in mean Ti concentrations and TitaniQ apparent temperatures may be interpreted as a proxy for gradients in cooling rates within these domes. Thus, in a rapidly exhuming body an area with predominantly high mean Ti concentrations would signify a zone of high cooling rate, and an area with predominantly low mean Ti concentrations could signify a zone of low cooling rate. For a steady-state scenario, such relative differences in cooling rates might also correspond to zones of higher and lower exhumation rates, and higher and lower finite exhumation levels. Exhumation in the D'Entrecasteaux Islands was near-isothermal from the mantle to the middle crust (Fig. 2.6), therefore any gradients in cooling rates observed across the domes (via proxy) would have been created as the gneiss domes in the middle to upper crust (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008). At the time of final dome emplacement, the Ti content was locked in when dynamic recrystallization by high-temperature GBM ceased, preserving the gradients in cooling rates and exhumation rates.

The inwardly increasing pattern of mean Ti concentrations across the D'Entrecasteaux Island gneiss domes implies that the most rapid rates of cooling and exhumation did not occur in proximity to the dome-bounding normal faults, but in the central part of each gneiss dome (Fig. 2.15a-e). When all samples are divided into core zone and carapace zone categories, the former averages a Ti concentration of $\sim 20 \pm 3$ ppm (2σ) and the latter averages 11 ± 1 ppm (2σ), implying that the core zones were “hotter” at the time of final quartz recrystallization relative to the carapace samples (Fig. 2.12b, 2.12e). Although the Ti concentrations gradients include significant variability or “noise”, all mean Ti concentrations gradients in Fig. 2.15 indicate a statistically robust increase of Ti content in quartz away from the dome margins. The dome with the highest increase in apparent cooling rates from the

margin into the interior is the Goodenough dome (Wakonai Fault; Fig. 2.15a), possibly because samples here originate from the Goodenough gorge (Fig. 2.13). This ~200 meter deep gorge has eroded the Goodenough dome more deeply than any of the other gorges sampled here. In other words, the samples from the Goodenough gorge represent the deepest exposed structural level in a dome, which has not been sampled in the other less eroded domes of the D'Entrecasteaux Islands. Alternatively, the high Ti content in the interior of the Goodenough dome may suggest that this area experienced a fast cooling and exhumation rate that relative to the other dome interiors. The second highest increase in relative cooling rates is seen in the southeast of the northwest Normanby dome (Fig. 2.15d), a locality that has five analyzed samples that are closely spaced. The transect orientation in the latter dome is nearly orthogonal to the main foliation, which dips particularly steeply on the dome margins. This steep dip would decrease the horizontal separation between samples of contrasting original structural depth. The other three transects (Fig. 2.15b,c,e) yielded similar inward increases in mean Ti content in quartz and apparent relative cooling rates. The low increase in mean Ti concentration within the Mailolo dome (Fig. 2.15b) may be the result of the shallow foliation dips within this dome relative to the other domes, and a low amount of erosion of that dome relative to the more deeply incised Goodenough dome.

I acknowledge that the linear relationship between Ti content and horizontal position in the domes (Fig. 2.15) is not strong, as is expressed by the small R^2 values for the regressed lines ($R^2 = 0.03 - 0.36$). The statistical probability that the signs of the slopes of the regressed lines in Fig. 2.15 are actually zero or negative was assessed using a one-sided t distribution. See Appendix B.3 for slope standard deviation and probabilities. This analysis indicates that the linear relationship between Ti concentration and distance from the fault has a <8% probability of having a negative slope (with Ti concentration increasing towards the dome margins) for the Wakonai, Mwadeia, Morima, and southeast Normanby faults and fault zones. The northwest Normanby regression has a 35% probability of an increase in Ti concentration towards the dome margins.

The low R^2 values of the linear regressions in Fig. 2.15 reflect up to 30 ppm of sample-to-sample variation in mean Ti concentration. The causes of such variability

include infiltration of local, chemically diverse Ti-bearing fluids, the composition of which affected the Ti content of quartz grains in the certain samples prior to the final high-temperature GBM recrystallization. Additionally, inclusions of Ti-bearing impurity phases (e.g. rutile exsolution needles) in the material measured by the LA-ICP-MS would have caused apparent differences in Ti concentrations that are unrelated to the temperature of quartz growth or recrystallization. Another possible source of sample-to-sample variation in Ti is the core and rim variations in Ti content in the quartz grains (Section 2.5.1). This zonation implies that post-growth GBM recrystallization did not cause a complete Ti equilibration to a uniform Ti concentration for all quartz grains in every lithology of the D'Entrecasteaux Islands. The thin rims (pattern a, Section 2.5.1) have a length scale of a few tens of microns at the extreme; therefore this within-grain Ti content variation is volumetrically insignificant and could not cause the observed sample-to-sample variation in Ti concentration (Fig. 2.15). Where observed, the relict growth zoning (pattern b and c, Section 2.5.1) has a length scale of 300 – 500 μm (Fig. 2.9f,h). Across one such zone in a sample of migmatitic gneiss the relative difference in Ti concentration is ~ 22 ppm (09-004civ; Fig. 2.9e,f). Relict (unrecrystallized) quartz grains in analyzed samples of metamorphic granodiorite (Fig. 2.9e,f) and retrogressed eclogite (Fig. 2.9g,h) would therefore contribute spot analyses with Ti concentrations that are high relative to the mean Ti content in a sample, which is volumetrically dominated by recrystallized quartz grains that are younger and have a lower Ti content.

2.6.5 Comparison of TitaniQ apparent temperatures to $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages

The majority of the $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages for white mica and biotite determined by (Baldwin et al., 1993) for samples in the D'Entrecasteaux Islands exhibit relatively flat age spectra, implying that the samples cooled rapidly ($200 - 400\text{ }^{\circ}\text{C Ma}^{-1}$) and were not disturbed once they cooled below the closure temperature (Dodson, 1973). The closure temperature for Ar is $350 - 450\text{ }^{\circ}\text{C}$ in white mica, and $300 - 350\text{ }^{\circ}\text{C}$ in biotite (Baldwin et al., 1993; McDougall and Harrison, 1999). Fig. 2.19 exhibits a plot of TitaniQ apparent temperatures as a function of white mica and biotite $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages for samples adjacent to samples used in the Baldwin et al., (1993) study. Fig. 2.19 implies a correlation may exist between the white mica and biotite $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages and the TitaniQ apparent temperatures (correlation

Figure 2.19 $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages from Baldwin et al. (1993) as a function of TitaniQ apparent temperatures calculated in this study using the Wark and Watson (2006) calibration. There is < 1 km vertical separation between the samples from which the $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages were calculated and the TitaniQ samples presented in this graph. Note that the higher TitaniQ apparent temperatures correspond to younger cooling ages (correlation coefficient = -0.54). The errors in the TitaniQ apparent temperatures are 95% confidence intervals and include analytical, calibration, and Ti activity uncertainty (Section 2.5.2, Table 2.1).

coefficient = -0.54). In other words, samples with the youngest cooling ages experienced the most rapid cooling and yielded the highest TitaniQ apparent temperatures. This relationship supports my inference that the Ti content in quartz was chiefly controlled by the rate of cooling in the rocks as they dynamically recrystallized. The $^{40}\text{Ar}/^{39}\text{Ar}$ data is, however, currently too sparse to make any clear inferences regarding spatial gradients in $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages across the gneiss domes (Baldwin et al., 1993).

2.6.6 Kinematics of gneiss dome emplacement in the D'Entrecasteaux Islands

The lack of evidence for any increase in exhumation rates or cooling rates outward towards the dome-bounding faults supports a symmetric doming (or diapiric) model of gneiss dome formation (Fig. 2.2a). Cooling rates within a rising diapir will be relatively slow compared to those near their margins (Faydon et al., 2004). Within an asymmetrical metamorphic core complex, cooling rates are predicted to be fastest immediately adjacent to the detachment, where the most rapidly exhumed and hottest footwall rocks will be juxtaposed against the relatively cold hanging wall (Faydon et al., 2004). This asymmetrical juxtaposition will result in a maximum predicted cooling rate immediately adjacent to the detachment faults. In the D'Entrecasteaux Islands, however, the highest Ti content and TitaniQ apparent temperatures are located in the interiors of the gneiss domes (Fig. 2.13).

The two models I have compared here are end-members and a continuum between detachment-related metamorphic core complexes and the pure-shear symmetric doming is likely to exist in nature (Leech, 2001; Little et al., 2011; Norlander et al., 2002; Whitney et al., 2004). This continuum may in part result from competition between localized slip on the normal dome-bounding faults and gravitational forces that affect the gneiss domes and metamorphic core complexes (Little et al., 2011). For example, Whitney et al. (2004) state that diapirism may have a passive role in extension, resulting in the exhumation of metamorphic core complexes. It is also possible for gneiss domes to be nested within metamorphic core complexes (i.e. the Thor-Odin dome within the Shuswap metamorphic core complex; Hinchey and Carr, 2006; Norlander et al., 2002; Whitney et al., 2004). For example, the Mailolo dome

contains a partial melt component that is low compared to that of the Goodenough dome (Section 2.2.2). This apparent difference in partial melt may have resulted in a lower buoyancy force and a greater component of localized slip affecting the uplift of the gneisses, and may have contributed to the unclear pattern of TitaniQ apparent temperatures shown in Fig. 2.13 and 2.15b.

A dominantly pure-shear symmetric diapiric origin for the gneiss domes is supported by the structural geology of the D'Entrecasteaux Islands (Little et al., 2011). Evidence for this includes stretching lineation trends that are nearly orthogonal to the direction of the rifting of the Woodlark and Australian plates, implying a gravitational driving force for the dome emplacement and decoupling of the domes from extensional plate tractions in the rift (Little et al., 2011). Moreover, shear-senses in the domes are bivergent, implying an approximate bulk pure-shear deformation (Little et al., 2011). In addition, the rocks in the D'Entrecasteaux Islands contain structural evidence of a pure-shear dominated deformation, including lattice preferred orientations of quartz that exhibits orthorhombic symmetry (Little et al., *in prep.*). In parallel with the TitaniQ apparent temperature trends shown here, quartz crystallographic preferred orientations suggest an inward temperature increase from 400 – 500 °C (type 1 crossed girdle) to temperatures of >650 °C (prism-c) from the dome margins to their interiors (Little et al., 2010; Little et al., 2011). Also the inward increase in abundance of leucosomes and pluton volume into the core of the gneiss domes implies higher temperatures (and greater exhumation rates) in the cores of the domes relative to the dome margins.

It is important to note that the models for dome development I have considered are concerned only with the mode of final emplacement into the crust, rather than any of the older and deeper UHP history. The recrystallization of quartz grains within the crust represents only the final phase of a progression in recrystallization, beginning at the original eclogite-facies crystallization and metamorphism at UHP depths in the mantle (Fig. 2.6). The dominant model proposed here for the crustal exhumation accords with the diapiric exhumation from the mantle to the lower crust inferred by Little et al. (2011) on the basis of structural data.

2.7 Conclusions

Based on the predominantly homogenous intra-granular Ti distribution observed here by CL, and the pervasive evidence of dynamic recrystallization by high-temperature GBM, I conclude that the Ti content in quartz in rocks from the D'Entrecasteaux Islands are related to the final crustal emplacement of the gneiss domes. The presence of a pervasive melt phase and of chessboard microstructures in quartz implies that the rocks in the D'Entrecasteaux islands were once heated to temperatures $>630^{\circ}\text{C}$. Based on these temperature constraints, and the evidence of dynamic recrystallization, I suggest that the sample-averaged Ti content within the quartz grains in a hot and rapidly exhuming body depend on the relative rates of cooling and recrystallization in the body in the final phase of its ascent. Where the recrystallization rate varies less than the cooling rate across the rising body, Ti concentrations in quartz and TitaniQ apparent temperatures may be used as a proxy for relative cooling rates and may help constrain the exhumational processes.

Spatial gradients in Ti concentrations and deformational TitaniQ apparent temperatures are used here to constrain exhumation and cooling rates across the D'Entrecasteaux Islands. This is a novel application of the TitaniQ, and is particularly useful given the absence of mappable metamorphic isograds or metamorphic field gradients in these domes. I have demonstrated that higher mean Ti concentrations (20 – >100 ppm) are found in the interior of the gneiss domes and relatively low mean Ti concentrations (2.5 – 25 ppm) are found near their margins. The Ti content in quartz is intrinsically variable from one sample to the next, suggesting competing causes for Ti variation. I conclude, however, that the mean Ti concentrations and TitaniQ apparent temperatures in all four of the gneiss domes studied here increase inward into the dome core and away from the dome-bounding normal faults in a statistically robust way. The occurrence of the highest cooling rates in the interior of the gneiss domes, and in particular the lack of any unidirectional increase in Ti concentration toward the bounding normal faults, suggests that the gneiss domes in the D'Entrecasteaux Islands are not detachment-driven but are diapiric in origin. The data presented here supports previous structurally based

arguments by Little et al. (2011) that these gneiss domes were emplaced within the crust by predominantly pure-shear symmetric doming.

3. Rb-Sr dating of eclogite- and amphibolite-facies metamorphism in the D'Entrecasteaux Islands, southeastern Papua New Guinea

3.1 Introduction

The exhumation of coesite-bearing eclogite-facies rocks from ultrahigh-pressure (UHP) depths can occur at plate tectonic rates (cm yr^{-1} ; Baldwin et al., 2008; Chopin, 1984; Chopin, 2003; Glodny et al., 2005b; Parrish et al., 2006; Rubatto and Hermann, 2001; Smith, 1984). For example, the Dora Maira UHP terrane in the western Alps was exhumed from depths of 110 km to depths of <20 km at rates of $3.4 - 1.6 \text{ cm yr}^{-1}$ (Rubatto and Hermann, 2001). This rapid speed of exhumation from UHP conditions (>28 kbar) to the lower crust results in a short time lag between the original eclogite-facies crystallization at >90 km and any subsequent metamorphic retrogression in the lower crust (Baldwin et al., 2008; Gordon et al., *in review*; Holm et al., 1967; Monteleone et al., 2007). Because of the short time lag between metamorphism in the mantle and emplacement in the upper crust for rapidly exhumed UHP terranes, a single process may be predominantly responsible for the bulk of this exhumation (Little et al., 2011).

The D'Entrecasteaux Islands in southeastern Papua New Guinea (PNG) are comprised of several gneiss domes that consist chiefly of amphibolite-facies quartzofeldspathic gneiss (Fig. 3.1, 3.2; *Chapter 2 this thesis*). This metamorphic terrane includes mafic blocks that preserve an eclogite-facies mineral assemblage (5 – 10% volume; Little et al., 2011). To date, U-Pb geochronology on zircons and Lu-Hf geochronology on garnets yields age estimates of 8 to 4 Ma for the timing of the (U)HP metamorphic crystallization in these regionally metamorphosed gneisses (Baldwin et al., 2004; Gordon et al., *in review*; Monteleone et al., 2007). One particularly well-preserved block of eclogite on west Fergusson Island contains coesite inclusions in garnet, which implies that some, or perhaps all, of the D'Entrecasteaux Island metamorphic terrane was subducted to UHP conditions (Baldwin et al., 2008; Little et al., 2011; Monteleone et al., 2007). Subsequent to their (U)HP crystallization, the rocks underwent rapid (cm yr^{-1}) and nearly

Figure 3.1 (a) Plate tectonic map of eastern Papua New Guinea. Adapted from Wallace et al. (2004), Webb et al. (2008), and Little et al. (2011): PAC, Pacific Plate; AUS, Australian Plate; WLK, Woodlark Plate, NBP; North Bismark Plate, SBP; South Bismark Plate. Direction of movement of the Pacific Plate relative to the Australian Plate shown by the bold red arrow. Pole of WLK-AUS relative rotation (with error ellipse) for the present-day (after Wallace et al., 2004). Pole of WLK-AUS relative rotation (with error ellipse) for 3.6–0.5 Ma (after Taylor et al., 1999). The small red arrows depict the current velocities of the Woodlark Plate relative to the Australian Plate (after Wallace et al., 2004). (b) Simplified tectonic map of southeastern Papua New Guinea. Background is a Digital Elevation Model from GeoMapApp (<http://www.GeoMapApp.org>). Location for figures 3.2 and 3.4 is shown in the dashed box. Location of Woodlark Rift zone after Baldwin and Ireland (1995).

Figure 3.2 Digital Elevation Model of the northwest D'Entrecasteaux Islands from GeoMapApp (<http://www.GeoMapApp.org>). Note locations of main dome-bounding normal faults (solid black lines) and faults zones (dashed black lines). See Figure 3.1b for location. Note locations of gneiss domes described in text.

isothermal decompression from mantle to lower crustal depths, arriving in the lower crust by 4 – 2 Ma (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008). The (U)HP terrane was finally emplaced into the upper crust as gneiss domes from ~2 Ma, at which time they underwent rapid cooling ($>100\text{ }^{\circ}\text{C Ma}^{-1}$; Baldwin et al., 2004). As these eclogites are late Neogene in age, this is the youngest known age of UHP metamorphic rocks on Earth. By contrast, other global examples of (U)HP terranes are generally Oligocene in age or older; for example the Western Gneiss Region in Norway experienced UHP conditions in the late Silurian and early Devonian (~425 – 400 Ma; e.g. Kylander-Clark et al., 2008) and the Dabie-Sulu UHP terrane in China in the mid-Triassic (235 – 225 Ma; e.g. Liu and Liou, 2011). The active, well-constrained geodynamic context and the limited metamorphic or deformational overprinting unrelated to the UHP exhumation process in the D’Entrecasteaux Islands, provides an opportunity to refine the current understanding of the kinematics of the (U)HP exhumation process.

The timing of the UHP eclogite-facies crystallization and the subsequent upper amphibolite-facies overprint in the lower crust within gneiss domes of the D’Entrecasteaux Islands (Fig. 3.3) has previously been approached by U-Pb and Lu-Hf geochronology. The U-Pb method has been used to date crystallization of zircon during both the eclogite- and amphibolite-facies metamorphism (i.e. Baldwin and Ireland, 1995; Baldwin et al., 2004; Gordon et al., *in review*; Monteleone et al., 2007), and Lu-Hf dating has constrained the timing of garnet crystallization at UHP conditions (Zirakparvar et al., 2011). In addition, white mica and biotite $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages and apatite fission track dating has constrained the timing of cooling through the crust (Baldwin et al., 1993; Fitzgerald et al., 2008). These techniques have dated either the growth or crystallization of zircon and garnet, or the late-stage cooling of the rocks through the crust. Direct dating of the *deformation* that accompanied the formation of eclogite- and amphibolite-facies rock fabrics of the youngest known UHP terrane on Earth has so far not been attempted.

The Rb-Sr internal mineral isochrons dating technique may be used to date syn-deformational mineral growth that results in the formation of a polyphase rock fabric (Glodny et al., 2002; Glodny et al., 2005b). Grain-scale fluid-rock interactions that take place during deformation and metamorphism are thought to cause Sr isotope re-

Figure 3.3 Grey shaded area shows pressure-temperature (P-T) path from the mantle to the surface of the ultra-high pressure gneiss in the Mailolo dome in the D'Entrecasteaux Islands: GS, greenschist; AM, amphibolite; BS, blueschist; EC, eclogite; GR, granulite.. Adapted from Baldwin et al. (2004, 2008) and Little et al. (2011). Timing of eclogite-facies (~5 Ma) and amphibolite-facies metamorphism (~2.5 – 3.0 Ma) after Rb-Sr ages presented here and Gordon et al. (*in review*). Note that the ~3.0 Ma upper bound of this metamorphic reaction represents the oldest syn-tectonic granitic dikes dated by U-Pb zircon ages, and the ~2.5 Ma lower bound represents Rb-Sr closure and late dike intrusion (see text). Exhumation path after P-T data from Hill and Baldwin (1993). P-T data for the solidus for H₂O-saturated crustal rocks after Hacker (2006) and Little et al. (2011).

distribution and re-equilibration between mineral phases (Glodny et al., 2003). Any preservation of minerals and fabrics attributed, to a particular metamorphic phase or fabric-forming event implies a corresponding Sr relict isotopic signature may also be preserved, provided that: (1) the sample selection allows differentiation between rock fabrics of different ages, and (2) the Sr isotopic system has remained closed (Glodny et al., 2002; Glodny et al., 2003). Dating by Rb-Sr internal mineral isochrons may therefore be used to constrain the timing of deformation and metamorphic events in poly-metamorphic terranes (Glodny et al., 2003; Glodny et al., 2005b).

I have analyzed nine samples from the D'Entrecasteaux Islands using Rb-Sr internal mineral isochrons. Constraints on the timing of the prograde UHP metamorphism and the retrogressive amphibolite-facies events allow us to measure the time lag between earlier and later metamorphic events, and apply a previously untried radiometric technique to the gneiss and eclogites in the D'Entrecasteaux Islands. Moreover, it provides a means of dating the ductile deformation that was coincident with these metamorphic phases. These new data sets are used here to place constraints on the unroofing rate during exhumation of the gneiss domes. In addition, I present new geothermobarometric estimates from five samples of quartzofeldspathic gneiss and quartzose rock, which refine the current constraints on pressure and temperature conditions that prevailed in the lower crust during the amphibolite-facies retrogression of the (U)HP terrane.

3.2 Geologic and tectonic setting

3.2.1 Regional tectonics

Eastern PNG is situated within a mosaic of microplates between the Pacific and Australian plates, which includes the Woodlark microplate (Fig. 3.1; Wallace et al., 2004). Motion between these microplates accommodates $\sim 110 \text{ mm yr}^{-1}$ of north-northwest to south-southeast horizontal motion (Wallace et al., 2004). The continental Woodlark Rift separates the Woodlark Plate to the north from the Australian plate to the south, and transitions eastward along strike into the Woodlark

Basin oceanic spreading center (Fig. 3.1; Taylor et al., 1999; Wallace et al., 2004). The D'Entrecasteaux Islands are situated ~100 km to the west of the tip of the Woodlark Basin spreading center (Fig. 3.1). This spreading center has been actively spreading since ~6 Ma and has propagated westward through previously thickened orogenic continental crust of the Papuan Orogen at a rate of ~150 km Ma⁻¹ (Taylor et al., 1999). The Papuan Orogen developed in the early to middle Eocene as the result of an arc-continent collision that emplaced the Cenozoic Papuan Ultramafic Body over Australian crustal material along the Owen Stanley Fault zone (Davies and Jacques, 1984; Lus et al., 2004). The shedding of metamorphic debris as conglomerate in the offshore region to the north of the D'Entrecasteaux Islands indicates that the gneiss domes had become emergent in the Pliocene (Baldwin et al., 1993; Davies and Warren, 1988). Elevated coral platforms of probable Holocene age on the southeast coast of Goodenough Island and incised flights of river terraces on the northeastern coastal plains of Goodenough Island indicate that uplift of the D'Entrecasteaux Islands has persisted, if only slowly, into the Late Quaternary (Little et al., 2011).

3.2.2 Structural geology of the D'Entrecasteaux Islands

The Goodenough, Mailolo, and Oiatabu gneiss domes are bounded by active north or northeast-dipping normal faults on the northeast margins of the domes (Fig. 3.2. 3.4). The Morima dome is bounded to the southwest by an active southwest-dipping normal fault (Fig. 3.2. 3.4). These faults separate un-metamorphosed late Quaternary alluvial sediments and volcanic rock in the hangingwall, from erosional remnants of the Cenozoic Papuan Ultramafic Body and underlying amphibolite-facies gneisses in their footwall (Fig. 3.4; Hill, 1994; Little et al., 2011). These normal faults are interpreted as late-stage faults that are related to the Woodlark Rift and post-date the UHP exhumation and most of the dome formation (Little et al., 2011). Where exposed in the northeast of Goodenough Island the Wakonai normal fault dips 35 - 40° (Fig. 3.4; Little et al., 2011). Structural data suggest that Goodenough and Mailolo Domes have been back-tilted ~20° to the southwest as a result of slip on the dome-bounding faults, implying an original dip for the faults of ~55 – 60° (Little et al., 2011).

Figure 3.4 Simplified tectonic and geologic map of the northwest D'Entrecasteaux Islands showing sample locations and sample lithology, adapted from Hill (1994) and Little et al. (2011): PUB, Papua Ultramafic Belt; Volc., volcanics. See Figure 3.1b for location. Inset: Schematic cross section along profile A-A' (no vertical exaggeration) after Little et al. (2011).

The footwalls of these normal faults consist of high-grade gneiss domes that are 2 – 2.5 km high at their crests (*Chapter 2 this thesis*). These domal culminations of gneiss are topographically well expressed, and are rounded or elongate in map view. The gneiss domes are separated by tight synforms (Fig. 3.4), and are comprised of amphibolite-facies quartzofeldspathic gneiss (~60%), much of it orthogneiss, and younger Pliocene-aged granodiorite to granitic dikes and plutons (35%; Fig. 3.5; Little et al., 2011 *and ref. therein*). Marbles and pelites are rare (<1%; Little et al., 2011 *and ref. therein*). The once continuously overlying sheet of ultramafic rock of the Cenozoic Papuan Ultramafic Body has now largely been eroded from the uplifted centers of the gneiss domes and is preserved in a scatter of small remnants exposed in structural lows (Fig. 3.4; Little et al., 2011). On the basis of their structural fabrics, the domes can be divided into two structural zones: a structurally higher carapace zone (up to ~ 1.5 km thick) and a deeper core zone (Fig. 3.4; Hill, 1994; Little et al., 2011). The migmatitic core rocks are typically banded on a cm-scale with an anastomosing foliation, and are cross-cut by granitic dikes (Fig. 3.5b,c; Little et al., 2011). By contrast, the carapace zone, which is also migmatitic and crosscut by granitic dikes, is characterized by a more planar, thinly laminated (mm-scale), and strongly lineated solid-state deformational fabric (Fig. 3.5a). The carapace and core zones have similar quartzofeldspathic and mafic protoliths. Thus, both preserve eclogite-facies assemblages in meter-scale eclogite boudins, and share an amphibolite-facies foliation that defines the gneiss dome culminations (Little et al., 2011). The foliation is sub-horizontal at the crest of the gneiss domes and elsewhere dips outward at 30 - 70° (Little et al., 2011). The main dome-defining foliation developed during a regionally widespread syn-exhumational upper amphibolite-facies metamorphism that widely retrogressed the gneiss terrane after it had risen from the mantle to the lower crust (Little et al., 2011).

The relict eclogites-facies metamorphic assemblage is preserved in the cores of mafic boudins, where it consists of garnet, omphacite, phengite, quartz, and rutile (Brownlee et al., *in prep*). The rinds of the boudins are generally retrogressed to an amphibolite-facies metamorphic assemblage (hornblende and plagioclase symplectite, garnet, quartz and ilmenite). The degree of this retrogressive event is quite variable as some boudins are completely retrogressed, whereas others preserve the eclogite-facies mineral assemblage (Baldwin and Ireland, 1995). Field

Figure 3.5 Photographs of typical lithologies in the D'Entrecasteaux Islands. Foliations have been rotated to the horizontal in the photographs. (a) Strongly foliated and lineated carapace zone quartzofeldspathic gneiss (lower Gulawata River gorge, Goodenough Island). (b) Quartzofeldspathic core zone gneiss (southeast Mailolo dome). Note patch of leucosome within the 0.25m x 0.25m grid. (c) Strongly deformed dm-thick granodiorite foliation-parallel sheets (upper left) with zircon U-Pb ages of 3.00 ± 0.02 Ma (2σ ; Gordon et al., *in review*). Relatively less deformed (younger) granodiorite intrusion with zircon U-Pb ages of ~ 2.4 Ma (single zircon ages range from 2.418 ± 0.004 Ma to 2.482 ± 0.007 Ma; 2σ ; Gordon et al., *in review*). Lower Mwadeia River gorge, Mailolo dome. (d) Core zone quartzofeldspathic gneiss with mafic eclogite boudins (southwest Goodenough Island).

relationships indicate that the eclogite boudins originated from meter-scale basaltic dikes that intrusively crosscut the quartzofeldspathic host gneiss (Baldwin et al., 2008). Both were later metamorphosed in eclogite-facies conditions prior to onset of the subsequent amphibolite-facies retrogression, at which time the mafic dikes were boudinaged and developed their retrogressed rinds (Baldwin et al., 2008). Although only the cores of these boudins preserve the eclogite-facies mineral assemblage, the entirety of the quartzofeldspathic gneisses in the D'Entrecasteaux Islands may once have experienced (U)HP eclogite-facies conditions (Little et al., 2011; Monteleone et al., 2007).

The gneiss domes were intruded by granodiorite and leucogranodiorite dikes and plutons of Pliocene age during the main amphibolite-facies deformation event in the lower crust (Fig. 3.5b,c; Hill et al., 1995; Little et al., 2011 *and ref. therein*). These dikes and plutons intruded both the carapace and core zones and are variably strongly to weakly deformed, with older phases being more deformed relative to younger melt phases. Little et al. (2011) interpret the youngest granodiorites as being intruded after the domes were emplaced in the upper crust. In addition, segregated partial melt is present as leucosomes. These partial melts are most abundant in the core region of the domes and may have been the result of decompression melting during the rapid ascent of the rocks (*Chapter 2 this thesis*; Little et al., 2011).

3.2.3 Previous thermobarometric studies in the D'Entrecasteaux Islands

Table 3.1 presents a summary of previously published pressure and temperature estimates for the UHP and high-pressure (HP) eclogite-facies metamorphism in the D'Entrecasteaux Islands. Previous temperature estimates for the UHP eclogite-facies metamorphism have a wide range of 612 °C to 930 °C. Pressure estimates for the eclogite-facies UHP metamorphism range between 18 and 27 kbar; however, the presence of coesite in one sample of eclogite (08-010a) implies a minimum pressure of 28 kbar for UHP conditions. Thus, the lower end of the range of UHP conditions shown in Table 3.1 may be an underestimate of the pressure during the UHP metamorphism (Baldwin et al., 2008; Holm et al., 1967; Monteleone et al., 2007). Temperature estimates for the HP (coesite not preserved or recognized) eclogite-

facies metamorphism range from 530 – 900°C. These estimates are slightly lower but similar to the range of temperature estimates for UHP conditions. Note that the upper end of the temperature estimates for the HP metamorphism (935 – 1015 °C) determined by Monteleone et al. (2007) was calculated using the Zr-in-rutile thermometer, and has not been reproduced by any other geothermometry study of the eclogite-facies rocks in the D’Entrecasteaux Islands. The range of pressure estimated for the HP eclogites is 12 – 25 kbar, which is considerably less than the minimum pressure estimate of 28 kbar required to stabilize coesite at UHP conditions.

Table 3.1 Summary of published pressure and temperature estimates for eclogite-facies metamorphism in the D’Entrecasteaux Islands.

Authors	Method	Temperature estimate (°C)	Pressure estimate (kbar)	Sample location	HP or UHP
Davies and Warren (1992)	garnet-cpx Fe-Mg exchange thermometer, two pyroxene thermometer (Na)	530 - 840	-	G, Mai, Mor, Oia, Kukuia	HP
	jadeite component in omphacite, phengite Si-Al ^{IV} exchange (minimum); Al content of opx	-	12 - 25	G, Mai, Mor, Oia, Kukuia	HP
Hill and Baldwin (1993)	jadeite component in omphacite	-	21 (minimum)	Mai, Oia	HP
	garnet-cpx Fe-Mg exchange thermometer	730 - 900	-	Mai, Oia	HP
Baldwin et al. (2004)	garnet-cpx Fe-Mg exchange thermometer	870 - 930	-	Mai	UHP
	jadeite-albite-quartz barometer	-	20 - 24	Mai	UHP
Monteleone et al. (2007)	garnet-cpx Fe-Mg exchange thermometer	677 - 810	-	G, Mai	UHP/HP
	Zr-in-rutile thermometer	677 - 1015	-	G	HP
	Zr-in-rutile thermometer	612 - 740	-	Mai	UHP
	Ti-in-zircon thermometer	740 - 870	-	G	HP
	Ti-in-zircon thermometer	650 - 680	-	Mai	UHP
	garnet-omphacite-phengite barometer	-	18 - 26 (coesite-bearing sample)	Mai	UHP
	jadeite component in omphacite	-	14 (minimum)	G	UHP/HP
Baldwin et al. (2008)	garnet-pyroxene thermometer	600 - 760	-	Mai	UHP
	Zr-in-rutile thermometer	695 - 743	-	Mai	UHP
	Ti-in-zircon thermometer	650 - 675	-	Mai	UHP
	garnet-pyroxene-phengite barometer	-	18 - 27	Mai	UHP

G, Goodenough dome; Mai, Mailolo dome; Mor, Morima dome.

The diversity in pressure and temperature estimates for the eclogite-facies metamorphism may reflect: (1) disequilibrium between mineral phases, (2) invalid

assumptions regarding the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, or (3) a diversity of pressure and temperature conditions during the (U)HP events (Monteleone et al., 2007). In addition, the exhumation from the mantle to the crust in the D'Entrecasteaux Islands is known to have been nearly isothermal, or associated with a slight increase in temperature during decompression (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008). Thus, temperatures of the eclogite-facies metamorphism were similar to the temperature of the subsequent amphibolite-facies metamorphism in the (U)HP terrane. This isothermal exhumation may have contributed to the poor preservation of eclogite-facies temperatures in the eclogites that are now strongly overprinted.

Table 3.2 presents a summary of previously published pressure and temperature estimates for the amphibolite-facies metamorphic retrogression in the D'Entrecasteaux Islands. Temperature estimates for the amphibolite-facies metamorphism have a range of 550 – 740 °C. I discount the lower bound of the paragonite to muscovite solubility temperature estimate by Davies and Warren (1992), as the paragonite component in the white mica analyzed in this study is minor (i.e. $\text{Na}/(\text{Na}+\text{K}) < 0.17$; Appendix D). Previous pressure estimates for the amphibolite-facies metamorphism have a range of 5 – 11 kbar, which is lower than the range in pressure estimates for the UHP or HP eclogite-facies metamorphic events.

Table 3.2 Summary of current pressure and temperature estimates for amphibolite-facies metamorphism in the D'Entrecasteaux Islands

Authors	Method	Temperature estimate (°C)	Pressure estimate (kbar)	Sample location	Structural zone
Davies and Warren (1992)	paragonite/muscovite solubility (A schist)	500 - 600	10	G, Mai, Mor	Core/ Carapace
	amphibole and rutile stability (amphibolite gneiss)	550 - 650	5- 10	G, Mai, Mor	Core/ Carapace
	Si substitution for Al^{IV} in phengite (Q gneiss)	-	8 - 11	G, Mai, Mor	Core/ Carapace
Hill and Baldwin (1993)	Fe-Mg garnet-biotite thermometer (C, A, M, Q gneiss)	570 - 730	-	G, Mai	Carapace
	Fe-Mg garnet-biotite thermometer (C, A, M, Q gneiss)	640 - 740	-	G	Core
	GASP barometer (C, A, M, Q gneiss)	-	7 - 11	Mai	Core/ Carapace
	GRIPS barometer (C, A, M, Q gneiss)	-	9 - 11	Mai	Carapace

C, calcic; A, aluminous; Q, quartzofeldspathic; M, micaceous; G, Goodenough dome; Mai, Mailolo dome; Mor, Morima dome.

3.2.4 Previous geochronological studies in the D'Entrecasteaux Islands

Current estimates for the timing of the eclogite-facies metamorphism within the D'Entrecasteaux Islands range from 8 to 4 Ma. Baldwin et al. (2004) dated *in-situ* zircons from a eclogite sample from the Mailolo dome UHP locality by the U-Pb method using a sensitive high-resolution ion microprobe. These authors determined a metamorphic age of 4.33 ± 0.36 Ma (2σ , MSWD = 3.3), which they infer to date the timing of zircon growth at eclogite-facies conditions. Monteleone et al. (2007) dated *in-situ* zircons from five samples of variably retrogressed eclogite from the Mailolo and Goodenough dome by the U-Pb method using a sensitive high-resolution ion microprobe. They determined a metamorphic age for UHP zircon growth of 7.9 ± 1.9 Ma (2σ ; MSWD = 9.2; four zircon grains) for the coesite-bearing eclogite from the UHP locality in the Mailolo dome. They also calculated a metamorphic age of 7.0 ± 1.0 Ma (2σ ; MSWD = 2.0; three zircon grains) for a eclogite that has been retrogressed under amphibolite-facies conditions. In addition, Monteleone et al. (2007) determined U-Pb zircon ages of 2.94 ± 0.41 Ma (2σ ; MSWD = 1.02; six zircon grains), 2.82 ± 0.27 Ma (2σ ; MSWD = 2.6; three zircon grains), and 2.09 ± 0.49 Ma (2σ ; MSWD = 4.2; three zircon grains) for three samples of retrogressed eclogites from the carapace zone of the Goodenough dome. Zirakparvar et al. (2011) dated garnets from the coesite-bearing eclogite sample from the Mailolo dome by the Lu-Hf method using a multi-collector inductively coupled plasma mass spectrometer (ICP-MS). These authors determined a Lu-Hf age of 7.1 ± 0.7 Ma (2σ , MSWD = 1.5), and interpret this age as the timing of garnet crystallization at UHP eclogite-facies conditions. Gordon et al. (*in review*) also dated zircons from a eclogite sample from the UHP locality in the Mailolo dome using U-Pb chemical-abrasion thermal-ionization mass spectrometry (TIMS), and determined a U-Pb zircon age range of 5.82 ± 0.20 Ma to 4.78 ± 0.17 Ma. In addition, Gordon et al. (*in review*) carried out 70 spot measurements of U-Th-Pb on zircon grains using a multi-collector ICP-MS. They determined that zircons in the fresh portion of the eclogite sample yield $^{238}\text{U}/^{206}\text{Pb}$ ages that range from 16.0 to 5.5 Ma, and zircons in the altered portion of the eclogite sample yield $^{238}\text{U}/^{206}\text{Pb}$ ages that range from 11.4 to 3.9 Ma. The two age ranges for the fresh and altered portions of the eclogite are within error of each other, and cluster around the more precise TIMS eclogite-facies U-Pb ages (~ 5 Ma;

Gordon et al., *in review*). Trace elements of zircons are similar between the core and the rim of the eclogite boudins (Gordon et al., *in review*). Based on the evidence from the U-Th-Pb spot measurements and the trace-element compositions of the zircons, Gordon et al. (*in review*) infer that the precise ~5 Ma TIMS U-Pb zircon age records the timing of the UHP metamorphism.

Previous geochronological studies have constrained the timing of the amphibolite-facies metamorphism for rocks in the Goodenough and Mailolo domes to 3.5 – 2.4 Ma. Baldwin and Ireland (1995) dated zircons from two samples of felsic gneiss in the Goodenough dome by the U-Pb method using a sensitive high-resolution ion microprobe, and determined ages of 2.63 ± 0.16 Ma (2σ) and 2.72 ± 0.28 Ma (2σ) respectively. These ages are interpreted as amphibolite-facies growth ages (Baldwin and Ireland, 1995). Gordon et al. (*in review*) carried out U-Pb chemical-abrasion TIMS for zircons extracted from a suite of variably deformed granodioritic dikes from the core and carapace of the Mailolo dome. A strongly deformed granodioritic orthogneiss from the core zone of the Mailolo dome (UHP locality) yielded U-Pb zircon ages that range from 3.50 ± 0.01 Ma to 3.41 ± 0.02 Ma (Gordon et al., *in review*). The most strongly deformed granodioritic orthogneiss dated by Gordon et al. (*in review*) is from the carapace zone of the Mailolo dome, and yielded a weighted mean TIMS U-Pb age of 3.082 ± 0.007 Ma (MSWD = 0.56; five zircon grains). Two nearby deformed granodioritic dikes yielded a TIMS U-Pb zircon age of 3.00 ± 0.02 Ma (2σ ; two zircon grains), with an age range of 2.418 ± 0.004 Ma to 2.482 ± 0.007 Ma (2σ), respectively. The ~2.4 Ma age for the relatively undeformed granodioritic gneiss is interpreted to date the timing of the final stages of the retrogressive amphibolite-facies ductile deformation in the Mailolo gneiss domes (Gordon et al., *in review*). The 2.09 ± 0.49 Ma (2σ ; MSWD = 4.2) U-Pb ion microprobe ages for zircons from eclogite samples from the Goodenough dome calculated by Monteleone et al. (2007) are younger than those attributed to the amphibolite-facies metamorphic growth in the Goodenough dome by Baldwin and Ireland (1995). Gordon et al. (*in review*) argue that the <3 Ma U-Pb zircon ages cannot date the growth of zircons at HP conditions.

White mica and biotite in gneiss samples from the Goodenough, Mailolo, Oiatabu, and Morima domes have yielded plateau and isochron $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages with a

spread of 3.0 – 1.5 Ma (white mica) and 1.9 – 1.4 Ma (biotite; Baldwin et al., 1993). These ages imply that there was rapid cooling of the rocks in the D'Entrecasteaux Islands below 400 – 300 °C in the crust over the 3.0 – 1.5 Ma time interval ($>100\text{ °C Ma}^{-1}$; Baldwin et al., 1993). Gneiss in the D'Entrecasteaux Islands yielded apatite fission track ages of 1.0 – 0.4 Ma, suggesting that final cooling of the rocks to below 130 °C took place during the last 1.0 Ma or less (Baldwin et al., 1993; Fitzgerald et al., 2008).

3.3 Rb-Sr dating of rocks by internal mineral isochrons

3.3.1 Rb-Sr isotope systematics

The exchange and interaction of isotopes between an intergranular fluid phase and rock-forming minerals during metamorphism and mineral growth is predicted to re-distribute and re-equilibrate Sr between the co-existing mineral phases (Freeman et al., 1997; Glodny et al., 2002; Glodny et al., 2003). Dynamic recrystallization and metamorphic mineral growth in a chemical system open to grain-scale fluid flow is predicted to cause homogenization of Sr during ductile deformation (Freeman et al., 1997). In such a case, the Rb-Sr isochron will reveal the timing of the metamorphic recrystallization event that caused final homogenization of the Rb-Sr system, provided that two conditions are met: (1) the temperatures during the Sr homogenization event were less than the effective blocking temperature for Sr in the mineral assemblage present in the rock, and (2) the blocking temperature of Sr was not exceeded during the later thermal history (Freeman et al., 1997). If the mineral fabric in a deformed metamorphic rock grew syn-tectonically, and there was no fluid access after mineral growth, then the Rb-Sr isotopic compositions would record the timing of mineral growth during ductile deformation regardless of the thermal history (Freeman et al., 1997). Because the eclogites boudin cores analyzed here were not retrogressed or hydrated by fluids during the fluid-present amphibolite-facies overprint, Rb-Sr ages for these eclogites should date the timing of their original eclogite-facies crystallization. The quartzofeldspathic gneiss and granitic rock that surrounds these boudins cores were retrogressed and hydrated during the

amphibolite-facies overprint; therefore, these rocks should yield Rb-Sr isochrons that date the timing of the final phase of fluid-present amphibolite-facies deformation during exhumation from the lower crust. The Rb-Sr method is thus an appropriate technique to date both the (U)HP metamorphism and the fluid-present amphibolite-facies overprint in the D'Entrecasteaux Islands, by careful selection of samples that preserve the eclogite- and amphibolite-facies mineral assemblages and fabrics.

The Sr blocking temperature of white mica is 550 – 650 °C (Blanckenburg et al., 1989; Giorgis et al., 2000; Glodny et al., 2005a). Rb-Sr diffusion within a rock is predicted to have modally-controlled closed system behavior so that the next-most-diffusive phase will determine the blocking temperature of Sr in the rock's multi-phase system, rather than the least retentive phase (Glodny et al., 2003; Glodny et al., 2002). Minerals with Sr blocking temperatures that are higher than that of white mica in the eclogites and quartzofeldspathic gneiss analyzed here include: apatite, ~650°C (Cherniak and Ryerson, 1993); Na-feldspar, 425 – 750 °C (Cherniak and Watson, 1992; Cherniak and Watson, 1994); K-feldspar, 650 – 900 °C (Cherniak and Watson, 1992; Cherniak and Watson, 1994); Ca-feldspar, 600 – 1000 °C (Cherniak and Watson, 1992; Cherniak and Watson, 1994); clinopyroxene and garnet, 800–1100°C (Burton et al., 1995; Cherniak, 1998; Sneeringer et al., 1984). As all samples analyzed here contain K-feldspar with the exception of the eclogites, the Rb-Sr ages may be interpreted as the time since the rock cooled to below ~650 °C (minimum closure temperature for K-feldspar), and would therefore be predicted to date the white mica mineral growth (formation age) rather than any later cooling event (Glodny et al., 2003).

3.3.2 Requirements for isotopic dating via Rb-Sr internal mineral isochrons

An internal mineral isochron plots $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for rock-forming minerals that are inferred to be in textural equilibrium with each other, in order to calculate a Rb-Sr isochron. For metamorphic rocks the existence of a valid multimineral isochron indicates closed system behavior and precludes the possibility that there has been post-recrystallization and re-distribution of radiogenic Sr between different mineral phases (Glodny et al., 2003; Glodny et al., 2005b). If, by contrast,

the internal mineral isochron yields a positive correlation between apparent age of white mica and the grain size of that white mica, this observation implies that there was post-growth diffusion of Sr from the crystal lattice (Glodny et al., 2002; Glodny et al., 2005b; Glodny et al., 2008b). Two advantages of the Rb-Sr internal mineral include: (1) the close tie between metamorphic reaction kinetics, ductile deformation, and isotopic re-equilibration implies that the isotopic distribution of Sr within co-existing minerals was homogenized during the metamorphic and deformation event that created the rock fabric in the sample; and (2) if the isotopic compositions do not plot on a linear isochron, the assumption of isotopic homogeneity and closed system behavior between the assemblage-forming minerals is known to be invalid (Glodny et al., 2002; Glodny et al., 2003; Glodny et al., 2008a; Thomson et al., 2009). Rb-Sr internal mineral isochrons therefore allow identification of relict isotopic signatures from previous growth events (i.e. a mixed white mica population), or of later resetting of the isotopic composition as a result of fluid-flux and diffusion or recrystallization (Glodny et al., 2008b).

Glodny et al. (2008c) argues that there are three key requirements for successful isotopic dating of deformation by Rb-Sr internal mineral isochrons. First, there must have been complete inter-mineral isotopic equilibration during the mineral growth event that created the rock fabric. The close link between textural and isotopic equilibration implies that samples that lack any textural relicts from earlier metamorphic events (such as boudins, porphyroclasts, or coarse mica fish) will contain a mineral assemblage that was homogenized with respect to Sr isotopes at the time of their growth. This isotopic equilibrium would have been established during the growth of the minerals that form the rock fabric, before closed system behavior began. Thus, Rb-Sr isotopic ages are interpreted as recording the end stages of deformation-induced recrystallization that created the mineral fabric of interest. Second, thermally driven diffusion subsequent to the fabric forming metamorphic growth must not have caused later alterations to the Sr isotopic composition of the constituent minerals. Third, there must not have been any post-growth alteration of the Sr isotopic composition of the mineral as a result of fluids or weathering. If late-stage fluid-present conditions occur within the two least retentive minerals in a sample, then Sr isotopes will be exchanged between these phases and a valid isochron will not be obtained (Freeman et al., 1997; Glodny et al., 2002; Glodny et

al., 2003). If no fluid is present, isotopic exchange between minerals is not possible regardless of the temperature (Freeman et al., 1997; Glodny et al., 2002; Glodny et al., 2003). In a poly-metamorphic rock, care must be taken to exclude late-stage phases such as biotite and chlorite that may have grown during retrogression and low-temperature fluid alteration, particularly along areas that act as fluid pathways (i.e. grain boundaries; Glodny et al., 2008c *and ref. therein*).

3.4 Analytical techniques

3.4.1 Thermobarometric and major element analytical technique

Quantitative major element analyses for white mica in eleven samples, and garnet, plagioclase, and ilmenite in five samples from the D'Entrecasteaux Islands were carried out on the JEOL JXA-8230 electron probe microanalyzer (EPMA) at Victoria University of Wellington, New Zealand. Quantitative standardization was carried out with 15 seconds for background measurement and 30 seconds for standard measurement with the exception of Ti for the white mica analyses, which was carried out with 30 second of background and 60 second of measurements. Analysis of unknowns included a background measurement of 15 seconds and a standard measurement of 30 seconds. Alkali elements were measured by the EPMA first. To ensure matrix effects of mass number (Z), absorbance (A), and fluorescence (F) did not lead to incorrect element concentration, a ZAF correction was used to automatically correct for these matrix effects.

All quantitative analyses were by wavelength dispersive spectrometry, which was calibrated with international mineral standards similar in composition to the phase analyzed for major elements, or with synthetic oxide standards for elements with <1 wt% (Table 3.3). The percent two standard deviation or analytical precision calculated from repeat analysis of calibrated standards was <3% for the oxides that are present in the standard at >1 wt%. Oxides analyzed for the Biotite PSU 5-110 standard yielded a range of percent two standard deviation of <5% for the oxides that are present in the standard at >1 wt%; with the exception of K₂O, which yielded

11.56%. The accuracy of the repeated analyses of oxides was <2.5 wt% (average of all repeat analyses of oxides in calibrated standards) for oxides that were present in the calibrated standards at >1 wt%. Precision and accuracy of all calibrated samples analyzed as unknowns is shown in Table 3.4 to 3.8 by oxide.

Table 3.3 Calibrated standards for quantitative major element analysis on the EMPA

Mineral Phase	Matrix-matched standards	Synthetic oxides
White mica	VG-A99 Basaltic Glass ^a (Ti*, Na, Si, Al, Fe) Biotite PSU 5-110 ^a (Ti*, Mg, Si, Al, Fe, K)	Wollastonite (Ca), MgO, MnO, Orthoclase Or-1A ^a (K) Wollastonite (Ca), MnO, Orthoclase Or-1A ^a (Na)
Garnet	Garnet USNM 110752 ^b (Ca, Mg, Si, Al, Fe)	MnO, TiO ₂
Plagioclase	Plagioclase ^b (Na, Si, Al, Ca)	TiO ₂ , Orthoclase Or-1A ^a (K), MgO, Fe ₂ O ₃
Fe-Ti oxides	Ilmenite ^b (Ti, Fe, Mn)	Wollastonite (Ca), MgO, Al ₂ O ₃

All elements were analyzed with 30 seconds of standard/sample measurement and 30 seconds of background measurements except were noted with an asterisk.

*, 60 seconds of standard/sample measurement and 30 seconds of background measurements.

^aIngamells, 1980

^bJarosewich et al., 1980

Table 3.4 Accuracy and precision of white mica major element analysis by EPMA

Standard: VG-A99 standard (n=4)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
Average	51.80	4.11	12.38	13.39	0.20	5.09	9.18	2.66	0.82	99.61
Min	50.80	4.08	12.23	13.35	0.18	4.99	9.16	2.63	0.81	98.34
Max	52.78	4.16	12.64	13.44	0.22	5.20	9.19	2.68	0.83	101.09
2 std. dev.	1.63	0.08	0.36	0.08	0.04	0.17	0.03	0.04	0.02	2.26
% 2 std. dev.	3.1	1.9	2.9	0.6	20.5	3.4	0.3	1.4	2.4	2.3
Ref. value^a	51.15	4.11	12.38	13.35	0.20	5.07	9.36	2.68	0.83	99.40
% offset	1.2	0.1	0.0	0.3	-2.6	0.3	-2.0	-0.9	-1.2	0.2

^aJarosewich et al., 1980

Table 3.5 Accuracy and precision of white mica major element analysis by EPMA

Standard: Biotite PSU 5-110 (n=115)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
Average	38.80	1.61	13.07	10.96	0.14	19.90	0.08	0.32	10.01	94.89
Min	36.85	1.44	12.30	10.27	0.10	18.61	0.02	0.03	8.22	92.85
Max	41.86	1.85	13.60	11.51	0.18	21.30	0.29	0.48	11.57	98.11
2 std. dev.	1.59	0.20	0.58	0.50	0.04	1.03	0.07	0.22	1.16	2.35
% 2 std. dev.	4.1	12.7	4.4	4.5	26.43	5.17	87.8	67.0	11.56	2.48
Ref. value^a	38.63	1.55	13.08	11	0.14	19.94	0.18	0.26	10	95.76
% offset	0.4	3.44	-0.1	-0.4	-0.56	-0.2	-128.6	19.45	0.09	-0.91

^aIngamells, 1980

Table 3.6 Accuracy and precision of garnet major element analysis by EPMA
Standard: Garnet USNM 110752 (n=24)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Total
Average	39.96	0.36	22.65	11.36	0.19	7.11	18.06	99.69
Min	39.34	0.32	22.38	11.18	0.16	6.94	17.85	99.08
Max	40.55	0.39	22.92	11.54	0.24	7.24	18.31	100.22
2 std. dev.	0.55	0.03	0.27	0.19	0.04	0.16	0.23	0.65
% 2 std. dev.	1.4	9.1	1.2	1.6	21.2	2.3	1.2	0.7
Ref. value^a	40.16	0.35	22.70	11.31	0.19	7.17	18.12	100.00
% offset	-0.5	3.0	-0.2	0.4	-0.6	-0.8	-0.3	-0.3

^aJarosewich et al., 1980**Table 3.7** Accuracy and precision of plagioclase major element analysis by EPMA
Standard: Plagioclase (n=25)

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total
Average	50.74	0.03	30.60	0.45	0.15	13.74	3.39	0.11	99.22
Min	49.29	0.00	29.89	0.40	0.12	13.43	3.25	0.10	97.05
Max	51.56	0.05	31.11	0.53	0.19	14.02	3.57	0.12	100.32
2 std. dev.	1.22	0.02	0.68	0.07	0.03	0.27	0.18	0.01	1.85
% 2 std. dev.	2.4	85.5	2.2	15.5	19.5	2.0	5.4	12.7	1.9
Ref. value^a	51.52	0.35	30.91	0.46	0.14	13.64	3.45	0.18	100.17
% offset	-1.5	-1244.1	-1.0	-2.1	5.0	0.7	-1.7	-59.4	-1.0

^aJarosewich et al., 1980**Table 3.8** Accuracy and precision of ilmenite major element analysis by EPMA
Standard: Ilmenite (n=12)

	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Total
Average	45.48	0.01	46.39	4.70	0.31	0.02	96.91
Min	44.02	0.00	45.72	4.44	0.26	0.00	96.25
Max	46.15	0.02	47.47	4.87	0.35	0.10	97.64
2 std. dev.	1.08	0.02	0.89	0.24	0.05	0.06	0.94
% 2 std. dev.	2.4	175.1	1.9	5.2	14.9	334.5	1.0
Ref. value^a	45.70	n/d	46.50	4.77	0.31	n/d	97.28
% offset	-0.5	-	-0.2	-1.5	-0.7	-	-0.4

^aJarosewich et al., 1980

n/d, not determined

Four samples of gneiss and one sample of quartzose rock were selected for thermobarometric analysis from the northwestern D'Entrecasteaux Islands (Fig. 3.4, 3.6). These samples were selected on the basis of identification of a mineral fabric that formed during the amphibolite-facies metamorphism. The location of all analyzed samples is shown in Fig. 3.4. A complete petrographic characterization for each sample analyzed by this study for thermobarometry is presented in Appendix D.

Pressure and temperature estimates on co-existing mineral assemblages were obtained using the computer program GeoThermoBarometry (Spear and Kohn, 1999). For kyanite-bearing samples (08-037a, 10-008a, 10-070a) pressures were estimated using the Newton and Haselton (1981), the Hodges and Spear (1982), the Ganguly and Sazena (1984), the Hodges and Crowley (1985), and the Kozoi (1989) calibrations of the garnet-Al₂SiO₅-plagioclase-quartz barometer. For non-kyanite bearing samples (06-018a, 08-032a), pressures were estimated using Hodges and Crowley (1985) and the Hoisch (1990) calibrations of the garnet-plagioclase-muscovite-quartz barometer. Temperatures for the five samples were estimated using the Krogh and Raheim (1978) and the Green and Hellman (1982) calibrations of the garnet-phengite Fe-Mg exchange thermometer. All gneiss and quartzose samples analyzed for pressure and temperature estimates contain an amphibolite-facies mineral assemblage and deformational fabric. Based on these fabrics garnet rim analyses, plagioclase matrix or rim analyses and white mica rim analyses (presented in Appendix D) were input into the GeoThermoBarometry program using the above cited calibrations.

3.4.2 Rb-Sr dating analytical technique

Five samples of quartzofeldspathic gneiss, two samples of granitic rock, and two samples of eclogites were selected for Rb-Sr analysis from the northwestern D'Entrecasteaux Islands (Fig. 3.4, 3.6). These samples were selected on the basis of identification of a mineral fabric that formed during either the amphibolite- or eclogite-facies metamorphism. A complete petrographic characterization for each sample analyzed for Rb-Sr isotopic composition in this study is presented in Appendix D.

Small (10-100 mg) lithologically homogeneous samples were analyzed for their ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr isotopic composition. A small rock sample size may ensure isotopic homogenization during metamorphism was effective throughout the entirety of the sample (Glodny et al., 2002; Glodny et al., 2008b; Glodny et al., 2008c). Rock samples of >100 mg were avoided as a larger size may introduce pre-metamorphic Sr compositional variations that are too significant to be canceled out by subsequent metamorphic events (Glodny et al., 2002). Crushed sample was separated into high

Figure 3.6 Photomicrographs of samples analyzed for Rb-Sr isotopic composition and pressure/temperature estimates. Sample locations shown in Fig. 3.4. Foliations have been rotated to the horizontal. (a) 03-086b, Rb-Sr sample, carapace zone of the Morima dome. (b) 06-018a, Rb-Sr and thermobarometry sample, from the Goodenough dome. (c) 08-010c, Rb-Sr sample, ultra-high pressure locality, core zone of the Mailolo dome. (d) 08-010a, Rb-Sr sample, ultra-high pressure locality, core zone of the Mailolo dome. Note that this sample preserves coesite (Baldwin et al., 2008). (e) 08-032a, Rb-Sr and thermobarometry sample, carapace of the Goodenough dome. (f) 08-037a, Rb-Sr and thermobarometry sample, core of the Mailolo dome. (g) 08-077a, Rb-Sr sample, core of the northwest Normanby dome. (h) 09-039biii, Rb-Sr sample, river cobble from the core of the Mailolo dome. Note the radial fractures surrounding the quartz inclusion in the central garnet grain, implying the possible presence of coesite. (i) 10-008a, thermobarometry sample, carapace of the northwest Normanby dome. (j) 10-070a, thermobarometry sample, carapace of the Mailolo dome. (k) 10-071a, Rb-Sr sample, carapace of the Mailolo dome. Note that all images were taken with crossed polars, with the exception of 09-039biii, which was taken in uncrossed polars to better illustrate the radial fractures.

(white mica) and low Rb-Sr isotopic ratio (plagioclase/quartz, omphacite) mineral splits using standard magnetic separation techniques. These mineral splits were hand picked to 99.9% purity under a binocular microscope, ground in ethanol, and sieved to further reduce any included impurities. A powdered whole rock specimen was prepared in a Tema mill to provide a weighted average isotopic composition of all minerals present within the rock (Glodny et al., 2003). All samples and standards were dissolved in a mixture of concentrated nitric (16M) and hydrofluoric (29 M) acid in a 1:3 ratio by volume. The hydrofluoric acid used here is Seastar™ grade ultra-pure (all key metals <10 ppt). All other acids are sub-boil distilled in Teflon (12 M HCl) and quartz (16 M HNO₃) stills. The resultant solutions were brought to incipient dryness on a hot plate and were then re-dissolved in 3 M nitric acid before being separated into two aliquots: one for measurement of the ⁸⁷Rb/⁸⁶Sr isotopic ratio (25% of solution), and one for measurement of the ⁸⁷Sr/⁸⁶Sr isotopic ratio (75% of solution). Purification of the ⁸⁷Sr/⁸⁶Sr isotopic ratio aliquot was carried out using pipette-tip columns with Eichrom™ Sr-spec resin. Rb was washed out of the columns with 5 ml of 3 M nitric acid and the purified Sr cut was collected in 5 ml of ultrapure Millipore water (resistivity >18.2 MW). The Sr separation step was carried out twice to ensure maximum separation of Sr from Rb, Ba and Ca. See Appendix E.2 for complete description of the chemical purification technique.

All ⁸⁷Rb/⁸⁶Sr values were analyzed with an Agilent© 7500 CS inductively coupled plasma mass spectrometer at Victoria University of Wellington, New Zealand (Appendix E.3). A 1 ppb Rb-Sr standard in 1% HNO₃ (Seastar™) was used to tune the lens parameters, torch position, and carrier gas flow of the ICP-MS to optimize instrument sensitivity and beam stability. Measurement of the 1 ppb Rb-Sr standard was repeated during analysis to correct for instrumental mass bias. Elemental oxide production was monitored (<1.5%) during the tuning of the plasma torch conditions using a 1 ppb Ce solution. Samples and standards were run on a looping sequence during analysis on the ICP-MS; each run of 2 – 4 mineral separates was bracketed with two measurements of the 1 ppb Rb-Sr standard. Each analytical run included one BHVO-2 measurement analyzed under conditions identical to those used to analyze the unknowns. Total procedural blanks were below background levels. An error of 1% was assigned to all ⁸⁷Rb/⁸⁶Sr values (i.e. Kullerud, 1991).

The international rock standard US Geological Survey Hawaiian basalt BHVO-2 was used as a secondary standard to ensure that the accuracy and precision of the solution ICP-MS was within acceptable levels. GeoReM preferred elemental compositions (<http://Georem.mpch-mainz.gwdg.de/>) were used to calculate the $^{87}\text{Rb}/^{86}\text{Sr}$ value for BHVO-2. The average of all measured BHVO-2 $^{87}\text{Rb}/^{86}\text{Sr}$ values is 0.062 ± 0.001 (2σ ; $n = 9$), which is within error of the reference value of 0.066 ± 0.007 . This reference value was calculated from Rb and Sr values in ppm by weight from the GeoReM website, and the error is a 1% error assigned by this study.

$^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios were measured on a Nu Plasma© multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at Victoria University of Wellington, New Zealand. MC-ICP-MS measurements were carried out in wet plasma conditions, and instrument sensitivity was tuned to attain ~ 5 V on the ^{88}Sr ion beam for a 300 ppb Sr solutions. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of BHVO-2 reference material was processed and analyzed in the same way as the unknowns during each analytical run, to assess the reproducibility and accuracy of the MC-ICP-MS. The average value of BHVO-2 obtained during the analytical period was 0.703472 ± 0.000017 (2σ , $n = 9$), which is within error of the GeoReM preferred reference value (0.703469 ± 0.000017 ; 1σ). Instrumental mass bias was internally corrected for by tuning the MC-ICP-MS to an $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. Repeated measurements of the bracketing Standard Reference Material NBS987 standard were carried out to correct for non-exponential mass bias ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$). Errors for the $^{87}\text{Sr}/^{86}\text{Sr}$ values are the internal error, which represents the precision of all measurements within a single analysis of a mineral separate solution. Procedural blanks were <30 pg and are therefore considered negligible. Isochron parameters and regression lines were calculated using Isoplot/Ex 3.71 (Ludwig, 2008).

3.5 Results of thermobarometry and white mica major element analyses

3.5.1 Petrography

Analysis on the electron probe microanalyzer (EPMA) was carried out to determine the major element composition of the white mica phase present in each sample analyzed. Representative major element composition data for the white mica phase is presented in Appendix D. All samples analyzed contain a white mica phase that plots between the muscovite and phengite end-member components (Fig. 3.7; Glodny et al., 2005b). The three white mica analytical categories (>500 μm core analysis, >500 μm rim analysis, and <500 μm analysis) are generally compositionally uniform with regards to their Al^{IV} , Al^{VI} , and $\text{Mg}+\text{Fe}_{\text{total}}$ compositions. Thus, there is no clear relationship between grain-size category and mineral composition. This homogeneity between grain size splits suggest that the white mica grains grew at the same time in each sample, and therefore yielded similar major element compositions. For example, for a case where phengite is present as coarse grains surrounded by a matrix of relatively finer grained muscovite, I would expect there to be a prevalence of >500 μm core grains that are phengitic in composition; the <500 μm grain analyses might be more muscovite-rich.

Garnet and plagioclase in five samples of gneiss and quartzose rock (06-018a, 08-032a, 08-037a, 10-008a, 10-070a) were analyzed for major element mineral compositions on the EPMA. Plagioclase was unzoned in most cases (95% of analyzed grains), with the albite number showing very little within-sample variation. The albite component varies between 75% and 80% for three samples of quartzofeldspathic gneiss (06-018a, 08-032a, 08-037a), and between 80 and 90% for the one sample of pelitic gneiss and one sample of quartzose rock (10-070a, 10-008a). Where zonation is present, there is a slight increase in albite number from the core to the rim of the grain (e.g. ~84% at the core and ~90% at the rim of one plagioclase grain; 10-008a). All garnets analyzed by this study are almandine-rich with 57 – 63 mol% almandine, with the exception of garnets in one sample of pelitic gneiss (10-008a), which contains 66 – 72 mol% almandine. Garnets in the three samples (10-008a, 10-070a, 06-18a) contain 8 – 13 mol% pyrope and 18 – 24 mol%

Figure 3.7 Ternary composition plot for phengite and white mica after Glodny et al. (2005). Note that the three white mica analytical categories are shown with three different symbols, and that the analyzed samples are shown with different colors. There is a large spread between the three white mica analytical categories and between analyzed samples; most plot between the phengite and muscovite end-member.

grossular in their cores and 15 – 20 mol% pyrope and 17 – 23 mol% grossular at their rims. Spessartine was a minor constituent in garnets from these latter three samples (1 – 5 mol% spessartine in their cores, 0.8 – 4 mol% spessartine at their rims). The garnets in these three samples (10-008a, 10-070a, 06-18a) therefore display prograde compositional zoning with a decrease in spessartine and an increase in pyrope components from core to rim. Garnets in a sample of quartzofeldspathic gneiss from the core zone of the Mailolo dome (08-037a) have a similar composition to the previously described three samples, but with a reversed core to rim relationship. Garnets in this sample yielded a high pyrope composition in the core relative to the rim, and spessartine and grossular components that are higher in the rim relative to the core. Garnet composition variations in this sample (08-037a) therefore imply a decrease in pressure during garnet crystallization. Garnets in a sample of quartzofeldspathic gneiss from the carapace of the Goodenough dome exhibit little zonation (08-032a; ~3.6 mol% pyrope, ~12.5 mol% spessartine, and ~23.5 mol% grossular component). Thus, garnets analyzed here are generally pyrope-almandine-grossular solid solutions and are weakly zoned, similar in compositions and zonation patterns to garnets hosted in eclogites from Goodenough and Fergusson Island (Davies and Warren, 1992).

3.5.2 Thermobarometry

Pressure and temperature estimates were determined for five samples of quartzofeldspathic gneiss and quartzose rock (06-018a, 08-032a, 08-037a, 10-008a, 10-070a) from the northwestern D'Entrecasteaux Islands. All analyzed samples were retrogressed during the amphibolite-facies overprint, so the pressure and temperature estimates presented below relate specifically to that syn-exhumational metamorphic event. Samples 06-018a, 08-032a, and 08-037a are amphibolite-facies retrogressed quartzofeldspathic gneiss from the Goodenough and Mailolo domes, with a mineral assemblage of quartz, plagioclase, K-feldspar, white mica, garnet (06-018a, 08-037a), biotite, and trace amounts of chlorite (06-018a, 08-037a). Sample 10-008a is a pelitic gneiss from the carapace of the northwest Normanby dome, Normanby Island, which contains plagioclase, K-feldspar, garnet, quartz, white mica, biotite and minor kyanite and oxides. Sample 10-070a is a strongly deformed quartzose sheet from the

carapace of the Mailolo dome, Fergusson Island, which contains quartz, K-feldspar, plagioclase, white mica, garnet, kyanite, biotite, and chlorite.

Pressure and temperature estimates for the amphibolite-facies metamorphism calculated here are presented in Table 3.9 and Fig. 3.8. The Krogh and Raheim (1978) calibration for the garnet-phengite thermometer yielded temperature estimates of 450 – 700 °C. The Green and Hellman (1982) calibration for the garnet-phengite thermometer yields temperature estimates of 560 – 760 °C. The Green and Hellman (1982) temperature estimate for sample 10-008a is lower than the other temperature estimates here by >100°C. This sample was collected in the northwest corner of the northwest Normanby dome, a location that is inferred to be subjacent to the contact between the upper plate and the lower plate of the northwest Normanby dome fault zone (Fig. 3.2, 3.4; Little et al., 2011). The low temperature estimate for sample 10-008 may have been the result of conductive cooling against the upper plate, and would therefore not represent an accurate estimate for the temperature during amphibolite-facies conditions in the D'Entrecasteaux Islands. I suggest a temperature range of 640 – 720 °C for the Green and Hellman (1982) calibration, which is slightly higher than the estimates calculated by the Krogh and Raheim (1978) calibration and is in better agreement with previous thermobarometric studies of the amphibolite-facies metamorphism (Section 3.2.3). The garnet-plagioclase-muscovite-quartz barometer yielded pressure estimates of 4 – 11 kbar for the Hodges and Crowley (1985) calibration and 12 – 17 kbar for the Hoisch (1990) calibration. These results are not as precise as the pressure estimates calculated for kyanite-bearing samples using the garnet-Al₂SiO₅-plagioclase-quartz barometer, which yielded pressure estimates of 10 – 17 kbar across all five calibrations and the five samples analyzed here.

Figure 3.8 Thermobarometry results for five amphibolite-facies samples from the D'Entrecasteaux Islands. Grey areas show approximate pressure and temperature estimates. (a) Sample 06-018a, non-kyanite bearing quartzofeldspathic gneiss (transitional zone between the core and carapace, Goodenough dome). (b) Sample 08-032a, non-kyanite bearing quartzofeldspathic gneiss (carapace, Goodenough dome). (c) Sample 08-037a, kyanite-bearing quartzofeldspathic gneiss, core, Mailolo dome. (d) Sample 10-008a, kyanite-bearing quartzofeldspathic gneiss (carapace, north Normanby dome). (e)

Sample 10-070a, mica-bearing quartz band with garnet and kyanite (carapace, Mailolo dome). For the complete petrographic characterization of each analyzed sample see Appendix D. Calibrations used: (1) garnet-phengite Fe-Mg exchange, Korch and Raheim (1978); (2) garnet-phengite Fe-Mg exchange, Green and Hellman (1982); (3) garnet- Al_2SiO_5 -plagioclase-quartz (GASP), Newton and Haselton (1981); (4) GASP, Hodges and Spear (1982); (5) GASP, Ganguly and Saxena (1984); (6) GASP, Hodges and Crowley (1985); (7) GASP, Koziol (1989); (8) garnet-plagioclase-muscovite-quartz (Fe), Hodges and Crowley (1985); (9) garnet-plagioclase-muscovite-quartz (Mg end-member), Hoisch (1990). Temperature and pressure estimates shown on Table 3.9 and sample locations are shown in Fig. 3.4.

Table 3.9 Summary of thermobarometric results

	Rock type	T (°C) Garnet-phengite		P (kbar) GPMQ		P (kbar) GASP
		1: Krogh and Raheim (1978)	2: Green and Hellman (1982)	8: Hodges and Crowley (1985)	9: Hoisch (1990)	Range of all calibrations ^a
06-018a	QG	575- 700	700 – 730	8 – 11	16 – 17	-
08-032a	QG	450 - 575	640 – 670	4 – 8	12 – 14	-
08-037a	QG	660 - 700	720 - 760	-	-	13 – 17
10-008a	QG	450 - 500	560 – 590	-	-	10 – 12
10-070a	QS	550 - 600	650 – 670	-	-	12 – 15

Temperature and pressure estimates have assigned uncertainties of $\pm 50^{\circ}\text{C}$ and ± 2 kbar respectively.

QG, quartzofeldspathic gneiss; QS, quartz sheet; P, pressure; T temperature; GPMQ, garnet-plagioclase-muscovite-quartz barometer.

^a Calibrations used for the garnet-plagioclase- Al_2SiO_5 -quartz (GASP) barometer are: Ganguly and Saxena, 1984; Hodges and Crowley, 1985; Hodges and Spear, 1982; Koziol, 1989; Newton and Haselton, 1981.

3.6 Results of Rb-Sr dating

Of the nine samples analyzed here for Rb-Sr isotopic compositions, only five yielded statistically-valid Rb-Sr isochrons, which I define to be an isochron with a mean square of weighted deviations (MSWD) of < 3.12 after Kullerud (1991). The MSWD is a measure of the ratio of the observed deviation of the data points from the best-fit line, and the deviation that is expected on the basis of the known errors in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (measured by the multi-collector ICP-MS) and the assigned 1% $^{87}\text{Rb}/^{86}\text{Sr}$ errors (Kullerud, 1991; Ludwig, 2008). This value represents a measure of the quality of linear fit (Kullerud, 1991; Ludwig, 2008). I have assigned a probability of fit of 0.05, which is the probability that the assigned data-point errors account for the observed scatter of the data-points about the regression line. Rb-Sr analytical results are listed by sample in Table 3.10 and sample locations are shown in Figure 3.4.

Table 3.10 Rb-Sr analytical data

Sample No.	Material	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr 2σ
ECLOGITE-FACIES						
08-010a	5.70 ± 2.00 Ma, Sr_i=0.703974 ± 0.000027, MSWD = 2.0					
	250-355 μm white mica	1591	399	0.912	0.704054	0.000021
	355-500 μm white mica	1232	226	1.237	0.704086	0.000023
	>500 μm white mica	1220	231	1.208	0.704052	0.000025
	whole rock	15	152	0.237	0.703991	0.000022
09-039biii	5.60 ± 1.60 Ma, Sr_i=0.704434 ± 0.000016, MSWD = 1.00					
	Omphacite	3	751	0.013	0.704431	0.000022
	250-355 μm white mica	772	244	0.855	0.704509	0.000023
	355-500 μm white mica	940	275	0.928	0.704516	0.000022
	>500 μm white mica	1018	276	1.007	0.704499	0.000022
	whole rock	34	708	0.126	0.704447	0.000022
AMPHIBOLOITE-FACIES						
08-010c	2.41 ± 1.40 Ma, Sr_i=0.703800 ± 0.000031, MSWD = 0.50					
	plagioclase/quartz	1	25	0.074	0.703819	0.000041
	250-355 μm white mica	32	34	2.304	0.703881	0.000040
	355-500 μm white mica	88	110	2.041	0.703871	0.000040
	>500 μm white mica	26	42	1.591	0.703853	0.000040
	whole rock	19	110	0.442	0.703797	0.000041
08-077a	3.90 ± 0.44 Ma, Sr_i=0.7044193 ± 0.000009, MSWD = 0.82					
	plagioclase/quartz	5	102	0.121	0.704423	0.000006
	250-355 μm white mica	74	84	2.028	0.704537	0.000006
	355-500 μm white mica	69	86	2.028	0.704531	0.000006
	>500 μm white mica	87	141	1.569	0.704514	0.000006
	whole rock	38	230	0.417	0.704444	0.000006
08-037a	12.0 ± 5.0 Ma, Sr_i=0.706160 ± 0.000120, MSWD = 5.5					
	plagioclase/quartz	5	48	0.255	0.706195	0.000019
	250-355 μm white mica	89	116	1.910	0.706432	0.000016
	250-355 μm white mica UC	94	124	1.831	0.706463	0.000017
	355-500 μm white mica	151	200	1.874	0.706499	0.000017
	355-500 μm white mica UC	90	117	1.892	0.706523	0.000015
	>500 μm white mica*	116	124	2.324	0.706894	0.000022
	>500 μm white mica UC*	415	450	2.283	0.706950	0.000020
	whole rock	30	62	1.193	0.706387	0.000014
06-018a	2.38 ± 0.29 Ma, Sr_i=0.704753 ± 0.000014, MSWD = 2.5					
	plagioclase/quartz	6	517	0.028	0.704739	0.000010
	250-355 μm white mica	2406	149	4.838	0.704911	0.000010
	355-500 μm white mica	1208	74	4.911	0.704924	0.000010
	>500 μm white mica*	1384	82	5.075	0.704971	0.000010
	whole rock	563	847	0.185	0.704774	0.000010

Table 3.10 Rb-Sr analytical data (cont.)

Sample No.	Material	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr} \ 2\sigma$
10-071a	3.70 ± 3.80 Ma, $\text{Sr}_i=0.706202 \pm 0.000095$, MSWD = 3.9					
	plagioclase/quartz	4	121	0.081	0.706213	0.000012
	250-355 μm white mica	3174	352	1.992	0.706294	0.000010
	355-500 μm white mica	2402	216	2.335	0.706347	0.000011
	>500 μm white mica	1768	229	1.714	0.706278	0.000011
	whole rock*	464	50	1.936	0.706375	0.000012
08-032a	0.22 ± 0.06 Ma, $\text{Sr}_i=0.705290 \pm 0.000270$, MSWD = 38					
	plagioclase/quartz	164	32	1.084	0.705349	0.000010
	250-355 μm white mica	760	9	19.142	0.706138	0.000010
	355-500 μm white mica	2627	1	660.627	0.707308	0.000036
	whole rock	715	91	1.686	0.705313	0.000009
03-086b	0.30 ± 0.39 Ma, $\text{Sr}_i=0.704650 \pm 0.00031$, MSWD = 152					
	plagioclase/quartz	8	60	0.030	0.704516	0.000011
	250-355 μm white mica	950	35	5.937	0.704783	0.000009
	355-500 μm white mica	1017	2	113.280	0.705122	0.000016
	>500 μm white mica	714	45	3.410	0.704684	0.000010

Error of 1% assigned to the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio. Typical sample weights are ~100 mg for all plagioclase, omphacite, and whole rock; ~50 mg for white mica.

*, not included in isochron age; UC, uncleaned white mica split.

Note: Italics denotes $^{87}\text{Rb}/^{86}\text{Sr}$ ratio was calculated using the correction method detailed in Appendix E.3).

Figure 3.9a presents a Rb-Sr internal mineral isochron for a sample of the unretrogressed core of the coesite-bearing eclogite boudin from the UHP locality in the core zone of the Mailolo dome (08-010a; Baldwin et al., 2008). The retrogressed amphibolite-facies rind of this boudin was excluded, and the core was free of veining and hydrous phases (Monteleone et al., 2007). This boudin is ~1 m in length with a ~20 cm rind, and occurs within a strongly foliated and folded host orthogneiss (08-010c; Baldwin et al., 2008). This sample contains garnet, omphacite, white mica, quartz, hornblende, and minor rutile (Fig. 3.6d; after Brownlee et al., *in prep.*). Mineral splits of whole rock, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. No mineral splits were excluded from this isochron (n = 4). This sample yielded a Rb-Sr age of 5.7 ± 2.0 Ma (2σ ; MSWD = 2.0; probability of fit >0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7040.

Figure 3.9b presents a Rb-Sr internal mineral isochron for a sample of the unretrogressed core of an eclogite cobble from the core zone of the Mailolo dome, collected ~3 km downstream of the main divide (09-039biii). The retrogressed amphibolite-facies rind of this cobble was excluded, and the core was free of veining

Figure 3.9 Rb-Sr internal mineral isochrons for two mafic eclogites from the core of the Mailolo dome, Fergusson Island: wm, white mica. Data-point error ellipses and errors in the age calculation are two standard deviations. Note that sample 08-010a is the only known coesite-bearing sample in the D'Entrecasteaux Islands, and that sample 09-039biii contains radial fractures around quartz inclusions in garnet (Fig. 3.6h; Baldwin et al., 2008). See Table 3.10 for analytical data and Fig. 3.4 for sample location.

and hydrous phases (Monteleone et al., 2007). This sample contains garnet, white mica, plagioclase, quartz, hornblende, rutile, and minor biotite (Fig. 3.6h). Garnets in this sample exhibit radial fractures around quartz inclusions in garnet, which implies that this sample once contained coesite (Fig. 3.6h). Mineral splits of whole rock, omphacite, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. No mineral splits were excluded from this isochron ($n = 5$). This sample yielded a Rb-Sr age of 5.6 ± 1.6 Ma (2σ ; MSWD = 2.0; probability of fit >0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7044. This Rb-Sr age is within error (2σ) of the previously discussed Rb-Sr age for the coesite-bearing eclogite (08-010a).

Figure 3.10a presents a Rb-Sr internal mineral isochron for a sample of granodioritic orthogneiss from the UHP locality in the core zone of the Mailolo dome (08-010c), which hosts the coesite-bearing eclogite (08-010a). This granodioritic orthogneiss is mappable at a kilometer-scale and is ductilely deformed. It includes foliation-parallel leucosomes (~10 cm in width) and is crosscut by foliated granitic dikes. This sample contains quartz, plagioclase, K-feldspar, white mica, and minor biotite and oxides (Fig. 3.6c). Mineral splits of whole rock, plagioclase and quartz, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. No mineral splits were excluded from this isochron ($n = 5$). This sample yielded a Rb-Sr age of 2.41 ± 1.40 Ma (2σ ; MSWD = 0.50; probability of fit >0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7038.

Figure 3.10b presents a Rb-Sr internal mineral isochron for a sample of granodioritic orthogneiss from the core of the northwest Normanby dome (08-077a). This granodioritic orthogneiss is a ductilely deformed granitic sheet (~20 cm thick), which crosscuts the main foliation in the host quartzofeldspathic gneiss. This sample contains quartz, plagioclase, K-feldspar, white mica, and minor biotite and oxides (Fig. 3.6g). Mineral splits of whole rock, plagioclase and quartz, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. No mineral splits were excluded from this isochron ($n = 5$). This sample yielded a Rb-Sr age of 3.90 ± 0.44 Ma (2σ ; MSWD = 0.82; probability of fit >0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7044.

Figure 3.10 Rb-Sr internal mineral isochrons for seven amphibolite-facies samples of quartzofeldspathic gneiss and granitic rock from the northwest D'Entrecasteaux Islands: wm, white mica; UC, uncleaned. Data-point error ellipses and errors in the age calculation are two standard deviations. See Table 3.10 for analytical data and Fig. 3.4 for sample location.

Figure 3.10c presents a Rb-Sr internal mineral isochron for a sample of quartzofeldspathic gneiss from the core of the Mailolo dome (08-037a). This quartzofeldspathic gneiss is ductilely deformed and finely layered, and hosts retrogressed eclogite boudins. This sample contains quartz, garnet, white mica, plagioclase, K-feldspar, with minor biotite and trace amounts of chlorite (Fig. 3.6f). I analyzed one cleaned and one uncleaned white mica split to test the efficiency of the previously discussed cleaning procedure for mineral separates. There was minimal difference in $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios for the cleaned and uncleaned white mica splits. Mineral splits of whole rock, plagioclase and quartz, 250 – 355 μm white mica (cleaned), 250 – 355 μm white mica (uncleaned), 355 – 500 μm white mica (cleaned), 355 – 500 μm white mica (uncleaned), >500 μm white mica (cleaned), and >500 μm white mica (uncleaned) were analyzed. This isochron does not include the >500 μm white mica split ($n = 6$), the lack of which cannot be explained by a low concentration of Rb and Sr, or by a small sample size (Table 3.10). The >500 μm white mica rim major element analysis for this sample is much closer to the muscovite end-member than the other two white mica analytical categories (>500 μm core, <500 μm ; Fig. 3.7). This dissimilarity may reflect disequilibrium between the analyzed white mica aliquots. This sample yielded a Rb-Sr age of 12.0 ± 5.0 Ma (2σ ; MSWD = 5.5; probability of fit <0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7062. The probability of fit for this sample is <0.05 and the isochron calculation therefore required a Model 3 fit (Ludwig, 2008). Although the Model 3 fit takes into account data-point errors, this fit assumes that excess scatter about the regression line results from uniform error in the Y parameter (Ludwig, 2008). In this case, the Isoplot program solves for the initial-ratio variation as well as for the best-fit line (Ludwig, 2008). The 2σ errors associated with this age are interpreted as the lower bound of the true errors (Ludwig, 2008). The isochron for this sample is older than any other amphibolite-facies Rb-Sr ages calculated by this study and any previous published U-Pb zircon ages for the amphibolite-facies metamorphism (Section 3.2.4). Based on the calculated MSWD, I suggest that the three key requirements for successful isotopic dating of deformation were not met for this sample (Section 3.3.2) and I reject this result.

Figure 3.10d presents a Rb-Sr internal mineral isochron for a sample of quartzofeldspathic gneiss from Goodenough dome, which is located in a transitional

zone between the core and the carapace (06-018a). This quartzofeldspathic gneiss contains a folded foliation, which is crosscut by abundant granitic dikes that were also tightly folded during subsequent deformation. Both the folded granitic dikes and the folded amphibolite-facies foliation are crosscut by late-stage and moderately deformed granitic dikes (~60 cm wide) which are at a high angle to the main foliation. This sample contains quartz, plagioclase, K-feldspar, biotite, white mica, with minor garnet, biotite, and chlorite (Fig. 3.6b). Mineral splits of whole rock, plagioclase and quartz, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. This isochron does not include the >500 μm white mica aliquot ($n = 4$), the lack of which cannot be explained by a low concentration of Rb and Sr or a small sample size (Table 3.10). White mica compositions for sample 06-018a are similar for all white mica analytical categories (Fig. 3.7), implying that the misfit of the >500 μm white mica aliquot to the rest of the data is not related to preserved zonation. This sample yielded a Rb-Sr age of 2.38 ± 0.29 Ma (2σ ; MSWD = 2.5; probability of fit >0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7048. This Rb-Sr age is within error (2σ) of the age calculated for the granodioritic orthogneiss that hosts the coesite-bearing eclogite from the UHP locality in the core of the Mailolo dome (08-010c).

Figure 3.10e presents an Rb-Sr internal mineral isochron for a sample of quartzofeldspathic gneiss from the carapace of the Mailolo dome (10-071a). This quartzofeldspathic gneiss is ductilely deformed. The gneiss includes pegmatite sheets and deformed granodiorite, sill-like bodies, and is crosscut by a late brittle-ductile shear zone. This sample contains quartz, white mica, biotite, K-feldspar, garnet, and oxides (Fig. 3.6k). Mineral splits of whole rock, plagioclase and quartz, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. The whole rock split for this sample was not included in the isochron ($n = 4$) as it includes pervasive biotite (5 – 7%) and minor chlorite (<2%; Appendix D). This sample yielded a Rb-Sr age of 3.7 ± 3.8 Ma (2σ ; MSWD = 3.9; probability of fit <0.05) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7062. This sample has a probability of fit of <0.05, and the isochron calculation required a Model 3 fit as previously discussed. Although this isochron yielded a geologically acceptable age of 3.7 Ma, the 2σ age uncertainty is larger than the calculated age. Based on this large error in the age and the MSWD of 3.9, I reject this result.

Figure 3.10f presents an Rb-Sr internal mineral isochron for a sample of quartzofeldspathic gneiss from the carapace of the Goodenough dome (08-032a). This quartzofeldspathic gneiss is ductilely deformed, and includes foliation-parallel leucosomes (3 – 5 cm in width). This sample contains quartz, plagioclase, K-feldspar, white mica, and biotite (Fig. 3.6e). Mineral splits of whole rock, plagioclase and quartz, 250 – 355 μm white mica, and 355 – 500 μm white mica were analyzed. No mineral splits were excluded from this isochron ($n = 4$). This sample yielded a Rb-Sr age of 0.22 ± 0.06 Ma (2σ ; MSWD = 38; probability of fit <0.05), which is younger than $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages for white mica and biotite (Baldwin et al., 1993). Based on the calculated MSWD, I suggest that the three key requirements for successful isotopic dating of deformation were not met for this sample (Section 3.3.2), and I reject this result.

Figure 3.10g presents an Rb-Sr internal mineral isochron for a sample of quartzofeldspathic gneiss from the carapace of the Mailolo dome (03-086b). This quartzofeldspathic gneiss is intruded by coarse-grained, deformed granodioritic dikes. This sample contains quartz, plagioclase, K-feldspar, white mica, and biotite (Fig. 3.6a). Mineral splits of plagioclase and quartz, 250 – 355 μm white mica, 355 – 500 μm white mica, and >500 μm white mica were analyzed. No mineral splits were excluded from this isochron ($n = 4$). This sample yielded a Rb-Sr age of 0.30 ± 0.39 Ma (2σ ; MSWD = 152; probability of fit <0.05), which is within error of the quartzofeldspathic gneiss from the carapace of the Goodenough dome (08-032a). Based on the calculated MSWD, I suggest that the three key requirements for successful isotopic dating of deformation were not met for this sample (Section 3.3.2), and I reject this result.

3.7 Discussion

3.7.1 Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

The Rb-Sr internal mineral isochrons presented here yielded an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio range of ~ 0.7038 to ~ 0.7048 (Fig. 3.9, 3.10). I note that these ratios are within the range of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for ocean island basalts ($0.7030 - 0.7060$; Hofmann, 1997). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of $0.7100 - 0.7130$ suggest additional contributions to the granite rock from melting of the pre-existing crustal source and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of <0.7100 in rocks of granitic composition implies derivation of these melts by partial differentiation directly from a mantle source (Singh and Chabria, 2002). Given these initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and that the primitive mantle today has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~ 0.7045 , the range of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated here indicate that the protolith of the rocks in the D'Entrecasteaux Islands was primitive (Hinchey and Carr, 2006).

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated here supports recent inferences that the protolith of both the eclogites and the quartzofeldspathic gneiss in the D'Entrecasteaux Islands was a segment of the isotopically primitive Whitsunday Volcanic Province of northeastern Australia (Zirakparvar et al., 2010; Zirakparvar et al., 2011). Part of this volcanic terrane, which was active between 120 and 105 Ma, was rafted into PNG by the opening of the Coral Sea Basin in 62 – 56 Ma (Davies and Jacques, 1984; Ewart et al., 1992; Weissel and Watts, 1979). Proterozoic and Siluro-Devonian igneous rocks in the Georgetown inlier of northeast Queensland, which occupies the 100,000 km² of northeastern Australia that is closest to southeastern PNG, have a range of initial $^{87}\text{Sr}/^{86}\text{Sr}$ of $0.7070 - 0.7150$ (average of 0.7100; Black and McCulloch, 1990 *and ref. therein*). This range is dissimilar to that determined here. The Whitsunday Volcanic Province in northeastern Australia has previously been inferred to be the protolith of metamorphic rock along the southern margin of the Woodlark Rift, based on the respective Nd isotopic compositions of these two areas (Zirakparvar et al., 2010). Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the volcanic and plutonic rocks through the Whitsunday, Cumberland and Northumberland Island groups along the central Queensland coast, yielded a range of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of $0.7031 - 0.7045$ (Ewart

et al., 1992). These results are from an area to the south of the Georgetown inlier, and are a near perfect fit to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ values measured by this study (0.7037 – 0.7048).

The Rb-Sr isochrons derived from the coesite-bearing eclogite (08-010a) and the granodiorite orthogneiss that hosts the UHP eclogite block (08-010c) of the Mailolo dome have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7040 and 0.7038 respectively (Fig. 3.9a, 3.10a). These ratios are at the lower end of the range observed for the data set as a whole, suggesting a ~5% more primitive source composition for the meta-basalts and meta-granite rock at the UHP locality. As the lower bound of the range of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Whitsunday Volcanic Province is 0.7031, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the UHP locality are within this range. Thus, the common initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for samples from the UHP locality is most easily interpreted as reflecting the derivation of these rocks from a section of the Whitsunday Volcanic Province that had a 5% more primitive Sr isotopic signature relative to the other samples analyzed here.

3.7.2 Rb-Sr constraints on the timing of the eclogite-facies metamorphic crystallization

The eclogites analyzed in this study yielded ages of 5.7 ± 2.0 Ma (2σ ; 08-010a) and 5.6 ± 1.6 Ma (2σ ; 09-039biii; Fig. 3.9). One sample has been proven to be coesite-bearing (08-010a) and the other contains radial fractures around quartz inclusions in garnet (09-039biii; Fig. 3.6h), which implies that the latter sample may once have been coesite-bearing (Baldwin et al., 2008; van der Molen and Paterson, 1979). The white mica mineral separates of the eclogite samples analyzed here are phengitic (Fig. 3.7). The unretrogressed interior of the eclogite boudins was used for analysis here, as these appear to have been shielded from the subsequent amphibolite-facies deformation that affected the surrounding quartzofeldspathic gneiss. From these data, I interpret these eclogite isochrons as dating the fluid-present mineral growth and deformation that took place at eclogite-facies UHP conditions (>90 km; Baldwin et al., 2008).

The eclogite-facies Rb-Sr results presented here agree with a new U-Pb chemical-abrasion thermal-ionization mass spectrometry study by Gordon et al. (*in review*). The single-crystal U-Pb zircon ages determined by Gordon et al. (*in review*) range from 5.82 ± 0.20 Ma to 4.78 ± 0.17 Ma (2σ ; Section 3.2.4). The Rb-Sr internal mineral isochrons presented here are within this range. Zircon U-Pb geochronology has high analytical precision relative to Rb-Sr dating and can therefore be used to precisely determine single-grain ages of the zircon crystallization (blocking temperature of $>900^\circ\text{C}$; Ireland and Williams, 2003; Reiners et al., 2005). By contrast, the Rb-Sr method is suggested to date fluid-present mineral growth during deformation, and has a lower isotope blocking temperature relative to the U-Pb system in zircon (Section 3.3.1). Prior to the study by Gordon et al. (*in review*), the age of the UHP metamorphism was interpreted to be 7 – 8 Ma. Gordon et al. (*in review*) argue that the ion microprobe ages for zircons determined by Monteleone et al. (2007) were a simplification of the history of the zircon grains, which may record multiple thermal events. Based on the Rb-Sr ages for the amphibolite-facies rock fabric development calculated here, I agree with this interpretation. The similarity between the new U-Pb zircon ages and Rb-Sr ages presented here strongly supports the recent revision of the timing of the UHP event to ~ 5 Ma (Gordon et al., *in review*).

3.7.3 Rb-Sr constraints on the timing of the amphibolite-facies metamorphic crystallization

Rb-Sr internal mineral isochrons calculated for samples that were retrogressed during the amphibolite-facies metamorphic event yielded an age range of 3.9 – 2.4 Ma (Fig. 3.10a,b,d). Modally controlled closed system behavior of the Rb-Sr system (Section 3.3.1) implies that the Rb-Sr ages for the deformed amphibolite-facies gneiss and granodiorite represent the timing of mineral growth and Sr equilibration in the presence of fluid at temperatures of $<650^\circ\text{C}$. Geothermobarometry for rocks that contain the typical amphibolite-facies mineral assemblage yielded an inferred temperature range of $>640 - 760^\circ\text{C}$ (Section 3.5.2; Table 3.9; Fig. 3.8). As $>640^\circ\text{C}$ is the lower bound of the temperature estimate for the amphibolite-facies metamorphism, I interpret these Rb-Sr ages as growth ages. The gneiss and granodiorite samples dated here therefore yield Rb-Sr isochron ages corresponding to

the time of mineral growth and fabric development during the final fluid-present stage of pervasive amphibolite-facies overprint that affected the (U)HP terrane upon its departure from the lower crust in the Woodlark Rift. The age of the cessation of the amphibolite overprint was therefore 3.90 ± 0.44 Ma (2σ) for rocks in the northwest Normanby gneiss dome and ~ 2.4 Ma for rocks in the Mailolo and Goodenough gneiss domes. These ages do not appear to be dependent on rock type and indicate that the main phase of retrogression and ductile flow in the lower crust took place from 3.90 ± 0.44 Ma to 2.38 ± 0.29 Ma (2σ) in the northwestern D'Entrecasteaux Islands.

Pressure estimates presented here indicate that the amphibolite-facies retrogression took place at 10 – 17 kbar (Table 3.9). This range is higher than the 7 – 11 kbar range of amphibolite-facies pressure estimates calculated by Hill and Baldwin (1993) study. These maximum pressure estimates have a difference of 6 ± 2.8 kbar (approximate 95% confidence interval), implying that the HP body, or “bolus”, was thicker when it ponded at the lower crust than previously inferred. The temperature estimates presented here, however, show good agreement with previous estimates for temperature conditions during the amphibolite-facies metamorphism (Table 3.9; Section 3.5.2). Temperature estimates presented here for the later amphibolite-facies metamorphism have a range of 640 – 720 °C (Table 3.9). Previous studies estimate that temperatures during the UHP eclogite-facies metamorphism had a range of 612 – 930 °C (Section 3.2.3). This is a minimal difference relative to the pressure difference between these two metamorphic events, and may reflect the nearly isothermal nature of the rapid exhumation process of the UHP rocks in the D'Entrecasteaux Islands (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008).

The amphibolite-facies Rb-Sr isochrons presented here may record an apparent westward decrease in age of retrogression of the (U)HP body in the lower crust. A deformed granodiorite in the northwest Normanby dome (08-077a) yielded a Rb-Sr age of 3.90 ± 0.44 Ma (2σ), whereas a granodiorite in the Mailolo dome that is located ~ 45 km to the west of sample 08-077a yielded a Rb-Sr age of 2.41 ± 1.40 Ma (08-010c; 2σ). Also, a quartzofeldspathic gneiss located an additional ~ 42 km to the west of sample 08-077a in Goodenough dome yielded a Rb-Sr age of 2.38 ± 0.29 Ma

(06-018a; 2σ ; Fig. 3.10a,b,d). Thus, the amphibolite-facies metamorphic retrogression may have affected rocks within the northwest Normanby dome first in the northwest D'Entrecasteaux Islands, followed by rocks in the Mailolo and Goodenough domes. This apparent westward younging may be an indication of the progression of the Woodlark Rift through the crust in southeastern PNG (Fitzgerald et al., 2008; Monteleone et al., 2007). The Rb-Sr ages for samples from the Mailolo and Goodenough gneiss domes imply that the timing of the amphibolite-facies metamorphic event may have been nearly simultaneous for rocks within these domes.

The new Rb-Sr ages presented here that date the timing of deformed in amphibolite-facies conditions compare favorably with previous U-Pb zircon ages and $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages for this metamorphic event (Fig. 3.10; Section 3.2.4). For example, U-Pb zircon ages for weakly deformed granodioritic dikes in the Mailolo dome are 2.418 ± 0.004 Ma to 2.482 ± 0.007 Ma (2σ ; Gordon et al., *in review*). These U-Pb zircon ages are within error of my amphibolite-facies Rb-Sr ages from the Mailolo dome (08-010c; 2.38 ± 0.29 Ma; 2σ) and the Goodenough dome (06-018a; 2.41 ± 1.4 Ma; 2σ). As the closure temperature of U-Pb in zircon is >900 °C, and the Rb-Sr closure is <650 °C for rocks analyzed here, Rb-Sr closure may have post-dated zircon growth in the dikes and that the Rb-Sr ages would therefore be slightly younger than the U-Pb zircon ages (Ireland and Williams, 2003; Reiners et al., 2005). There is, however, good agreement between these two data sets, which is an excellent result as both these ages are inferred to date the timing of the final stages of the retrogressive amphibolite-facies ductile deformation in the Mailolo gneiss domes (Gordon et al., *in review*). The amphibolite-facies Rb-Sr ages presented here are also within error of the Baldwin and Ireland (1995) U-Pb zircon age of 2.63 ± 0.16 Ma (2σ) and 2.72 ± 0.28 Ma (2σ) for two samples of felsic gneiss from Goodenough Island. These latter ages are interpreted as dating zircon growth subsequent to the eclogite-facies metamorphism. Thus, there is good agreement between the U-Pb and the Rb-Sr dating technique, similar to the agreement between the Rb-Sr ages and the U-Pb zircon ages that date the timing of the eclogite-facies metamorphism as discussed above. The available white mica and biotite $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages for Goodenough dome (3.0 – 1.5 Ma) are interpreted to date cooling of the rock below 400 – 300 °C, subsequent to the peak of the amphibolite-facies metamorphism. The

overlap between the $^{40}\text{Ar}/^{39}\text{Ar}$ cooling ages on mica and the new Rb-Sr (growth) ages indicates very rapid exhumation and cooling of the (U)HP terrane ($>100\text{ }^{\circ}\text{C Ma}^{-1}$), similar to that previously suggested by Baldwin et al. (1993, 2004, 2008; Glodny et al., 2002).

3.7.4 Time scale for decompression of the (U)HP terrane from the mantle to the crust

The Rb-Sr ages presented in this study indicate that the eclogite-facies crystallization event predated the amphibolite-facies retrogressive event by $2.2 \pm 1.2\text{ Ma}$ (error is the approximate 95% confidence interval) in the Mailolo dome. Rb-Sr ages for the Mailolo dome indicate that the UHP metamorphism took place at $5.62 \pm 1.2\text{ Ma}$ ($n = 2$, error is the approximate 95% confidence interval for the weighted mean). The $\sim 3.4\text{ Ma}$ calculated by Gordon et al. (*in review*) is interpreted to date the early phases of the amphibolite-facies deformation when the (U)HP terrane reached lower crustal levels (six zircons analyses that yielded a clustering of ages from $3.50 \pm 0.01\text{ Ma}$ to $3.41 \pm 0.02\text{ Ma}$; 2σ). Thus, the Rb-Sr ages for the UHP metamorphism presented here (Fig. 3.9) and the new U-Pb zircon age calculated by Gordon et al. (*in review*) imply a time lag from the mantle to the crust of $2.2 \pm 1.2\text{ Ma}$ (error is the approximate 95% confidence interval) for rocks within the Mailolo dome. This time lag indicates that eclogite-facies metamorphism at HP and UHP conditions was followed very quickly by exhumation to lower crustal levels, where the terrane ponded, thinned and flowed laterally parallel to the rift margins (Little et al., 2011).

Based on the time lag between UHP and amphibolite-facies metamorphism, and the new pressure estimates presented here, we calculate a minimum unroofing rate of the UHP terrane of $19 \pm 11\text{ mm yr}^{-1}$ (approximate 95% confidence interval) from the mantle to the lower crust for rocks within the Mailolo dome. I estimate that the pressure during amphibolite-facies metamorphism for a core sample from the Mailolo dome was $\sim 12.5 \pm 2\text{ kbar}$ (assigned $\pm 2\text{ kbar}$ uncertainty). This is a minimum pressure estimate calculated using the garnet- Al_2SiO_5 -plagioclase-quartz barometer (Fig. 3.8c; Holm et al., 1967). Assuming a rock density of 2.7 g cm^{-3} , the pressure estimate at amphibolite-facies compositions corresponds to a depth estimate of $47 \pm 7\text{ km}$ (approximate 95% confidence interval; Harkness, 1891; Hinze, 2003). Based

on the preservation of coesite in one sample, pressure estimates for the UHP eclogite-facies metamorphism in the D'Entrecasteaux Islands has a minimum bound of 28 kbar (08-010a; Baldwin et al., 2008; Holm et al., 1967). I therefore calculate a minimum of 43 ± 10 km of unroofing from UHP conditions (>90 km) to the lower crust between 5.62 ± 1.2 Ma and ~ 3.4 Ma for rocks in the Mailolo dome (Gordon et al., *in review*). This estimate of unroofing rate is similar to previously inferred exhumation rates for the rocks in the D'Entrecasteaux Islands (cm yr^{-1} ; Baldwin et al., 1993; Baldwin et al., 2004).

3.7.5 Ages and P-T estimates for fabric formation in the core and carapace zones

One of the original aims of this study was to determine if the core and the carapace zones in the D'Entrecasteaux Island gneiss domes were deformed diachronously or contemporaneously. Structural data from the gneiss domes implies that exhumation of the gneiss was diapiric (Little et al., 2011). The carapace of the dome absorbed the greatest amount of pure shear-dominated thinning and solid-state ductile flow as it was structurally the uppermost part of the body of diapir and was highly attenuated (Little et al., 2011). I note that all carapace samples analyzed for Rb-Sr ages here (03-086b, 08-032a, 10-071a) are statistically invalid based on previously stated criteria (Section 3.3.2). The lack of evidence for isotopic homogeneity in the carapace samples suggests that the carapace rocks were affected by fluid-present deformation during the final phases of crustal emplacement. Thus, late-stage isotopic exchange occurred between low Rb-Sr ratio minerals (plagioclase) and high Rb-Sr ratio mineral (white mica) in the carapace rocks. Little et al. (2011) observe talc- and biotite-bearing phyllonite in shear zones near the southeast coast of Fergusson Island and the northwest tip of Normanby Island. These authors therefore interpret these locations to expose the D'Entrecasteaux Island Fault Zone (a boundary at the base of the upper plate of the dome-bounding normal faults; Fig. 3.2, 3.4), which was altered with extensive fluid flow during the final juxtaposition of the carapace gneiss against the ophiolitic cover rocks. If this extensive fluid flow was pervasive throughout the majority of the carapace rocks in the D'Entrecasteaux Islands, it may have caused the Sr isotopic disequilibrium between constituent minerals in the carapace observed here.

The new geothermobarometry data implies that the carapace rocks crystallized at lower pressure and temperature conditions relative to the subadjacent core rocks during the lower crustal amphibolite-facies metamorphism (Table 3.9; Fig. 3.8). Temperatures estimates presented here for the core and carapace rocks of the Mailolo gneiss dome are 720 – 760 °C (sample 08-037a) and 640 – 670 °C (sample 10-070a), respectively (estimates were derived using the Green and Hellman, 1982 thermometer). Pressure estimates presented here show a corresponding apparent decrease from the core zone relative to the carapace zone. The garnet-plagioclase- Al_2SiO_5 -quartz barometer yielded a pressure estimate of 13 – 17 kbar for the core of the Mailolo dome (08-037a) and 12 – 15 kbar for the carapace of the Mailolo dome (10-070a; Fig. 3.8c,e). This apparent difference in pressure between the core and the carapace zones is also present in the Goodenough dome (Fig 3.8a,b; Table 3.9), where the rocks yielded pressure estimates of 16 – 17 kbar for the core zone and 12 – 14 kbar for carapace zone. Estimates for the pressure of fabric formation in the carapace of the northwest Normanby dome are 10 – 12 kbar (10-008a), which is ~2 kbar less than the pressure estimate for carapace rocks from the Mailolo dome and the Goodenough dome (Fig. 3.8d). This pressure estimates supports previous inferences that the northwest section of the northwest Normanby dome represents a structural level of the gneiss dome that is not observed elsewhere in the D'Entrecasteaux Islands (Little et al., 2011).

3.7.6 Post-metamorphic ductile thinning estimates

The original foliation-orthogonal separation between core and carapace samples within the Mailolo dome is uncertain, as there has been post-metamorphic thinning during deformation of the regionally flat lying amphibolite-facies foliation in the lower crust (Little et al., 2011). The intersection of the Green and Hellman (1982) thermometer and the garnet-plagioclase- Al_2SiO_5 -quartz barometry allows us to determine an apparent difference in pressure between a core sample (08-037a; 16 ± 2 kbar) and a carapace sample (10-070a; 13 ± 2 kbar) in the Mailolo dome (Fig. 3.8c,e). A similar relative difference in pressure is also shown by the intersection of the Krogh and Raheim (1978) thermometer and the garnet-plagioclase- Al_2SiO_5 -quartz barometer (Fig. 3.8c,e). Thus, this apparent difference in pressure between the

Mailolo dome core and carapace samples is reproducible between gneiss domes and barometers. I therefore suggest that the original difference in pressure that separated the core sample (08-037a) and the carapace sample (10-070a) in the Mailolo dome, prior to the amphibolite-facies ductile thinning, was 3 ± 2.8 kbar (approximate 95% confidence interval). This pressure difference equates to 10 ± 9.3 km (approximate 95% confidence interval) of foliation-orthogonal distance (assuming a rock density of 2.7 g cm^{-3} as previously discussed; Harkness, 1891; Hinze, 2003). The current foliation-orthogonal distance separating these samples is 1.1 ± 0.25 km (assigned 2σ uncertainty; *Chapter 2 this thesis*). These apparent differences in foliation-orthogonal distance imply 9 ± 9.3 km (approximate 95% confidence interval) of exhumation as the result of ductile thinning between the crust and the carapace in the (U)HP terrane during doming in the upper crust.

This estimate is poorly constrained to the point of being meaningless because of the large errors associated with the original difference in pressure between the core and carapace samples (± 2.8 kbar). These errors would decrease if the ± 2 kbar error I have assigned to pressure estimates calculated here were correlated, possibly through the assumptions related to the thermobarometric calculation. Although the estimates I have presented here are not constrained by meaningful errors, I suggest that a detailed geobarometric study on the core and carapace zones in the D'Entrecasteaux Islands may refine our understanding of the final phases of dome development and emplacement in the mid to upper crust in the D'Entrecasteaux Islands. Structural evidence in the gneiss domes suggests significant contribution of ductile thinning to the exhumation of the gneiss domes through the crust, and constraining the pressure conditions of the formation of the core and carapace zones would help to constrain the magnitude of this ductile thinning (Little et al., 2011).

3.8 Conclusions

The Rb-Sr internal mineral isochrons presented here are the first attempt to directly date deformation related to the eclogite- and amphibolite-facies metamorphic events in the D'Entrecasteaux Islands, using a radiometric technique that has never been

applied to these rocks. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated here (0.7037 – 0.7047) are primitive and support previous inferences that the protolith of the UHP and HP metamorphic rock was the igneous Whitsunday Volcanic Arc Province in northeastern Australia. This province is currently separated from PNG by the Coral Sea Basin ocean floor (Paleocene to early Eocene).

Two samples of eclogite, five samples of quartzofeldspathic gneiss, and two samples of granitic rock were analyzed for Rb-Sr isotopic composition. Five of these samples yielded statistically valid isochrons. A coesite-bearing sample of eclogite yielded a Rb-Sr age of 5.7 ± 2.0 Ma (2σ). The other sample of eclogite, which may have once contained coesite based on radial fracturing around quartz inclusions in garnets, yielded an age of 5.6 ± 1.6 Ma (2σ). These two samples of boudins cores retain their eclogite-facies rock fabric and mineral assemblage, and have remained a closed system since the crystallization of eclogite-facies minerals. These new Rb-Sr ages support recent U-Pb zircon ages by Gordon et al. (*in review*) that indicate the UHP metamorphism took place at ~ 5 Ma, ~ 2 Ma younger than previously suggested (Baldwin et al., 2004; Monteleone et al., 2007; Zirakparvar et al., 2011). Based on Rb-Sr ages presented here, and previous U-Pb zircon ages on granitic dikes by Gordon et al. (*in review*), I calculate a time lag of 2.2 ± 1.5 Ma (approximate 95% confidence interval) between UHP metamorphism in the mantle and amphibolite-facies metamorphism and ductile thinning in the lower crustal for rocks within the Mailolo dome. The Rb-Sr ages of three samples of amphibolite-facies quartzofeldspathic gneiss and granodiorite range from 3.90 ± 0.44 Ma (2σ) in the northwest Normanby dome, to 2.41 ± 1.40 Ma (2σ) and 2.38 ± 0.29 Ma (2σ) in the Mailolo dome and Goodenough dome respectively. I interpret these three Rb-Sr ages as recording the timing of the final stage of fluid-rock interaction during the amphibolite-facies retrogression. The latter two ages are remarkably similar to U-Pb zircon ages calculated by Gordon et al. (*in review*), which are similarly interpreted.

I conclude that the estimate of temperature during the amphibolite-facies metamorphism determined by this study ($>640 - 760$ °C) is in agreement with previous studies that suggest that the exhumation from the mantle to the surface was nearly isothermal (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008; Little et al., 2011; Monteleone et al., 2007). The pressure estimates for the

amphibolite-facies metamorphism presented here (10 – 17 kbar) are 3 – 6 kbar higher than previous estimates, an apparent increase in pressure that implies the body of gneisses was thicker during ponding at the lower crust. Based on the 2.2 ± 1.5 Ma (approximate 95% confidence interval) time lag and the pressure estimates for the amphibolite-facies metamorphism calculated here, I estimate a minimum unroofing rate for the (U)HP gneisses of 19 ± 11 mm yr⁻¹ (approximate 95% confidence interval) from UHP depths to the lower crust.

4. Thesis conclusions

This thesis utilizes geochronology and geothermobarometry to refine the current understanding of the kinematics of exhumation and the timing of deformation in gneiss domes in the D'Entrecasteaux Islands, southeastern Papua New Guinea (PNG). I present two main analytical data sets for this (U)HP terrane, which contains the youngest known eclogite-facies rocks on Earth. First, I undertook a detailed study of the variation of Ti content in quartz across four gneiss domes in the northwestern D'Entrecasteaux Islands. I conclude that spatial gradients of Ti content in quartz are a valid tectonic tool to discern cooling and exhumation rates in a rapidly exhuming body of rock. Second, nine new Rb-Sr ages are presented here, which are interpreted as constraining the previously undetermined timing of rock fabric development during the ultrahigh-pressure (UHP) metamorphism and the subsequent amphibolite-facies metamorphism in the D'Entrecasteaux Island. Based on these new data sets, and on the cathodoluminescence and thermobarometric analysis undertaken here, I present the following conclusions:

1. Rb-Sr isochrons calculated for two samples of the cores of eclogite boudins yield a mean Rb-Sr age of 5.6 ± 1.2 Ma (approximate 95% confidence interval). As one of these samples has been shown to preserve coesite (08-010a; Rb-Sr age of 5.7 ± 2.0 Ma; 2σ) and the other contains radial fractures around quartz inclusions in garnet (09-039biii; Rb-Sr age of 5.6 ± 1.6 Ma; 2σ), these new Rb-Sr ages support recent U-Pb zircon ages that revise the age of the UHP metamorphism to ~ 5 Ma (Gordon et al., *in review*). This new age is ~ 2 Ma younger than previous estimates for the timing of this UHP metamorphism (Baldwin et al., 2004; Monteleone et al., 2007; Zirakparvar et al., 2011).
2. I present statistically valid Rb-Sr isochrons for three samples of granodiorite and quartzofeldspathic gneiss, which constrain the timing of mineral fabric formation during the amphibolite-facies overprint in the northwestern D'Entrecasteaux Islands to 3.9 – 2.4 Ma. These three ages are 3.90 ± 0.44 Ma (2σ) for a granodiorite from the northwest Normanby dome, 2.41 ± 1.40 Ma

(2σ) for a granodiorite from the Mailolo dome, and 2.38 ± 0.29 Ma (2σ) for a quartzofeldspathic gneiss from the Goodenough dome. These ages imply a westward younging in age of the amphibolite-facies overprint, which may be related to the propagation of the Woodlark Rift through the crust of eastern PNG.

3. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios calculated here are primitive (0.7037 – 0.7047), and supports previous inferences that the protolith of the metamorphic rock in the D'Entrecasteaux Islands was the igneous Whitsunday Volcanic Province in northeastern Australia. The Whitsunday Volcanic Province is located on the opposite flank of the oceanic Coral Sea Basin, which was actively spreading from 62 to 56 Ma.
4. Based on the Rb-Sr age for the UHP metamorphism presented here and a U-Pb zircon age for the initial phase of the amphibolite-facies metamorphism in the lower crust determined by Gordon et al. (*in review*), I calculate a time lag of 2.2 ± 1.2 Ma (approximate 95% confidence interval) between UHP conditions at mantle depths and metamorphism and ductile thinning at lower crustal depths.
5. Pressure and temperature estimates for the amphibolite-facies metamorphism are 10 – 17 kbar and $>640 - 760$ °C respectively. The presence of coesite in one sample of eclogite in the Mailolo dome and a pressure estimate for a core sample from the Mailolo dome of 12.5 ± 2 kbar, implies that this gneiss dome was exhumed from >90 km to $\sim 47 \pm 7$ km (approximate 95% confidence interval). These pressure estimates imply a difference in depth between UHP metamorphism and metamorphism in the lower crust of 43 ± 10 km (approximate 95% confidence interval). Based on this difference in depth, and the time lag between these two metamorphic events calculated here, I estimate an unroofing rate of 19 ± 11 mm yr⁻¹ (approximate 95% confidence interval) during exhumation from the mantle to the lower crust.
6. I present a pressure estimate of 16 ± 2 kbar for a core sample and 13 ± 2 kbar for a carapace sample from the Mailolo dome. Based on these estimates, I

calculate an apparent difference in pressure of 3 ± 2.8 kbar (approximate 95% confidence interval) between these samples, which are currently separated by a vertical distance of $\sim 1.1 \pm 0.25$ km (assigned 2σ uncertainty). This apparent separation implies post-metamorphic ductile thinning of the gneiss body as it was exhumed through the crust.

7. I analyzed 90 samples by LA-ICP-MS, and determine that the average range of Ti content in quartz in the D'Entrecasteaux Islands is 10 – 20 ppm. In the D'Entrecasteaux Islands, the final Ti equilibration in quartz occurred during dynamic recrystallization by high-temperature grain-boundary migration during the final stage of exhumation of the gneiss domes. Based on this dynamic recrystallization and on temperature constraints from the presence of a partial melt phase in the domes and chessboard microstructures in quartz, I conclude that the sample-averaged Ti content within the quartz grains in a hot and rapidly exhuming body depends on the relative rates of cooling and recrystallization during final ascent. Assuming that the recrystallization rate across the exhuming body varied less than the cooling rate, the sample-averaged Ti concentrations may be used as a proxy for cooling rates, and by inference, exhumation rates between samples.
8. I have mapped an increase in Ti content in quartz from 2.5 – 25 ppm at the margins to 20 – >100 ppm in the interiors of four gneiss domes in the D'Entrecasteaux Islands. I conclude that this increase is statistically robust based on regression analysis and probabilities determined by a one-sided Student's t test. If the assumption of a constant recrystallization rate is valid for quartz grains within the D'Entrecasteaux Islands, the occurrence of high Ti concentrations in the interior of the gneiss domes implies that this area was subjected to the fastest relative cooling rates. I conclude that the gneiss domes in the D'Entrecasteaux Islands are diapiric in origin, and were exhumed through the crust via pure-shear dominated symmetric doming.

The unroofing rate presented here (19 ± 11 mm yr⁻¹; approximate 95% confidence interval) between UHP conditions at mantle depths and metamorphism and ductile thinning at lower crustal depths implies that exhumation in the D'Entrecasteaux

Islands occurred at plate tectonic rates (cm yr^{-1} ; Baldwin et al., 2008; Monteleone et al., 2007). In addition, the minimal difference between previously published temperature estimates for the UHP metamorphism and the amphibolite-facies temperature estimates presented here support previous inferences that exhumation from mantle depths to the lower crust was nearly isothermal (Baldwin et al., 1993; Baldwin et al., 2004; Baldwin et al., 2008). This rapid and nearly isothermal exhumation strongly supports my conclusion that the crustal exhumation is predominantly affected by pure-shear (diapiric) symmetric doming. I note that this conclusion is in accordance with a previous structural study by Little et al. (2011), who argue that the (U)HP terrane in the D'Entrecasteaux Islands was exhumed from the mantle to the lower crust diapirically.

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Appendix B

Ti-in-quartz methods

B.1 Methods

Hand samples were cut into sub-samples ~5 mm in size and then pressed onto tape with the epoxy mould. EPO-TEK epoxy was used to mount the samples into 25 mm half-moons briquettes for the laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS). Once the epoxy was dry, the mounts were ground down on a diamond cup-wheel until a large sample surface area was exposed, and then polished using 6 μm , 3 μm , and 1 μm Kemet International Ltd. liquid diamond polish on an ATM Saphir 560 polishing machine. Before analysis, sample mounts were coated with ~25 nm of carbon in a JEOL vacuum evaporator.

Two sets of pre-analyses images were obtained to facilitate sample location during LA-ICP-MS. Reflected light microscopy was carried out on an Olympus BX51 microscope with an Olympus DP70 camera (which contains in-built scale bars) at Victoria University of Wellington (VUW), in order to create a background to the map of quartz grains selected for analysis. Back-scattered electron images were captured on the JEOL JXA-733 SuperProbe and the new JEOL JXA-8230 electron probe microanalyzer at VUW. Back-scattered electron images were used to locate quartz for analyses. These two images sets were combined to create the final map for LA-ICP-MS analysis.

The New Wave 193 μm solid-state Nd-YAG laser at VUW causes trace element-poor and Si-rich material to fracture during interaction of the laser with the target. Ideally, this interaction should create a round crater. This fracturing results in the creation of mineral shards in the first few seconds of laser ablation that are subsequently blown away by the gas flow, and may result in unwanted mineral phases being incorporated into the signal and the destruction of the area immediate to the shot. Laser settings (such as optional gas flow, extract voltage, and torch position) were tuned during ablation of the NIST 612 standard to ensure that: (1) the quartz ablated as well as possible, and (2) the ICP-MS was at optimum sensitivity

and low internal errors (Table B.1). The switch between pulse (P; $<1 \times 10^6$ counts per second; ^{43}Ca , ^{47}Ti , ^{49}Ti , ^{27}Al) and analog (A; $>1 \times 10^6$ counts per second; ^{29}Si) counting modes was carried out by the ICP-MS. The P/A factor was measured on all analyzed elements during tuning to ensure the switch between high and low signal was performed correctly. Elemental oxide production was maintained below 1.5% by tuning the conditions of the plasma torch, and was monitored by ThO^+/Th^+ .

Table B.1 Analytical conditions of the LA-ICP-MS

ICP-MS	
System	Agilent 7500CS
Acquisition mode	Peak-hopping
Detection mode	pulse (^{43}Ca , ^{47}Ti , ^{48}Ti , ^{27}Al) and analogue (^{29}Si)
Laser ablation	
System	New Wave 193 nm (deep UV) solid state laser
Laser power	65% for NIST 612, ~85% for quartz grains
Ablation mode	Static spot analysis
Repetition rate	10 Hz
Standards	
Bracketing/Calibration standards	NIST 612
Analysis method	
Standard/sample acquisition	60 seconds
Wash out/background acquisition	90 seconds
Measured isotopes and integrations times	^{29}Si , ^{43}Ca , ^{47}Ti , ^{49}Ti , ^{27}Al ; all 0.01 seconds
Tuning	
Tuning standards	NIST 612
Monitored isotopes during tuning	^{29}Si , ^{43}Ca , ^{47}Ti , ^{49}Ti , ^{27}Al
Ablation mode	50 μm diameter spots
Monitored isotopes during ablation	^{29}Si , ^{43}Ca , ^{47}Ti , ^{49}Ti , ^{27}Al
Background	^{47}Ti <400 counts per second*
Oxides	$<1.5\%$ (checked during tuning)
Carrier gas (Ni)	0.75 -0.85 L min^{-1}
Optional gas (He)	75 - 85%
RF Power	1500 W
RF matching	1.96 V
Sample depth	3 – 4 mm

*Counts per second or signal measure by the LA-ICP-MS

B.2 Errors and uncertainties calculations

The total uncertainty related to the Ti-in-quartz apparent temperature (Table 2.1) is derived from three sources. First, there is an uncertainty in the slope and intercept of

the least-squares regression-analysis carried out during calibration of the thermometer ($\sim 5^\circ\text{C}$ of uncertainty; Thomas et al., 2010; Wark and Watson, 2006). Secondly, there is the analytical uncertainty, which is a 95% confidence interval of the average Ti concentration. Thirdly, there is an assigned uncertainty of ± 0.2 in the Ti activity (α_{TiO_2}). I suggest that the three sources of uncertainty are independent of each other as they arise from different contributions. Wark and Watson (2006) and Thomas et al., (2010) determined the calibration uncertainty. The analytical uncertainty is calculated from the ICP-MS measurement statistics. The α_{TiO_2} uncertainty is an assigned value.

B.2.1 Wark and Watson (2006) uncertainty

The combination of the three sources of uncertainties into the single value was determined as a 95% confidence interval of the quotient. The calibration uncertainty ($c^1 = \pm 24$ and $c^2 = 0.02$), the analytical uncertainty (ϵ_j), and the Ti activity uncertainty (α) were all incorporated into the original Wark and Watson (2006) equation:

$$T = \frac{-(3765 + c^1)}{\left(\log_{10} \left(\frac{\text{Ti} + \epsilon_j}{\alpha_0 + \alpha} \right) - (5.69 - c^2) \right)} - 273.$$

Expanding the logarithm and converting to base e gives the denominator as

$$0.4343 \left(\text{Ln}(\text{Ti} + \epsilon_j) - \text{Ln}(\alpha_0 + \alpha) \right) - (5.69 - c^2),$$

which can be rearranged to

$$0.4343 \left(\text{LnTi} - \text{Ln}\alpha_0 + \text{Ln} \left(1 + \frac{\epsilon_j}{\text{Ti}} \right) - \text{Ln} \left(1 + \frac{\alpha}{\alpha_0} \right) \right) - (5.69 - c^2).$$

Approximating $\text{Ln}(1+x)$ by the first term of its power series is valid if $x^2 \ll x$. Thus, the denominator is approximately

$$0.4343 \left(\text{LnTi} - \text{Ln}\alpha_0 + \frac{\epsilon_j}{\text{Ti}} - \frac{\alpha}{\alpha_0} \right) - (5.69 - c^2).$$

The variance of the denominator is

$$= 0.4343^2 \left(\frac{\sigma_\epsilon}{\text{Ti}} \right) + 0.4343^2 \left(\frac{1/2\alpha}{\alpha_0} \right)^2 + \left(\frac{0.02}{2} \right)^2.$$

The variance of the numerator is

$$= \left(\frac{c^1}{2} \right)^2,$$

where I have taken the ranges c^1 , c^2 , and α to be 2σ . The two variances were then input in the equation for the 95% confidence interval of a quotient:

$$\text{var}\left(\frac{A}{B}\right) = \frac{1}{B^2} \text{var } A + \frac{A^2}{B^4} \text{var } B,$$

in order to determine the combined uncertainty. This equation is valid provided A and B are independent and var B is small ($< \sim 0.1$) compared to B.

B.2.2 Thomas et al. (2010) uncertainty

The combination of the three sources of uncertainties into the single value for the calculated Thomas et al. (2010) TitaniQ apparent temperatures was accomplished with a method similar to that discussed in Section B.2.1. The calibration uncertainty ($c^1 = \pm 3122$, $c^2 = \pm 0.04$, $c^3 = \pm 63$), the analytical uncertainty (ϵ_j), and the Ti activity uncertainty (α) were all incorporated into the original Thomas et al., (2010) equation:

$$T(^{\circ}\text{C}) = \frac{(60952 \pm c^1) + (1741 \pm c^3)P}{(1.520 \pm c^2) - R(\ln X_{\text{TiO}_2}^{Qtz} \pm \epsilon_j) + R(\ln \alpha_{\text{TiO}_2} \pm \alpha)} - 273.15$$

Expanding the denominator gives

$$(1.520 \pm c^2) - R \left\{ \ln \left(\frac{X_{\text{TiO}_2}^{Qtz}}{\alpha_{\text{TiO}_2}} \right) + \ln \left(1 + \frac{\epsilon_j}{X_{\text{TiO}_2}^{Qtz}} \right) - \ln \left(1 + \frac{\alpha}{\alpha_{\text{TiO}_2}} \right) \right\}.$$

Approximating $\ln(1+x)$ by the first term of its power series is valid if $x^2 \ll x$. If

$$\frac{\sigma_{\epsilon}}{X_{\text{TiO}_2}^{Qtz}} \text{ and } \frac{\alpha}{\alpha_{\text{TiO}_2}} \ll 1, \text{ the denominator is approximately}$$

$$(1.520 \pm c^2) - R \left\{ \ln \left(\frac{X_{\text{TiO}_2}^{Qtz}}{\alpha_{\text{TiO}_2}} \right) + \frac{\epsilon_j}{X_{\text{TiO}_2}^{Qtz}} - \frac{\alpha}{\alpha_{\text{TiO}_2}} \right\}.$$

So the variance of the denominator is

$$= -R^2 \left\{ \text{var} \left(\frac{\epsilon_j}{X_{\text{TiO}_2}^{Qtz}} \right) + \text{var} \left(\frac{\alpha}{\alpha_{\text{TiO}_2}} \right) \right\} + \left(\frac{c^2}{2} \right)^2,$$

which expands to

$$= R^2 \left\{ \frac{1}{\left(X_{TiO_2}^{Q_{Tz}}\right)^2} \sigma_\epsilon^2 + \frac{\left(\frac{\alpha}{2}\right)^2}{\left(\alpha_{TiO_2}\right)^2} \right\} + \left(\frac{c^2}{2}\right)^2.$$

The variance of the numerator is

$$= \left(\frac{c^1}{2}\right)^2 + \left(\frac{c^3}{2}\right)^2,$$

where I have taken the ranges c^1 , c^2 , and α to be 2σ , and c^3 to be $\ll c^1$. The two variances were then input in the equation for the 95% confidence interval of a quotient:

$$\text{var}\left(\frac{A}{B}\right) = \frac{1}{B^2} \text{var } A + \frac{A^2}{B^4} \text{var } B,$$

in order to determine the combined uncertainty, with the same requirements as before.

B.3 One-sided t distribution

A one-sided t distribution was used to determine the probability that the slopes for the linear regressions in Fig. 2.15 were negative or zero (Table B.2). I assume that the uncertainties or scatter in the data, and hence the slope estimates, are Normal/Gaussian random variables (Fig. B.1).

Table B.2 Results of one-sided t distribution

Fault	Slope (m)	Standard Deviation m (sd)	No. of data ^a	m/sd	p0 (Probability slope is negative or zero)	p0
Wakonai	0.00826	0.00283	21	2.92260	0.00437	< 1%
Mwadeia	0.00109	0.00072	14	1.51883	0.07735	< 8%
Morima	0.00046	0.00005	5	9.29280	0.00132	< 1%
NW Norm.	0.00054	0.00127	5	0.42839	0.34863	< 35%
SE Norm.	0.00321	0.00126	5	2.53610	0.04248	< 5%

^a df = no. of data -2

Figure B.1. A Normal or Gaussian distribution. The probability that the slope listed in Table B.3 is zero or negative is the probability that the slope will fall into the shaded area of the graph (one-sided test). If it did so, this area gives the corresponding probability that the slope of the linear regressions on Figure 2.15 is zero or negative.

Appendix C

MATLAB™ script

C.1 MATLAB™ input file formatting

The MATLAB™ script presented here was used to calculate averages and standard deviations of all the inductively coupled plasma mass spectrometry (ICP-MS) analyses undertaken by this study. This script was written by Euan Smith (Victoria University of Wellington). The MATLAB™ script requires the user to set the initial wait, which is the length of time before the first analysis of the standard. There was some variation in this value for certain analytical sessions undertaken by this study. If the initial wait is inaccurate, the average and standard deviation of the ICP-MS analyses will be inaccurate as well. This parameter is marked “sampwait=84;.....%%%%%%%%%%TUNABLE !!” in the MATLAB™ script. The input file must be a csv file, and must be formatted as in Fig. C.1.

C.2 MATLAB™ script

```
%_____
%
% LAICPMS output averaging
%
% Euan Smith 110908
%
% with some code borrowed from an unpublished MatLab script by Brian
Anderson (february 2009)
%
%_____
```

	A	B	C	D	E	F
1	Time [Sec]	Al27	Si29	Ca43	Ti47	Ti48
2						
3	0.259	4500.73	59729.22	833.36	120	316.67
4	0.508	3200.37	66459.94	766.69	60	166.67
5	0.757	4100.61	65153.72	666.68	80	300
6	1.006	3900.55	67062.86	683.35	110	333.34
7	1.255	4900.87	63847.63	833.36	50	266.67
8	1.504	3100.35	64952.78	633.35	60	250
9	1.753	3700.5	61938.94	533.34	60	333.34
10	2.002	2700.26	61336.26	600.01	110	450.01
11	2.251	3700.5	65857.06	666.68	70	233.34
12	2.5	3100.35	62642.12	750.02	90	216.67
13	2.749	2100.16	65555.64	766.69	100	383.34
14	2.998	3400.42	67163.34	600.01	60	350
15	3.247	4000.58	58524.07	566.68	110	300
16	3.496	4100.61	64651.37	583.35	70	300
17	3.745	4200.64	59026.19	766.69	40	266.67
18	3.994	4100.61	62240.3	800.02	70	350
19	4.243	3100.35	60130.97	983.37	60	316.67
20	4.492	3900.55	64249.49	516.68	70	233.34
21	4.741	4000.58	68369.25	666.68	90	266.67
22	4.99	4600.77	74500.92	850.03	20	283.34
23	5.239	3200.37	65254.21	716.69	80	183.33
24	5.488	4000.58	61436.7	716.69	70	366.67
25	5.737	3600.47	64048.56	583.35	60	333.34
26	5.986	3900.55	58724.91	466.67	100	150
27	6.235	3800.52	59628.78	733.35	60	266.67
28	6.484	2600.25	68771.25	900.03	90	200
29	6.733	3200.37	59126.63	616.68	50	233.34
30	6.982	3600.47	61838.51	683.35	120	200
31	7.231	3400.42	59227.05	550.01	40	250

Figure C.1 MATLAB™ program input file formatting. There must be no data or notations after the end of the ICP-MS measurements.

```

clear all

%-----

%

% parameters

%

%-----

headlines=2;

initialwait=80;    %default now overwritten by dialogue prompt

sampwait=84;      %%%%%%%%%%%TUNABLE !!

stdwait=90;

backwait=40;

nsample=60;

nstd=60;

nback=30;


%_____

%

% Get and read datafile (.csv)

%_____


fd = dir;

fnstr = {fd.name};

[s,ok] = listdlg('PromptString','Select data file (.csv):',...

                'SelectionMode','single',...

                'ListString',fnstr);

```

```
if ~ok error('user pressed cancel'); end

ss=getfield(fd,{s});

fdata=ss.name;

M=csvread(fdata,headlines,0);

%now read those headerlines

fid=fopen(fdata);

% read all text to the end of line, including whitespace

header = textscan(fid,'%s%*[^\\n]',headlines,'whitespace','\\t');

fclose(fid);

%

% extract field names

fn=textscan(strvcat(header(Blanckenburg et al.)(1)),'%s','delimiter',',');

field_names=fn(Blanckenburg et al.);

%

% plot all data and draw legend

%

% Modification 11/2010 get starting wait

%

prompt = {'Enter initial wait'};

dlg_title = 'wait(s)';
```

```
num_lines = 1;

initial = inputdlg(prompt,dlg_title,num_lines);

initialwait=str2num(initial(Blanckenburg et al.));

clf

time=M(:,1);

nelements=length(field_names)-1; %process each element

nd=length(time);

dt=max(time)/(nd+1);

%convert wait times to indices

nextstd=ceil(nstd/dt);

nextsamp=ceil(nsamp/dt);

nextback=ceil(nback/dt);

nsampwait=ceil(sampwait/dt);

nstdwait=ceil(stdwait/dt);

nbackwait=ceil(backwait/dt);

for iel=2:nelements+1

    clear back
```

```
clear sample
```

```
clear stnd
```

```
dataleft=1;
```

```
ip=ceil(initialwait/dt);
```

```
h=0;%processed samples and standards
```

```
jstd=0;
```

```
jsample=0;
```

```
jback=0;
```

```
%method: rrecord background before each std or sample
```

```
while dataleft
```

```
    h=h+1;
```

```
    if mod(h,5) == 1 %standard
```

```
        jstd=jstd+1;
```

```
        jback=jback+1;
```

```
        %1st background
```

```
        if ip+nextback-1 <= nd
```

```
            samplemask=zeros(nd,1);
```

```
            samplemask(ip:ip+nextback-1,1)=ones(nextback,1);
```

```
            sett=samplemask'*(M(:,iel).^2); %squares
```



```

    back(jback,1)=(1/nextback)*samplemask'*M(:,iel);
    varr=(1/nextback)*sett-back(jback,1)^2;
    back(jback,1)=(1/nextback)*samplemask'*M(:,iel);
    back(jback,4)=sqrt(varr/nextback);
    back(jback,2)=ip;
    back(jback,3)=ip+nextback-1;
    ip=ip+nextback+nbackwait;
end

%now std
if ip+nextstd-1 <= nd
    samplemask=zeros(nd,1);
    samplemask(ip:ip+nextstd-1,1)=ones(nextstd,1);

    sett=samplemask'*(M(:,iel).^2); %squares
    stnd(jstd,1)=(1/nextstd)*samplemask'*M(:,iel);
    varr=(1/nextstd)*sett-stnd(jstd,1)^2;
    stnd(jstd,1)=(1/nextstd)*samplemask'*M(:,iel);
    stnd(jstd,4)=sqrt(varr/nextstd);
    stnd(jstd,2)=ip;
    stnd(jstd,3)=ip+nextstd-1;
    ip=ip+nextstd+nstdwait;
end
else
    jsample=jsample+1;

```

```

jback=jback+1;

%1st background
if ip+nextback-1 <= nd
    samplemask=zeros(nd,1);
    samplemask(ip:ip+nextback-1,1)=ones(nextback,1);

    sett=samplemask'*(M(:,iel).^2); %squares
    back(jback,1)=(1/nextback)*samplemask'*M(:,iel);
    varr=(1/nextback)*sett-back(jback,1)^2;
    back(jback,1)=(1/nextback)*samplemask'*M(:,iel);
    back(jback,4)=sqrt(varr/nextback);
    back(jback,2)=ip;
    back(jback,3)=ip+nextback-1;
    ip=ip+nextback+nbackwait;
end

%now sample
if ip+nextsamp-1 <= nd
    samplemask=zeros(nd,1);
    samplemask(ip:ip+nextsamp-1,1)=ones(nextsamp,1);

    sett=samplemask'*(M(:,iel).^2); %squares
    sample(jsample,1)=(1/nextsamp)*samplemask'*M(:,iel);
    varr=(1/nextsamp)*sett-sample(jsample,1)^2;

```

```

        sample(jsample,4)=sqrt(varr/nextsamp);

        sample(jsample,2)=ip;

        sample(jsample,3)=ip+nextsamp-1;

        ip=ip+nextsamp+nsampwait;

    end

end

if nd-ip < min([nextsamp nextstd nextback])

    dataleft=0;

end

end

figure

ph=semilogy(time,M(:,iel),'-c');

legend(ph,field_names(iel));

hold on

Nsamp=length(sample(:,1));

Nstd=length(std(:,1));

Nback=length(back(:,1));

for j=1:Nsamp

    errorbar(time(sample(j,2):sample(j,3),1),sample(j,1)*ones(nextsamp,1),...

        sample(j,4)*ones(nextsamp,1),'-m');

end

for j=1:Nstd

```

```
errorbar(time(std(j,2):std(j,3),1),std(j,1)*ones(nextstd,1),std(j,4)*ones(ne
xtstd,1),'-r');
```

```
end
```

```
for j=1:Nback
```

```
errorbar(time(back(j,2):back(j,3),1),back(j,1)*ones(nextback,1),back(j,4)*ones(
nextback,1),'-k');
```

```
end
```

```
%-----
```

```
%
```

```
% write data to .xls
```

```
%
```

```
%-----
```

```
lf=length(fdata);
```

```
fout=[fdata(1:lf-4) 'out.xls'];
```

```
datout=[std;zeros(1,4);sample;zeros(1,4);back];
```

```
xlswrite(fout,datout,field_names{iel},'A2');
```

```
end %of file
```

C.3 MATLAB™ output

The output of the MATLAB™ script is shown in Fig. C.2. The user must check the position of each ICP-MS measurement on the graphs output by the program, in order to determine if the average and standard deviation of the ICP-MS analysis and the background is accurate. If they are not accurate, the initial wait time must be adjusted.

Figure C.2 MATLAB™ program results. (a) Example of one of the five graphs for each mass measured by ICP-MS (Al27, Si29, Ca43, Ti47, Ti48) that is output by the MATLAB™ script presented here. These can be saved as Adobe Illustrator (Adobe Systems Incorporated. San Jose, CA, USA) files. The position and length of the red bars is the average and standard deviation respectively of each ICP-MS analysis. The position and length of the black bars is the average and standard deviation respectively of each background measurement. If the position of these markers is inaccurate, they can be adjusted by changing the initial sample wait (see text). (b) A screen shot of the Microsoft Excell (Microsoft. Redmond, WA, USA) file that is output by the MATLAB™ script, labeled as MKiout. The last five tabs shown at the bottom left of the image are for each mass analysed by the ICP-MS. The columns contain the following data: A, average counts per second or signal of the ICP-MS; B, start of the indices on the input csv file; C, end of the indices on the input csv file; D, standard deviation the ICP-MS measurements for that analysis. The first set of data (row 2 - 4 here) are the standard measurements, the second set of data (row 6 - 13 here) are the unknown measurements, and the third set of data (row 15 - 28 here) are the background measurements.

Appendix D

Rb-Sr and thermobarometry sample petrology

D.1 Mailolo dome, Fergusson Island

08-010c, coarse-grained granodioritic host orthogneiss, core zone, 2.41 ± 1.40 Ma

Assemblage: quartz, plagioclase, K-feldspar, and white mica with minor orthopyroxene, biotite, oxides, and clinozoisite.

Quartz (300 – 1000 μm) exhibits a well-developed subgrain structure with deformation bands and rounded interlobated grain boundaries. Plagioclase grains (200 – 600 μm) are inequigranular and exhibit lamellar twinning with minor white mica inclusions (<1%). White mica is fresh, coarse-grained (300 – 900 μm), and has been affected by minor regression to biotite at the grain boundaries (<2%).

08-010a, ultra-high pressure eclogite, core zone, 5.7 ± 2.0 Ma

Assemblage: garnet, omphacite, white mica, quartz, and hornblende with minor rutile, orthopyroxene, zoisite, and apatite.

Petrology after Brownlee et al. (*in prep.*). Garnets (200 – 400 μm) are rounded and equigranular. Omphacite is coarse-grained (>500 μm) and retrogressed to a fine symplectite of plagioclase and hornblende at grain boundaries. Phengite is coarse-grained (500 – 1000 μm) and retrogressed to biotite and plagioclase at the grain boundaries. Phengite and has been affected by retrogression to biotite between the mica sheets (<1%). Hornblende grains are present (200 – 500 μm ; 5% volume). Rutile grains (200 – 300 μm) exhibit minor retrogression to ilmenite at the grain boundaries. This rock contains coesite (Baldwin et al., 2008).

08-037a, quartzofeldspathic gneiss, core zone, 12.4 ± 5.0 Ma

Assemblage: quartz, garnet, white mica, plagioclase, and K-feldspar with minor biotite, chlorite, rutile, ilmenite, and kyanite.

Quartz is coarse-grained (~1000 μm) with rounded polygonal grain boundaries and sweeping deformational bands. Garnets are rounded and equigranular, and vary from

coarse- (1000 μm ; fractured with biotite and quartz inclusions) to fine-grained (<400 μm). White mica is coarse-grained (500 – 1000 μm) and has been affected by retrogression to biotite at grain boundaries (20%) and between mica sheets (1%). Plagioclase and K-feldspar are fine-grained (200 – 300 μm), relative to the elongate quartz grains. Biotite grains (<5% volume) have been affected by minor retrogression to chlorite at grain boundaries (<<1%).

09-039biii, eclogite float, core zone, 5.6 ± 1.6 Ma

Assemblage: garnet, white mica, plagioclase, quartz, hornblende, and rutile with minor biotite, ilmenite, apatite and oxides.

Garnets (700 – 1200 μm) are rounded and fractured, with some radial fracturing around quartz inclusions. Garnets exhibit fine rutile exsolution needles and white mica inclusions, and are retrogressed to hornblende at grain boundaries. At the grain boundaries of hornblende there is a symplectite of plagioclase, quartz, biotite, albite, and pyroxene. Phengite (300 – 500 μm) has been retrogressed to muscovite and biotite at the grain boundaries (~15%). Plagioclase (where not included in a symplectite) is coarse-grained (400 – 600 μm) with lamellar twinning. Quartz is coarse-grained (500 – 1000 μm) with interlobate boundaries. Rutile (100 – 200 μm) is retrogressed to ilmenite at grain boundaries (~1%). Albite is fine-grained (<100 μm) with dentate margins.

10-070a, mica-bearing quartz sheet, carapace zone, thermobarometry sample

Assemblage: quartz, K-feldspar, plagioclase, white mica, garnet, kyanite, biotite, and chlorite with minor rutile and ilmenite.

Quartz (500 – 700 μm) exhibits undulose sweeping extinction and has rounded to dentate grain boundaries. Plagioclase (600 – 700 μm) exhibits lamellar twinning. Garnets (2000 – 2500 μm) are fractured and euhedral, and in some cases completely replaced by chlorite and biotite. Coarse-grained white mica (~1000 μm) exhibits minor (<<1%) retrogression to biotite on the grain boundaries. Kyanite grains are fractured.

10-071a, quartzofeldspathic gneiss, carapace zone, 3.7 ± 3.8 Ma

Assemblage: quartz, white mica, biotite, K-feldspar, garnet, and hornblende with minor oxides.

White mica is coarse-grained (800 – 1200 μm) with retrogression to biotite and chlorite at the grain boundaries (<2%). Coarse-grained white mica grains form large aggregates (>2000 μm). Quartz grains (400 – 600 μm) occur in aggregates and have polygonal grain boundaries with sweeping deformational bands. Plagioclase (<10% volume) exhibits lamellar twinning. Biotite grains (400 – 500 μm ; ~5 – 7% volume) show retrogression to chlorite at grain boundaries (<2%). Garnets (1000 – 2000 μm) are fractured with quartz and rutile inclusions.

D.2 Morima dome, Fergusson Island**03-086b, leucocratic orthogneiss, carapace zone, 0.30 ± 0.39 Ma**

Assemblage: quartz, plagioclase, K-feldspar, and white mica with minor epidote.

Quartz is coarse-grained (600 – 1000 μm) with round to dentate margins and undulose extinction. Plagioclase porphyroclasts (400 – 700 μm) show lamellar twinning and contains quartz and epidote inclusions. K-feldspar porphyroclasts are coarse-grained (2000 – 4000 μm), and contains quartz, white mica, and epidote inclusions. White mica occurs as coarse-grained mica fish (~1000 μm) and finer-grained matrix grains (400 – 600 μm), and is retrogressed to biotite near grain boundaries (<5%) and between mica sheets (<1%). White mica occurs as large (>4000 μm) aggregates. Fine-grained white mica occurs on the margins of plagioclase and K-feldspar and is in some cases completely retrogressed to biotite. Epidote occurs as two habits: (1) a coarse-grained (500 – 600 μm) and fractured matrix phase, and (2) fine-grained inclusions.

D.3 Goodenough dome, Goodenough Island

06-018a, quartzofeldspathic gneiss, transition zone between the core and carapace, 2.38 ± 0.29 Ma

Assemblage: quartz, plagioclase, K-feldspar, biotite, and white mica with minor garnet, sphene, chlorite, and oxides.

This sample contains mica-rich and quartz-rich domains. Quartz (300 – 600 μm) grain boundaries are interlobate, and the grains exhibit a well-developed subgrain texture. Plagioclase occurs in two habits: (1) a coarse-grained (1000 – 1200 μm) with lamellar twinning and irregular grain boundaries; or (2) a fine-grained matrix grains (400 – 600 μm) that can exhibit lamellar twinning. K-feldspar (500 – 800 μm) exhibits deformational crosshatched twinning. Garnets (400 – 600 μm) are rounded and fractured, with biotite and quartz inclusions. Garnets occur only in the mica-rich domains. White mica is coarse-grained (600 – 1200 μm) and has been affected by retrogression to biotite between mica sheets ($<<1\%$). White mica is slightly zoned under transmitted light. Biotite grains (500 – 700 μm) are retrogressed to chlorite at grain boundaries (10% of biotite grains by volume).

08-032a, leucocratic gneiss, carapace zone, 0.22 ± 0.06 Ma

Assemblage: quartz, plagioclase, K-feldspar, white mica, and biotite with minor apatite, orthopyroxene, clinozoisite, epidote, and garnet.

Quartz is fine-grained (300 – 500 μm) and exhibits a well-developed subgrain texture with deformation bands. Plagioclase is coarse-grained (800 – 1000 μm) and exhibits lamellar twinned and anti-perthite (exsolution texture). Plagioclase grains are intergrown with adjacent quartz grains. K-feldspar ($<2\%$ volume) contains quartz inclusions and is perthitic (exsolution texture). White mica is coarse-grained (600 – 1200 μm) and retrogressed to biotite at the grain boundaries ($<2\%$). Garnets (300 – 500 μm ; $<4\%$ volume) are fractured and intergrown with biotite.

D.4 Northwest Normanby dome, Normanby Island

•08-077a, foliated 20 cm granitic sheet hosted by quartzofeldspathic gneiss, core zone, 3.90 ± 0.44 Ma

Assemblage: quartz, plagioclase, K-feldspar, and white mica with minor biotite and oxides.

Quartz (200 – 500 μm) has polygonal to interlobate grain boundaries, and can form ribbons aggregates. Quartz exhibits inclusions of fine-grained biotite needles. Plagioclase is coarse-grained (400 – 600 μm) with irregular grain boundaries and lamellar twinning. White mica occurs as coarse-grained fish (700 – 1300 μm) with retrogression to biotite between mica sheets (<3%). Fine-grained biotite (100 – 200 μm) is present at white mica grain boundaries. White mica grains (500 – 1300 μm) occur in large (>4000 μm) aggregates.

•10-008a, pelitic gneiss, carapace zone, thermobarometry sample

Assemblage: plagioclase, K-feldspar, garnet, quartz, white mica, and biotite with minor kyanite, rutile, ilmenite, and oxides.

Extremely coarse-grained garnets (>1cm) were once euhedral and are now fractured with rutile, ilmenite, quartz, and oxides inclusions. Quartz occurs as fine-grained matrix grains (75 – 200 μm) and coarse-grained (800 – 1300 μm) ribbon aggregates with a well-developed subgrain texture. Quartz grain boundaries are primarily polygonal and interlobate. White mica is coarse-grained (700 – 1000 μm) and wraps the coarse-grained garnets. Mica-rich domains contain biotite, white mica, and oxides. White mica is retrogressed to biotite at the grain boundaries and between mica sheets. Fine-grained biotite (200 – 300 μm) occurs in the mica-rich domains.

Table D.1 Representative white mica major element compositions of samples analyzed for Rb-Sr isotopic composition and thermobarometry

Point	1	2	3	4	5	6	7	8	9	10	11	12
Sample No.	03-086b	03-086b	03-086b	06-018a	06-018a	06-018a	10-019a	10-019a	10-019a	08-032a	08-032a	08-032a
Grain Size	~500 μm	~500 μm	~250 μm	~1 mm	~1 mm	~350 μm	~2 mm	~2 mm	~300 μm	~700 μm	~700 μm	~250 μm
Notes	rim	core	core/rim	rim	core	core/rim	rim	rim	core	rim	core	core
SiO₂	47.59	48.09	48.73	46.28	45.47	45.76	49.11	51.47	47.52	45.68	46.35	46.08
TiO₂	0.80	0.50	0.51	0.75	1.55	1.60	0.83	0.58	1.11	0.76	0.97	0.91
Al₂O₃	33.09	28.40	28.74	32.49	31.37	32.15	29.06	27.21	31.22	30.77	28.33	29.12
FeO	3.61	4.23	4.06	2.61	2.85	2.81	3.61	3.88	3.86	5.56	6.93	6.50
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	1.47	2.83	2.96	1.77	1.76	1.56	3.15	3.55	2.58	1.35	1.54	1.54
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na₂O	0.37	0.20	0.17	0.41	0.44	0.38	0.32	0.31	0.35	0.38	0.27	0.36
K₂O	9.75	9.70	10.47	11.04	10.85	11.09	10.84	10.83	11.02	10.94	10.97	10.99
Anhydrous Total	96.69	93.95	95.65	95.34	94.29	95.34	96.92	97.82	97.67	95.44	95.36	95.48
Si	3.14	3.28	3.27	3.12	3.10	3.09	3.26	3.38	3.14	3.12	3.19	3.17
Ti	0.04	0.03	0.03	0.04	0.08	0.08	0.04	0.03	0.06	0.04	0.05	0.05
Al	2.57	2.28	2.28	2.58	2.53	2.56	2.27	2.10	2.43	2.48	2.30	2.36
Fe	0.20	0.24	0.23	0.15	0.16	0.16	0.20	0.21	0.21	0.32	0.40	0.37
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.14	0.29	0.30	0.18	0.18	0.16	0.31	0.35	0.25	0.14	0.16	0.16
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.05	0.03	0.02	0.05	0.06	0.05	0.04	0.04	0.05	0.05	0.04	0.05
K	0.82	0.84	0.90	0.95	0.94	0.96	0.92	0.91	0.93	0.95	0.96	0.96
Fe/(Fe + Mg)	0.71	0.60	0.58	0.60	0.62	0.64	0.53	0.52	0.60	0.80	0.82	0.81
Na/(Na+K)	0.04	0.02	0.02	0.04	0.04	0.03	0.03	0.03	0.03	0.03	0.02	0.03
Cel (Si-3)	0.14	0.28	0.27	0.12	0.10	0.09	0.26	0.38	0.14	0.12	0.19	0.17

Normalized to 12 oxygens

Table D.1 Representative white mica major element compositions of samples analyzed for Rb-Sr isotopic composition and thermobarometry (cont.)

Point	13	14	15	16	17	18	19	20	21	22	23	24
Sample No.	10-008a	10-008a	10-008a	10-008a	03-118a	03-118a	03-118a	09-039biii	09-039biii	09-039biii	10-071a	10-071a
Grain Size	~1.2 mm	~1.2 mm	~250 µm	~250 µm	~1.2 mm	~1.2 mm	~250 µm	~2 mm	~2 mm	~400 µm	~1.4 mm	~1.4 mm
Notes	rim	core	rim	inclusion garnet	rim	core	core	rim	core	rim	rim	core
SiO ₂	47.07	47.30	47.90	46.14	46.90	47.56	48.73	49.19	47.12	47.41	48.89	50.45
TiO ₂	0.63	0.64	0.64	0.45	0.93	1.21	0.51	1.14	1.13	1.13	0.85	0.65
Al ₂ O ₃	30.07	30.29	31.10	36.82	32.85	32.25	28.74	30.80	29.88	30.39	32.54	30.08
FeO	1.96	1.72	1.88	1.18	4.72	4.66	4.06	2.34	2.60	2.71	1.27	1.64
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	2.40	2.28	2.40	0.96	1.10	1.22	2.96	2.31	3.02	2.33	2.20	2.97
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	1.44	1.37	1.05	1.89	0.33	0.39	0.17	0.88	1.04	0.94	0.94	0.63
K ₂ O	9.62	9.44	9.00	9.15	9.76	9.67	10.47	9.60	9.29	9.51	9.97	10.02
Anhydrous Total	93.18	93.06	93.97	96.60	96.59	96.95	95.65	96.26	94.08	94.42	96.65	96.44
Si	3.22	3.22	3.22	3.02	3.12	3.15	3.27	3.24	3.19	3.20	3.20	3.31
Ti	0.03	0.03	0.03	0.02	0.05	0.06	0.03	0.06	0.06	0.06	0.04	0.03
Al	2.42	2.44	2.46	2.84	2.58	2.52	2.28	2.39	2.39	2.42	2.51	2.32
Fe	0.11	0.10	0.11	0.06	0.26	0.26	0.23	0.13	0.15	0.15	0.07	0.09
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.24	0.23	0.24	0.09	0.11	0.12	0.30	0.23	0.30	0.23	0.21	0.29
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.19	0.18	0.14	0.24	0.04	0.05	0.02	0.11	0.14	0.12	0.12	0.08
K	0.84	0.82	0.77	0.76	0.83	0.82	0.90	0.81	0.80	0.82	0.83	0.84
Fe/(Fe + Mg)	0.45	0.43	0.44	0.55	0.81	0.79	0.58	0.50	0.46	0.54	0.37	0.36
Na/(Na+K)	0.13	0.13	0.10	0.17	0.03	0.04	0.02	0.08	0.10	0.09	0.09	0.06
Cel (Si-3)	0.22	0.22	0.22	0.02	0.12	0.15	0.27	0.24	0.19	0.20	0.20	0.31

Normalized to 12 oxygens

Table D.1 Representative white mica major element compositions of samples analyzed for Rb-Sr isotopic composition and thermobarometry (cont.)

Point	25	26	27	28	29	30	31	32	33	34	35	36
Sample	10-071a	08-077a	08-077a	08-077a	08-037a	08-037a	08-037a	10-031a	10-031a	10-031a	10-070a	10-070a
Grain Size	~450 μ m	~1.2 mm	~1.2 mm	~400 μ m	~1.3 mm	~1.3 mm	~300 μ m	~1 mm	~1 mm	~250 μ m	~1.2 mm	~1.2 mm
Notes	rim	rim	core	core/rim	rim	core	core	rim	core	core/rim	core	rim
SiO ₂	49.10	47.26	49.67	47.39	46.23	49.01	48.40	47.96	46.66	38.34	50.07	49.88
TiO ₂	0.85	0.62	0.63	0.66	1.10	1.02	1.01	0.67	0.68	1.71	0.70	0.59
Al ₂ O ₃	32.58	29.01	30.06	29.27	35.35	31.00	31.21	30.92	32.45	19.12	36.09	36.69
FeO	1.32	3.44	3.70	3.59	2.04	2.87	2.65	2.39	2.51	12.43	1.03	0.84
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	2.16	2.37	2.36	2.41	0.78	2.36	2.11	2.42	1.98	14.90	1.11	0.90
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.42	0.37	0.41	0.34	1.11	0.70	0.74	0.36	0.43	0.32	1.36	1.47
K ₂ O	10.75	9.98	9.91	9.90	8.93	9.34	9.29	10.43	10.51	9.85	8.24	8.16
Anhydrous Total	97.17	93.06	96.75	93.56	95.52	96.30	95.42	95.13	95.22	96.81	98.60	98.53
Si	3.20	3.25	3.28	3.24	3.06	3.23	3.22	3.21	3.13	2.77	3.16	3.15
Ti	0.04	0.03	0.03	0.03	0.05	0.05	0.05	0.03	0.03	0.09	0.03	0.03
Al	2.50	2.35	2.34	2.36	2.76	2.41	2.45	2.44	2.57	1.63	2.69	2.73
Fe	0.07	0.20	0.20	0.21	0.11	0.16	0.15	0.13	0.14	0.75	0.05	0.04
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Mg	0.21	0.24	0.23	0.25	0.08	0.23	0.21	0.24	0.20	1.60	0.10	0.09
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.05	0.05	0.05	0.04	0.14	0.09	0.10	0.05	0.06	0.05	0.17	0.18
K	0.89	0.88	0.83	0.86	0.75	0.79	0.79	0.89	0.90	0.91	0.66	0.66
Fe/(Fe + Mg)	0.38	0.59	0.61	0.60	0.72	0.55	0.56	0.50	0.56	0.45	0.48	0.48
Na/(Na+K)	0.04	0.04	0.04	0.03	0.11	0.07	0.07	0.03	0.04	0.03	0.14	0.15
Cel (Si-3)	0.20	0.25	0.28	0.24	0.06	0.23	0.22	0.21	0.13	-0.23	0.16	0.15

Normalized to 12 oxygens

Table D.1 Representative white mica major element compositions of samples analyzed for Rb-Sr isotopic composition and thermobarometry (cont.)

Point	37	38	39	40	41	42	43
Sample	10-070a	08-010a	08-010a	08-010a	08-010c	08-010c	08-010c
Grain Size	~450 μ m	~600 μ m	~600 μ m	~350 μ m	~600 μ m	~600 μ m	~250 μ m
Notes	core/rim	core	rim	core	core	rim	core
SiO₂	50.10	48.19	50.25	48.11	48.38	52.91	49.52
TiO₂	0.79	0.38	0.34	0.36	0.77	0.67	0.70
Al₂O₃	35.74	29.55	29.08	29.59	31.11	26.04	29.27
FeO	1.08	4.48	4.64	4.66	2.30	2.04	2.15
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	1.48	1.49	1.48	1.44	2.31	3.89	2.93
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na₂O	1.63	0.39	0.39	0.48	1.31	0.81	1.56
K₂O	7.92	10.30	10.40	10.33	9.49	9.75	9.12
Anhydrous Total	98.74	94.78	96.58	94.97	95.68	96.10	95.25
Si	3.16	3.27	3.34	3.26	3.21	3.48	3.29
Ti	0.04	0.02	0.02	0.02	0.04	0.03	0.04
Al	2.66	2.36	2.28	2.37	2.44	2.02	2.30
Fe	0.06	0.25	0.26	0.26	0.13	0.11	0.12
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.14	0.15	0.15	0.15	0.23	0.38	0.29
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.20	0.05	0.05	0.06	0.17	0.10	0.20
K	0.64	0.89	0.88	0.89	0.80	0.82	0.77
Fe/(Fe + Mg)	0.42	0.75	0.76	0.76	0.50	0.34	0.42
Na/(Na+K)	0.17	0.04	0.04	0.04	0.12	0.08	0.15
Cel (Si-3)	0.16	0.27	0.34	0.26	0.21	0.48	0.29

Normalized to 12 oxygens

Table D.2 Representative mineral compositions for plagioclase in samples used for thermobarometric analysis.

Point	1	2	3	4	5	6	7	8	9	10
Sample No.	06-018a	06-018a	08-032a	08-032a	08-037a	08-037a	10-008a	10-008a	10-070a	10-070a
Notes	core	rim	core	rim	core	rim	core	rim	core	rim
SiO₂	62.87	62.86	64.37	63.77	61.88	62.23	65.93	66.79	64.76	64.50
Al₂O₃	24.03	24.14	23.48	23.40	24.95	24.57	23.05	22.72	23.19	23.07
TiO₂	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00
FeO	0.00	0.00	0.05	0.04	0.09	0.06	0.05	0.02	0.02	0.02
MgO	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00
CaO	4.60	4.51	3.88	3.89	5.52	5.15	3.38	2.96	3.36	3.23
Na₂O	8.05	8.12	8.70	8.68	7.83	7.95	9.39	9.50	8.87	8.82
K₂O	0.33	0.28	0.38	0.17	0.11	0.12	0.10	0.09	0.16	0.16
Total	99.89	99.91	100.85	99.96	100.39	100.08	101.91	102.08	100.37	99.80
Si	2.62	2.62	2.66	2.65	2.56	2.59	2.69	2.72	2.68	2.69
Al	1.51	1.51	1.46	1.46	1.55	1.54	1.41	1.39	1.45	1.45
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe total	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.21	0.20	0.17	0.17	0.24	0.23	0.15	0.13	0.15	0.14
Na	0.65	0.66	0.70	0.70	0.63	0.64	0.74	0.75	0.71	0.71
K	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.01
TOTAL	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
An%	24.01	23.46	19.76	19.85	28.04	26.36	16.57	14.67	17.32	16.82
Ab%	75.99	76.54	80.24	80.15	71.96	73.64	83.43	85.33	82.68	83.18
Or%	2.64	2.24	2.77	1.27	0.88	0.99	0.72	0.62	1.17	1.17

Normalized to 5 cations and 12 oxygens. Explanation: bd, below detection limits.

Table D.3 Representative mineral compositions for garnet in samples analyzed for thermobarometric analysis.

Point	1	2	3	4	5	6	7	8	9	10
Sample No.	10-008a	10-008a	10-070a	10-070a	06-018a	06-018a	08-032a	08-032a	08-037a	08-037a
Notes	rim	core	rim	core	rim	core	rim	core	rim	core
SiO₂	38.38	37.81	38.56	37.97	38.61	38.32	37.50	37.82	38.82	38.80
Al₂O₃	21.94	21.90	21.93	21.91	22.00	21.96	20.99	20.91	22.41	22.52
FeO total	30.73	32.61	29.02	27.88	26.33	27.33	27.26	27.03	28.53	28.88
Fe₂O₃(calc)	0.82	0.99	1.05	1.13	0.40	0.55	1.34	2.02	0.58	0.85
MgO	3.90	2.19	5.21	2.83	4.07	3.16	0.93	0.89	5.66	6.41
MnO	0.37	0.43	0.24	1.44	1.71	2.27	5.48	5.75	1.00	0.68
TiO₂	bd	bd	bd	0.12	bd	bd	bd	bd	bd	bd
CaO	6.12	6.44	5.90	8.69	8.47	8.25	8.10	8.41	5.30	4.22
Total	102.26	102.37	101.92	101.95	101.59	101.84	101.60	102.83	102.30	102.35
Si	5.95	5.92	5.95	5.91	5.97	5.96	5.96	5.94	5.94	5.92
Al	4.01	4.04	3.99	4.02	4.01	4.02	3.93	3.87	4.05	4.05
Fe total	3.98	4.27	3.74	3.63	3.41	3.55	3.62	3.55	3.65	3.69
Fe³⁺ (calc)	0.10	0.12	0.12	0.13	0.05	0.06	0.16	0.24	0.07	0.10
Mg	0.90	0.51	1.20	0.66	0.94	0.73	0.22	0.21	1.29	1.46
Mn	0.05	0.06	0.03	0.19	0.22	0.30	0.74	0.77	0.13	0.09
Ti	bd	bd	bd	0.01	bd	bd	bd	bd	bd	bd
Ca	1.02	1.08	0.97	1.45	1.40	1.37	1.38	1.42	0.87	0.69
Total	16.00	16.00	16.00	16.00	16.00	16.00	16.00	16.00	16.00	16.00
Almandine	66.95	72.14	62.95	61.26	57.03	59.64	60.79	59.78	61.46	62.26
Pyrope	15.16	8.64	20.14	11.07	15.71	12.28	3.70	3.52	21.73	24.61
Spessartine	0.81	0.97	0.53	3.21	3.75	5.02	12.37	12.88	2.18	1.48
Grossular	17.08	18.24	16.38	24.46	23.51	23.06	23.13	23.82	14.63	11.65

Normalized to 16 cations. Explanation: bd, below detection limits.

Appendix E

Rb-Sr dating and thermobarometry methods

The chemical purification of mineral separates is complex and involves several steps. The method used in this study was adapted from the method of Dr. Johannes Glodny (Glodny et al., 2003; Glodny et al., 2002), with consultation from Dr. Marc Alban-Millet (VUW, pers. comm.), Dr. Julie Vry (VUW, pers. comm.), and Dr. Joel Baker (VUW, pers. comm.).

E.1 Sample selection and preparation

Rock samples of <100 g were used to obtain material for mineral separates. In addition, a small amount of rock sample (<30 g) was crushed using a tungsten carbide lined Tema mill in order to obtain a whole rock split. The Tema mill was cleaned with two washes of acetone and processing a load of quartz sand between samples. The <100 g rock sample was crushed with a steel percussion mortar, which was cleaned with two washes of acetone between samples. This study used white mica separates that differ in size (250 – 355 μm , 355 – 500 μm , >500 μm), and the crushed material was sieved in order to separate the bulk rock sample into ≥ 500 μm , 250 – 500 μm , ≤ 250 μm size splits. Sieves were cleaned by two acetone washes between samples. This crushed and sieved material was then separated using standard magnetic separation techniques on a Franz isodynamic separator in order to obtain mineral separates that were purified by hand picking on an Olympus SZX7 binocular microscope. The 250-500 μm mica separate was then split into 250-355 μm and 355-500 μm using nylon mesh sieves that were discarded after use.

Mineral separates were cleaned before being weighted into clean beakers (Section E.2). White mica mineral separates were ground by hand in an agate mortar with Ar-grade methanol and dried, sieved with nylon mesh sieves to remove impurities. Before acid was introduced into the beakers, all mineral separates were washed three times in > 18.2 M Ω ultra-clean water (Millipore: MQ H₂O).

E.2 Chemical purification

All chemical purification of mineral separates was performed in a Picotrace© Class 10 laminar flow hood in an ultra-clean laboratory (positively pressured with air continuously filtered to Class 100). All HF used by this study was Seastar™ grade ultra-pure (29M; all key metals <10 ppt). All acids used in this study (unless otherwise stated) were sub-boil distilled in Teflon (12 M HCl) and quartz (16 M HNO₃) stills. Dilute acids were prepared by dilution of concentrated acids (both sub-boiled and Seastar©) with MQ H₂O. An electronic density meter was used to calibrate dilute acid molarities (assume density of MQ H₂O as 0.9998 at 18°C). Eppendorf pipette tips were used during chemical purification and were rinsed three times with MQ H₂O before use.

The beakers used were 23 ml, 7 ml, and 3 ml Teflon Savillex© beakers and were first pre-cleaned by wiping the outside with Ar-grade methanol and then rinsing both the beaker and the lid in tap water. The beakers were then rinsed with MQ H₂O and each beaker and lid was individually dipped into a glass beaker of 6 – 8 M HCl and left for >24 hours at 90°C. The beakers and lids were then rinsed three times in MQ H₂O and each beaker and lid was individually dipped into a glass beaker full of 6 – 8 M HNO₃ and left for >24 hours at 90°C. The beakers were rinsed out 3 times in MQ H₂O and filled with enough 7 M HNO₃ to cover the bottom of the beaker. The filled beakers were left at 120°C for ≥24 hours to reflux. The beakers were then rinsed out three times with MQ H₂O, and left open to dry on a hot plate (120°C).

Mineral separates are measured into cleaned beakers using a high precision balance (± 0.00001 g), which was tarred to the weight of the beaker before introduction of the mineral separate. As a rule of thumb, ~40 mg of mica separates and ~100 mg of all other mineral separates and standards was used. All sample material were then refluxed with ~1 ml concentrated HF and ~0.25 ml concentrated HNO₃ in sealed beakers at 120°C for ~72 hours. In the case of mineral separates of garnet and omphacite with garnet inclusions, concentrated HF and HNO₃ was evaporated and 3

ml concentrated HCL was added to beakers. These were sealed and refluxed at 120°C for >12 hours and then evaporated. The garnet and omphacite separates were then once more refluxed in 1 ml concentrated HF and 0.25 ml concentrated HNO₃ in sealed beakers at 120°C for ~72 hours.

The resultant solution was evaporated to incipient dryness to avoid sample loss, followed by two more evaporations with concentrated HNO₃ and one of 2ml 3 M HNO₃. Once the samples were dry 2 ml of 3 M HNO₃ was added to the beakers and they were refluxed at 120°C for 24 hours. It is essential that the samples were completely dissolved, as an incomplete dissolution would result in fractionation of Rb and Sr between the solutions and the solid residues. The solution was therefore visually checked for any remnant solute and if needed additional 3 M HNO₃ is added in 2 ml steps. Once the solution was free of solids to the naked eye, it was spun on a Heraeus© Millifuge 1s at 5000 revolutions per minute for five minutes and once more carefully examined for any remaining solute. In some cases, the samples were not solute-free even when >20 ml of 3 M HNO₃ was introduced; these samples were evaporated and re-dissolved with concentrated HF and HNO₃. If a sample contained oxides that could not be dissolved, it was re-centrifuged at 5000 revolutions per minute for five minutes and care was taken in extracting the solution for the ⁸⁷Rb/⁸⁶Sr and ⁸⁸Sr/⁸⁶Sr aliquots in order to avoid the oxides.

The completely dissolved mineral separate was split into an ⁸⁷Rb/⁸⁶Sr aliquot, which was set aside for analysis, and an aliquot used to obtain a purified Sr cut through column chemistry. In the case of samples which required >10 ml of 3 M HNO₃ to completely dissolve, three steps were taken to split the sample: (1) 25 % of the completely dissolved sample was extracted for the ⁸⁷Rb/⁸⁶Sr aliquot, (2) the remainder of the sample was evaporated down and brought back into solution in 3 ml of 3 M HNO₃, (3) 2 ml of the partially dissolved sample was extracted with a pipette, and was used for column chemistry. Before analysis, the ⁸⁷Rb/⁸⁶Sr aliquot was evaporated in a 3 ml Teflon beaker at 120°C. The evaporate was then brought into solution with 1 ml 1 M HNO₃ (Seastar™) for analysis on the inductively coupled plasma mass spectrometer (ICP-MS).

The remaining 75% of the completely dissolved mineral separate was used to separate Sr with a double pass through Eichrom™ Sr-specific resin. Sample solutions were left at 120°C for ~ 1 hour. Columns were constructed from Eppendorf 1 ml pipette tip columns with polypropylene frits fitted at the bottom of the pipettes. The columns were pre-cleaned by soaking in 1 M HCl, and were then individually rinsed six times with MQ H₂O. The columns were loaded with Eichrom© strontium resin (50 – 100 µm) to create a >5 mm bed of resin. The resin was cleaned with 1.5 ml MQ H₂O followed by 1.5 ml 3 M HNO₃ three times, followed by equilibration with 3 ml 3 M HNO₃. The sample was loaded with a disposable 10 ml pipette and matrix elements were eluted with 4.5 ml 3 M HNO₃. The beakers (which were free of solution at this point) were cleaned by: (1) rinsing three times with MQ H₂O, (2) adding ~1 ml 6 M HCl and refluxing the beaker for 20 minutes at 120°C, and (3) rinsing out three times with MQ H₂O. The cleaned beakers were used to collect the Sr cut in 4.5 ml MQ H₂O. The Sr cut was evaporated at 120°C, and three drops of concentrated HNO₃ was evaporated at 120°C. The Sr cut was evaporated once more in 1.5 ml 3M HNO₃ at 120°C, was then brought into solution with 1.5 ml 3 M HNO₃ at 120°C for >12 hours for a second column pass with new pipette tip columns. The double-pass technique reduces the amount of matrix elements in the solution, thus minimizing any analytical artifacts. After the second column pass, the Sr cuts were evaporated with three drops of concentrated HNO₃ at 120°C, and brought into solution with 2 ml 0.5% HNO₃ (Seastar™) at 120 °C for ≥24 hours.

E.3 Solution ICP-MS analysis

An Agilent© 7500 CS inductively coupled plasma mass spectrometer (ICP-MS) at Victoria University of Wellington, New Zealand was used to analyze the ⁸⁷Rb/⁸⁶Sr solution. The ⁸⁷Rb/⁸⁶Sr solution was diluted with 50 µl of sample into 5 ml 1% HNO₃ (Seastar™). Analytical conditions for the ICP-MS are given in Table E.1.

Table E.1 ICP-MS analytical and instrumental conditions

ICP-MS	
System	Agilent 7500CS
Acquisition mode	Peak-hopping
Detection mode	Pulse and analogue
Standards and calibration	
Bracketing standards	1 ppb Rb/Sr standard in 1% HNO ₃ (Seastar™), 50 ppb ⁴⁴ Ca standard in 1% HNO ₃ (Seastar™)
Secondary standards	BHVO-2
Analysis method	
Background acquisition	30 seconds
Standard/sample acquisition	120 seconds
Washout times	Water wash out: 30 seconds; 1% HNO ₃ (Seastar™): 90 seconds
Measured isotopes and integrations times	⁸⁵ Rb, ⁸⁶ Sr, ⁸⁷ Sr, ⁸⁸ Sr, ⁴⁴ Ca; 0.01 seconds
Tuning	
Tuning standards	1 ppb Rb/Sr standard in 0.5% HNO ₃ (Seastar™)
Monitored isotopes during tuning	⁸⁵ Rb, ⁸⁶ Sr, ⁸⁷ Sr, ⁸⁸ Sr, ⁴⁴ Ca (%RSD <3%)
Calibration standard	1 ppb Rb/Sr standard in 0.5 % HNO ₃ (Seastar™)
Monitored isotopes during calibration	⁸⁵ Rb, ⁸⁶ Sr, ⁸⁷ Sr, ⁸⁸ Sr, ⁴⁴ Ca (%RSD <3%)
Background	⁸⁵ Rb < 800 CPS, ⁸⁶ Sr < 1000 CPS, ⁸⁷ Sr < 500 CPS, ⁸⁸ Sr < 2000 CPS, ⁴⁴ Ca < 200000 CPS *
Oxides	<1.5% (checked during tuning)
Carrier gas	1.08 - 1.12 L min ⁻¹
Make up gas	0 L min ⁻¹
RF Power	1500 W
RF matching	1.68 - 1.72 V
Sample depth	7 mm

* “CPS” is the counts per second or signal measure by the ICP-MS

Two washouts were used: (1) MQ H₂O for 30 seconds, and (2) 1% HNO₃ (Seastar™) for 90 seconds. Acquisition time for standards/unknowns was 120 seconds. The mean background was subtracted from the counts per second of the ⁸⁵Rb, ⁸⁶Sr, and ⁸⁸Sr before during raw data processing before calculation of the ratios.

The majority of the ⁸⁷Rb/⁸⁶Sr ratios (see Table 3.10) were calculated using the ⁸⁵Rb/⁸⁸Sr ratios of samples and standards and the relative abundance of ⁸⁷Rb and ⁸⁶Sr. Interference from ⁴⁴Ca dimer on ⁸⁸Sr was monitored using ⁸⁸Sr/⁸⁶Sr ratio during data processing. Measured ⁸⁸Sr/⁸⁶Sr ratios of samples and standards are tightly clustered at ~8.8 across all analytical sessions, regardless of the sample composition (whole rock, pyroxene, white mica). This measured ⁸⁸Sr/⁸⁶Sr ratio is very close to the natural value of 8.3752 and this interference was considered

negligible. The $^{87}\text{Rb}/^{86}\text{Sr}$ ratio and its 1% error is normally calculated by: (1) calculating the standard-corrected $^{85}\text{Rb}/^{88}\text{Sr}$ ratio as measured by the ICP-MS, (2) correcting this value to the natural value of $^{85}\text{Rb}/^{88}\text{Sr}$, and (3) correcting this $^{85}\text{Rb}/^{88}\text{Sr}$ ratio to the abundance of ^{87}Rb and ^{86}Sr . There was, however, inaccuracy in the calculated $^{87}\text{Rb}/^{86}\text{Sr}$ ratios because of uneven pulse/analogue (P/A) switching of the ^{85}Rb , ^{86}Sr , and ^{87}Sr isotopes measured during a single analysis. The P/A factor is an automatic empirical correction that the Agilent© 7500 CS ICP-MS instrument performs to ensure that the switch from pulse mode ($<1 \times 10^6$ counts per second) to analogue mode ($>1 \times 10^6$ counts per second) is linear. The P/A factor switch, however, was malfunctioning during some analytical sessions, which lead to inaccurate ratios between isotopes that are not counted on the same mode of the detector. Typically, ^{85}Rb , ^{86}Sr and ^{87}Sr would be counted on the Pulse mode, while ^{88}Sr would be counted on the analog mode. This difference in modes lead to measured $^{88}\text{Sr}/^{86}\text{Sr}$ ratios of 91 – 100 in some samples and standards affected by the uneven P/A switch. Thus, for the mineral splits that were affected by this inaccuracy in the P/A factor, $^{87}\text{Rb}/^{86}\text{Sr}$ ratios were estimated by calculated a ratio of total mass 87 signal over the ^{86}Sr measured by the ICP-MS. I then subtracted the accurate multi-collector ICP-MS $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that correspond to each inaccurate mineral split analysis to determine an $^{87}\text{Rb}/^{86}\text{Sr}$ ratio. Accuracy of this correction method was assessed with repeated measurements of the BHVO-2 standard.