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Grain-scale dependency of metamorphic reaction on crystal plastic strain

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Grain-scale dependency of metamorphic reaction on crystal plastic strain

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ABSTRACT

The Breaksea Orthogneiss in Fiordland, New Zealand preserves water-poor intermediate and mafic igneous rocks that were partially recrystallized to omphacite granulite and eclogite, respectively at $P \approx 1.8$ GPa and $T \approx 850$°C. Metamorphic reaction consumed plagioclase and produced grossular-rich garnet, jadeite-rich omphacite, clinozoisite and kyanite. The extent of metamorphic reaction, identified by major and trace element composition and microstructural features, is patchy on the grain and outcrop scale. Domains of re-equilibration coincide with areas that exhibit higher strain suggesting a causal link between crystal plastic strain and metamorphic reaction. Quantitative orientation analysis (EBSD) identifies gradual and stepped changes in crystal lattice orientations of igneous phenocrysts that are surrounded by homophase areas of neoblasts, characterized by high grain boundary to volume ratios and little to no internal lattice distortion. The limited, peripheral chemical modification of less deformed garnet and omphacite phenocrystal grains reflects limited lattice diffusion in areas that lacked 3D networks of interconnected low-angle boundaries. Low-angle boundaries appear to have acted as elemental pathways (pipe diffusion) that enhanced in-grain element diffusion. The scale of pipe diffusion is pronounced in garnet relatively to clinopyroxene. Strain-induced mineral transformation largely controlled the extent of high-*T* metamorphic reaction under relatively fluid-poor conditions.

KEYWORDS: element diffusion; recrystallisation; metamorphic equilibration; crystal plastic strain; deformation; microstructures

INTRODUCTION

Deformation is generally thought to assist metamorphism overcoming kinetic impediments and achieve reaction progress, based on both experimental and field observation (e.g. Brodie & Rutter, 1985; Austrheim, 1987; Rutter & Brodie, 1995). However, the nature of causal grain-scale mechanisms remains largely unconstrained in regional metamorphic terranes that experienced high-grade conditions. Microstructures in granulite facies rocks commonly involve ~~chemically~~ homogeneous minerals of low-energy grain form that lack obvious reaction relationships (Powell, Guiraud & White, 2005; Vernon, Collins & Cook, 2012). Such features are assumed to reflect a point of thermodynamic equilibrium whereby rates of intra-crystalline diffusion approached rates of grain boundary diffusion, enabling equilibrium to be maintained on a scale larger than that of the grain (e.g. Marmo, Clarke & Powell, 2002; Powell et al., 2005). Persistent high temperature conditions are also conducive to the deformation of many common rock-forming minerals plastically via mechanisms such as dislocation creep (Bürgmann & Dresen, 2008).

Microstructures indicative of incomplete reaction and strain localization can be common in exceptionally dry rocks and/or the products of short-lived tectonic events (e.g. Williams & Jercinovic, 2012). Sites that record partial metamorphism enable the identification of kinetic limitations to reaction progress and present phenomena that can be queried to assess the link between crystal plastic strain and metamorphic reaction. Related processes that contribute to reactions overcoming kinetic barriers, such as fluid ingress and/or mechanical reductions in grain size, can result in a decrease in the time- and length-scale of grain-boundary diffusion (Austrheim, 1987; Yund & Tullis, 1991). More pervasive feedback mechanisms can potentially involve the direct coupling of intra-crystalline element mobility, dislocation movement and the production of strain-induced lattice defects. The latter may be difficult to verify in geological samples on account of the time scales involved, which are amenable to physical recovery and secondary ~~chemical~~ change (Urai, Means & Lister, 1986; Powell et al., 2005). However, a number of reported observations present a compelling link between the production and migration of low- and high-angle boundaries and the formation of new chemically-distinct (equilibrated) grains (e.g. Brodie & Rutter, 1985; Stünitz, 1998; Svahnberg and Piazolo, 2010; Williams & Jercinovic, 2012; Satsukawa et al. 2015).

The generation, movement and annihilation of dislocations during crystal plastic deformation can also enhance intra-grain element diffusion (Cottrell, 1953; Ruoff & Ballufi, 1963). This may take the form of a sweeping motion of high solute concentrations adjacent to dislocations, as has been observed in zircon (Piazolo et al., 2016). In conjunction with comparatively rapid “pipe” diffusion — the process of diffusing elements along dislocation cores (low-angle boundaries) — pronounced ~~chemical~~ change can be achieved within volumes of strained lattice (Hart, 1957; Love, 1964). Whereas solid state change through pipe diffusion has been detected in metals (e.g. Legros, Dehm, Arzt & Balk, 2008), the interpretation of equivalent change in silicates has been largely restricted to accessory minerals (Lund, Piazolo & Harley, 2006; Reddy et al., 2006; Piazolo, Austrheim & Whitehouse, 2012). However, based on work we present her[illegible]e occurrence and efficiency of such diffusion in silicates is fundamental to models of ionic diffusion and scale of equilibration (Lasaga, 1979; Marmo et al., 2002; Powell et al., 2005; Ague & Carson, 2013). An iss[illegible]ot explored here is the potential of non-hydrostatic stress to additional influence the nature of chemical equilibrium (e.g. Wheeler, 2014; Powell, Evans, Green & White, 2017). ~~We present a quantitative analysis assessing~~ the spatial correlation between chemical modification and the dependency on the presence of deformation induced low-angle boundary networks, gradual lattice distortion and high-angle boundaries in a natural example of lower crustal rocks from New Zealand (Clarke, Daczko & Miescher, 2013; Chapman, Clarke, Piazolo & Daczko, 2017). Low angle boundary networks are shown to provide channel ways ~~of~~ accelerated intra-grain diffusion in garnet and pyroxene during metamorphism compared with the relative restricted length scales recorded along high-angle boundaries in relics of formerly homogeneous igneous phenocrysts. The results from our case-study highlight the fundamental role crystal plastic deformation plays in enhancing metamorphic re-equilibration during solid-state reaction in rock-forming mineral[illegible]

THE BREAKSEA ORTHOGNEISS

The *c*. 124–110 Ma Breaksea Orthogneiss is exposed in Breaksea Sound (Fig. 1) and immediate north thereof (Allibone et al., 2009; De Paoli, Clarke, Klepeis, Allibone & Turnbull, 2009; Milan, Daczko, Clarke & Allibone, 2016; Stowell et al., 2017). It is the highest-grade part of the Western Fiordland Orthogneiss, a suite of intermediate to mafic plutons emplaced during an early Cretaceous arc flare-up event (Bradshaw, 1989; Allibone et al., 2009; Chapman, Clarke & Daczko, 2016; Milan, Daczko & Clarke, 2017). The Breaksea Orthogneiss ~~comprises~~ [illegible]rmediate and mafic layers, thought to have been emplaced into thickened arc crust (De Paoli et al., 2009). Monzodioritic layers are patc[illegible]metamorphosed to garnet–omphacite granulite (65%) or omphacite–orthopyroxene granulite (5%) with decametre layers and pods of peridotgab[illegible] eclogite (25%), and minor garnetite, clinopyroxenite, harzburgite and hornblende peridotite (collectively 5%: De Paoli et al., 2009; Clarke et al., 2013; Chapman, Clarke, Daczko, Piazolo & Rajkumar, 2015). Metamorphic assemblages in both intermediate and mafic protoliths reflect *c.* 1.8 GPa and 850˚C (De Paoli et al., 2009, De Paoli, Clarke & Daczko, 2012; Clarke et al., 2013; Chapman et al., 2017).

~~Distinctions~~ in the proportions of garnet, clinopyroxene, plagioclase and orthopyroxene throughout the Breaksea Orthogneiss are primarily attributed to cumulate processes and magma redox conditions that preceded ~~high-grade~~ deformation (De Paoli et al., 2009; Chapman et al., 2015). Interlayered near-monomineralic garnetite and clinopyroxenite retain igneous microstructures and mineral chemistry (Clarke et al., 2013). Garnet in eclogite layers is interpreted as igneous on the basis of its major and rare earth element (REE) content being similar through the spectrum of ultrabasic–intermediate compositions, and ~~it~~ lacking a positive Eu anomaly (Clarke et al., 2013). As garnet and o[illegible]acite collectively form 90% of eclogite, omphacite in the eclogite layers is also interpreted to be of cumulus origin (Clarke et al., 2013). Despite having an intense, shallowly dipping gneissic foliation, the orthogneiss preserves compositional layering in all rock types (De Paoli et al., 2009; Betka & Klepeis, 2013; Chapman et al., 2015; Klepeis, Schwartz, Stowell & Tulloch, 2016). This layering is inferred to be mainly an igneous feature, presumably cumulate, and was transposed into S_1. In low strain zones, monzodioritic gneiss preserves igneous microstructures consistent with the parental magma having crystallised Ca–Na clinopyroxene with or without garnet or orthopyroxene (Clarke et al., 2013; Chapman et al., 2015). Metamorphic assemblages of omphacite, garnet, plagioclase, kyanite and rutile that define S_1 in monzodioritic gneiss are consistent with metamorphic equilibration at the omphacite granulite sub-facies (De Paoli et al., 2012; Chapman et al., 2017). A series of late magmatic garnet-monzonite veins cross-cut S_1 (Clarke et al., 2013). The whole-rock major and trace element compositions throughout the strained monzodioritic (now granulite) components of the orthogneiss are remarkably consistent, defining a restricted range in silica and total alkali content (SiO_2 = 50–55 wt %O and (Na_2O+K_2O) = 5–7 wt %O: Clarke et al., 2013; Chapman et al., 2015).

Igneous and metamorphic paragenesis have been distinguished using a combination of mineral chemistry and microstructural relationships, the overall extent of relict mineralogy varying with strain intensity (Clarke et al., 2013; Chapman, Clarke, Piazolo & Daczko, submitted). Igneous garnet defines large granoblastic garnet grains in clusters with omphacite (Fig. 2a), that retain heavy-REE-enriched patterns overlapping with igneous garnet in eclogite and garnetite (Clarke et al., 2013). In contrast, metamorphic garnet form small idioblastic grains in necklace-style structures between omphacite and plagioclase (Fig. 2b), are heavy-REE depleted and have positive Eu anomalies consistent with metamorphic growth (Clarke et al., 2013). Similarly, igneous clinopyroxene form large calcic grains in clusters with igneous garnet, retaining pronounced lattice distortion and fine exsolution lamellae (Fig. 2f). These contrast with small neoblastic grains that are free of substructure and are richer in sodium (Fig. 2). The distinct microstructural form of the relict and neoblastic phases corresponds with differing crystallographic orientations (Chapman et al., submitted). Omphacite neoblasts have orientations consistent with their formation during rotational recrystallization from the larger porphyroclasts. The S_1 grain form present[illegible]ucleation sites for the subsequent epitaxial growth of metamorphic garnet (Chapman et al., submitted). Concurrently, the surrounding feldspar-quartz-rich matrix was extensively recrystallized and chemically modified (Fig. 2). Across differing strain domains in the orthogneiss these distinctions in microstructural extent of relict and neoblastic phases has been quantified on a thin-section scale (Chapman et al., submitted).

The finer s extent of intra-grain chemical modification in deformed porphyroclasts of the Breaksea Orthogneiss has not been assessed. The recovery of petrogenetic information, either through traditional thermobarometic methods or by analysing mineral reaction textures through the pseudosection approach, are dependent on appropriate microstructural interpretations at these scal .g. Powell & Holland, 2008; Vernon, White & Clarke, 2008). Establishing the link between thermodynamically controlled mineral chemistry and deformation-induced crystal plastic microstructure in common rock-forming minerals is therefore fundamental to understanding the tectonometamorphic and rheology of the lithosphere. This paper specifically assesses the link between crystal plastic strain and in-grain chemical zoning from garnet and pyroxene phenocrysts from the dioritic component of the Breaksea Orthogneiss

METHODS

Petrographic and microstructural observations were coupled with quantitative crystallographic orientation mapping. All thin sections were prepared perpendicular to the foliation (XY plane) and parallel to the lineation (X direction). Representative examples were analysed at high-resolution using the electron back-scatter diffraction (EBSD) technique (e.g. Prior et al. 1999). ~~Mineral chemical analysis~~ was undertake oss the scale of EBSD mapping to correlate to features of recrystallisation and crystal plastic deformation.

Quantitative crystallographic orientation analysis

Electron back-scatter diffraction (EBSD) investigation was performed using a Zeiss Ultra Plus SEM at the Australian Centre for Microscopy and Microanalysis at the University of Sydney. Etched polished thin sections (~30 µm) were analysed at an accelerating voltage of 20 kV, with a beam current of 8 nA and a working distance of ~9–14 mm. Electron backscatter diffraction patterns were automatically acquired and indexed using Oxford Instruments AzTEC software (https://www.oxford-instruments.com/). The EBSD patterns were collected in regular grids where the sampling step size varied from 1–3 µm for grain-scale analysis and 0.3– 0.5 µm for detailed sections of the crystals. Post-processing was undertaken in the HKL Channel 5 TANGO software (Oxford Instruments) following procedures that are designed to remove false data and to enhance data continuity over the microstructures as described by Prior, Wheeler, Peruzzo, Spiess & Storey (2002). In the following analysis, grains are defined as areas enclosed by boundaries of greater than 10° of misorientation; boundaries with misorientations less than 10° but greater than 1° are referred to as low-angle boundaries. The extent of crystal lattice strain in a defined grain area was determined by the average distribution of misorientation, inclusive of the low-angle boundaries in Channel 5.

Mineral Chemistry

Major elements

Quantitative chemical X-ray maps of crystalline minerals were obtained using the Cameca SX100 electron microprobe housed at the Electron Microscopy and X-ray Microanalysis facility at the University of Tasmania, Hobart. Additional data ~~was~~ also collected on the Cameca SX100 electron microprobe housed at the Research School of Earth Sciences, Australian National University, Canberra. Operating conditions for the analysis involved a 15 kV accelerating voltage, 40 nA beam current and 2 µm beam-diameter with dwell times of

300 milliseconds per point. The analyses at the University of Tasmania were collected on five wavelength-dispersive spectrometers (WDS) using TAP, LPET, PET and LLIF crystals. The raw ~~data~~ was processed using the in house ‘*Probe for EMPA* (Probe Software Inc. Eugene, USA)’ and using the Phi-Rho-Z matrix correction method of Love & Scott (1978). X-ray intensities were converted to maps of oxide weight percent using the algorithm of Clarke, Daczko & Nockolds (2001) and visualized following data manipulation procedures described in Marmo et al. (2002).

Trace elements

The distribution of trace elements in relation to lattice defects and low-angle boundaries cannot be robustly resolved with point source data [illegible] broad perspective is obtainable by comparing grain regions with lattice distortion and low-angle boundaries to those that lack appreciable substructure. The trace element concentrations of garnet and omphacite were determine though *in-situ* analysis using an Agilent 7700cs quadrupole Inductively Coupled Plasma Mass Spectrometer (ICPMS), attached to a New Wave UP-213 Nd:YAG laser ablation microprobe (LAM) housed at Macquarie Geoanalytical, Macquarie University, Sydney. Data acquisition parameters involved a *c*. 60 second background count prior to laser ablation and a *c*. 100–120 second signal analysis period. Operating conditions involved a 55 μm beam diameter and a 5 Hz pulse repetition that produced ~40 μm deep flat bottom pits. Calcium content determined by the electron microprobe was used to calibrate trace element spectra. The analysis of NIST 610 glass during each session provided an external standard, with individual analysis required to fall within error of long-term laboratory compilations. The internal standards BRC2 and MONGOL garnet were analysed in sampling brackets to the unknowns throughout the session. Precision was calculated at less than 10% relative standard deviation based on 1σ distribution of the presented trace elements.

Correlative Chemical and Microstructural Analysis

Image analysis was performed on the corrected X-ray intensity (wt %) and the EBSD maps to correlate and quantify the extent of element zoning associated with low-angle boundary development. This analysis was undertaken in MATLAB (https://au.mathworks.com/products/matlab.html). Chemically-distinct regions of the mineral (for both garnet and omphacite) in the elemental maps were isolated and masked using appropriate thresholds (z, see below) following methods outlined by Marmo et al. (2002). Additional binary masks were created to delineate regions of ~~chemical~~ change within garnet and omphacite and smoothed by a factor of 4 to remove noise below the analytical step size (of the element maps). The analysis focused on prominent (metamorphic) elemental zoning, primarily: for garnet, MgO ($z < 5.5$ wt %) and CaO ($z > 6$ wt %); and for omphacite, Na_2O ($z < 1.5$ wt %), CaO ($z < 3.5$ wt %O) and Al_2O_3 ($z < 1.75$ wt %). The binary matrices were rectified to EBSD maps of crystal lattice strain. Euclidean distance measurements were calculated for three crystal regions with distinct substructure (based on misorientation distributions) and chemistry: (1) igneous cores; (2) metamorphic rims adjacent to high-angle boundaries but with low lattice distortion (<1.5° misorientation/μm^2); and (3) highly distorted metamorphic rims with abundant low-angle boundaries (>1.5° misorientation/μm^2). The effect of fractures and incidental defects in the dataset were reduced by smoothing using Fourier transform methods. A defined buffer of 4 pixels (~2 µm) around the low-angle boundaries was utilised to account for the step size of the EBSD analysis. The Euclidean distances were calculated from the high- and low-angle boundaries to each pixel in regions of elemental change to define the length scales. The calculation produced matrices infilled with an intensity gradient proximal to the boundaries, wh[illegible]ncreases towards the edge of the chemical zonation. Statistical analysis involved the determination of the mean distance over the defined pixel area to the 1σ level, accounting for the inherent intensity gradient produced in the Euclidean distance maps. These gradients result in the systematically higher standard deviation (σ) in areas with extensive mineral zonation, and therefore does not simply reflect the calculation error. The variance thus provides a measure ~~on~~ the likely extent of the zonation in relation to the interconnectivity of the boundaries. To directly compare the length-scales of zonation associated with high distortion rims (mainly low-angle boundaries) and low distortion rims (mainly high-angle boundaries) a ratio was calculated between the two regions (d*l* = low-angle boundary distance/high-angle boundary distance). All analyses and map values were converted to micrometres (μm) from pixels. All the Euclidean distance maps are provided in the supplement (Fig. S1).

RESULTS

Microstructure and Mineral Chemistry

Detailed characterisations of microstructural relations and mineral chemistry are presented for the omphacite granulite elsewhere (De Paoli et al., 2009; Clarke et al., 2013; Chapman et al. 2015, 2017, submitted; Miranda & Klepeis (2016). This study focuses on relating the mineral chemical variations to recrystallisation microstructure an[illegible]ystal substructure.

Garnet

Large euhedral garnet phenocrysts (1000–3000 μm: Grt_i) form mm-scale mafic grain cl[illegible]s intergrown with omphacite. The cores of large grains have faceted and euhedral inclusions of omphacite and antiperthite in addition to fine rutile exsolution lamellae consiste[illegible]ith unimpeded igneous growth (Fig. 2a) (after Vernon et al., 2012). In contrast, garnet neoblasts (Grt_m) form coronae on attenuated omphacite grain clusters ~~(Figs 2b, c & 3).~~ They have rounded and vermicular quartz inclusions and c. 120° hom[illegible]ase grain triple-junctions (Fig.

2c). These features are consistent with late-S_1 metamorphic growth. The outermost parts of most garnet phenocrysts are comparatively grossular-rich and pyrope-poor and are compositionally equivalent to the garnet neoblasts (Fig. 4). The scale and s[illegible]f the compositional changes are spatially irregular: polyphase boundaries of garnet and feldspar are commonly marked by a narrow (*c*. 25–50 µm) rim of distinct ~~chemistry;~~ polyphase boundaries of garnet with omphacite commonly show minimal or no compositional change; and *c*. 250–500 µm-scale, grossular-rich pyrope-poor patches may be associated with inclusion-rich parts of garnet or simply cover broad areas of what are inferred to be relic "phenocryst" (Fig. 4). The narrow rims and irregular larger patches are interpreted as being mostly phenocrystal material that was chemically modified by element exchange during metamorphism. Polyphase (garnet-feldspar) overgrowths ~~to~~ some large garnet grains include lobate boundaries consistent with metamorphic overgrowth (Fig. 2b). These ~~coronate~~ intergrowths are more common in higher-strain domains.

Most lattice distortion in garnet is restricted to the relict phenocrysts, with neoblasts generally being free of substructure (<2°). Large garnet cores record up to 4° degrees of crystal lattice distortion that occurs progressively over a distance of ~200–2000 µm (Figs 3a). Small high-strain regions (~300 µm) at elongated grain tips or adjacent to neighbouring garnet crystals have ~~appreciable~~ lattice misorientation of greater magnitude (above 20°) (Fig. 3a). In detail, most distortion ~~is focussed~~ in a series of closely spaced step-like low-angle boundaries (each of 1–5°), with limited or no misorientation between the stepped [illegible]nges (Fig. 3d & e). These low-angle boundaries vary in length (200–500 µm) and generally adjoin nearby high-angle grain boundaries consistent with them forming an interconnected 3D network. Progressive lattice rotation (<100>) across these boundaries supports the interpretation of their formation through crystal plastic deformation generating common crystallographic orientations (Prior et al., 2002; Cyprch, Piazolo & Almqvist, 2017). A series of post-S_1 rectilinear fractures cut some of the garnet grains.

Omphacite

Omphacite typically forms in complex aggregates with igneous garnet that preserve S_1 flaser structures (Figs 2b–c, e–f & 5). Cores of large omphacite grains (~2000 μm: Omp_i) have faceted plagioclase inclusions and delicate titano-hematite exsolution lamellae (Figs 2e & f). These cores are typically calcic and enveloped by near-concentric jadeite-rich rims (F[illegible]5) that may or may not be coherent with the core. The calcic grains also preserve interlocking euhedral microstructures of low dihedral angles consistent with mutual impingement (fig. 2 Chapman et al., 2017). Such features are consistent with these omphacite porphyroclasts mostly reflecting growth from a magma (after Vernon et al., 2012). The phenocryst~~al~~ cores are surrounded by hom[illegible]ase polygonal grain aggregates of comparatively calcium-poor omphacite (50–400 μm: Omp_m) formed of smaller high-angle grains with limited internal substructure, most consistent with [illegible]tamorphic origin (Figs 2e, f & 5, 6; Vernon et al., 2012). Such neoblastic aggregates are commonly attenuated into flaser tails on igneous garnet or omphacite grains, in places forming high-aspect ratio ribbons (Fig. 2b & e). In all instances, grains forming these neoblastic tails are jadei[illegible]ch compared with the larger igneous grains (Chapman et al., submitted). Omphacite neoblasts with the highest jadeite contents occur in the aggregate tips (Fig. 6).

Omphacite porphyroclasts can show pronounced elongation and progressive crystal lattice distortion of up to 12° (Fig. 5a & d). This is distinct from relationships in the fine-grained neoblastic aggregates, where grains have minimal internal substructure (<2°: Fig. 5a & d). Progressive misorientation occurs across large distances in porphyroclast~~ic grain~~ cores (>1000 μm) through a series of step-like low-angle boundaries (~1°) (Fig. 5a & d). The spacing between the low-angle boundaries reduces, and lattice distortion is more focused (4°), towards the elongated edges of the grains (Fig. 5d). A succession of curved low-angle boundaries (100–300 µm in size) ~~concentrate the overall lattice distortion~~ (1–2°) (Fig. 5a). The low-angle boundaries display step-like misorientations separated by regions of progressive distortion (<1°) (Figs 5a & e). The size of the sub-grain enclosed by the low-angle boundaries (~50–400 µm) matches the size of the equant neoblasts that make up the homophase flaser tails (Fig. 5a). The variation in crystallography between these crystals defines a progressive rotation in orientation into the S_1 fabric (Fig. 5c). The majority of dispersion appears to be accommodated by rotation on both the [001] or the [110] axes, consistent with the overall preferred orientations of omphacite (Fig. 5b & c: Brenker, Prior & Müller, 2002; Chapman et al., submitted).

Correlating lattice strain to chemical zonation

Major and trace element distinctions between garnet types can be spatially correlated with crystal substructure. Calcium and magnesium zoning in garnet is more extensively developed in localized crystal volumes that record appreciable distortion. The length scales of modified (i.e. metamorphic) Ca and Mg compositions in regions of abundant low-angle boundaries (distorted regions) ranges from near parity with, to up to 2.5 times greater than, that recorded by high-angle rims with limited lattice distortion (d*l*: Fig. 7). This is reflected in the systematically higher mean distances in the lattice regions with appreciable distortion (Fig. 7). Together with the higher standard deviation (σ) from these domains (Fig. 7), the calculations reflect greater length scales of diffusion related to crystal plastic strain and imply that the crystallographic boundaries were at least partially interconnected in 3D. Grain size has no appreciable influence on the scale of chemical change; in all grains, the average distance from igneous cores to regions of chemical change is similar. The result represent~~s~~

the overall maximum length scale of intra-crystalline diffusion from both high- and low-angle boundary networks (Fig. 7).

Correlations between regions of chemical change and the development of low-angle boundaries in omphacite are less distinct. Typically, zoning in omphacite has a regular concentric habit. There is no apparent dependence between the extent of zoning and grain size of the porphyroclast (Fig. 8). Generally, areas of comparatively calcic omphacite have similar length scales (mean distances and d*l* ratios) in both low- and high-angle boundary regions. The length scales for Na and Al zonation in regions with abundant low-angle boundaries (high distortion) is greater (d*l* = 1.1–1.6) consistent with subtly more extensive change (metamorphism) (Fig. 8). These differences between elements are also apparent in the variance (σ), which is higher for Na and Al compared with Ca. The observations would appear to indicate that the low-angle boundaries provided the greatest influence on Na and Al diffusion, in association with the interconnected nature of the crystallographic boundaries in 3D. However, this affect is less pronounced in omphacite than in garnet.

The influence of crystal plastic strain on intra-grain trace element diffusion can be broadly assessed through spatial trends in concentration. At the first order, highly distorted regions of garnet have lower concentrations of Zr and Ti, but similar Y content, when compared with grain rims that lack lattice distortion (Fig. 9). Other transition metals, such as Cr and Ni, record a general decrease in concentration from the core to the rim of garnet grains, similar to variations in elemental concentration in regions recording crystal lattice strain (Figs 9 & S2). A concentric style of zoning is apparent for some trace elements in omphacite: Ti, Nd and Sr content transitions in a generally linear fashion from high core concentrations to low rim concentrations (Figs 10 & S3 for Mn & Zr). However, areas with the lowest concentrations tend to occur in neoblasts or grain regions with abundant low-angle boundaries (Fig. 10). Chromium concentration increases progressively towards the rim, with the highest concentrations in the distorted regions with abundant low-angle boundaries, but the lowest concentrations are generally observed in neoblasts (Fig. 10b). Nickel concentrations are largely consistent (~140 ppm) throughout crystal form (core, rim or neoblasts) (Fig. 10c).

DISCUSSION

High-grade metamorphic rocks commonly preserve grain-scale variability in microstructures and mineral chemistry that reflect dynamic changes in intrinsic and/or extrinsic variables including recrystallization (Powell et al., 2005; Williams & Jercinovic, 2012). In the Breaksea Orthogneiss, there is a marked grain-scale association between deformation microstructure and metamorphic reaction. Low-strain regions commonly preserve phenocrysts of omphacite and garnet with delicate microstructural and ~~chemical~~ features retained from the high-*T* recrystallization of the igneous protolith (*T*>1000°C), such as exsolution lamellae and facetted inclusions (Clarke et al., 2013; Chapman et al., 2017). Rims ~~to~~ porphyroclasts and neoblastic minerals in high-strain domains have ~~chemical~~ compositions that match ~~better~~ predictions from mineral equilibria modelling of metamorphosed intermediate protoliths at the inferred peak conditions (~850°C, 1.8 GPa: De Paoli et al., 2012; Chapman et al., 2017). The occurrence of domainal metamorphic equilibration in regions of high-strain and the generation of gneissic foliation is common to other high-grade terranes (e.g. Austrheim, 1987; Williams, ~~Dumond, Mahan, Regan & Holland,~~ 2014). The spatial association begs the question as to what variables control this dependency at the grain-scale? Establishing this context becomes particular relevant in extracting appropriate information to establish plausible petrogenetic histories (e.g. Vernon et al., 2008; cf. Stowell et al., 2017).

Low-angle boundary networks as elemental pathways of enhanced diffusivity

An intrinsic link between recrystallisation and metamorphic reaction progress in the Breaksea Orthogneiss can mostly account for the grain-scale development of comparatively grossular-rich garnet, jadeite-rich omphacite, clinozoisite and kyanite, and the consumption of plagioclase. Peripheral regions of the porphyroclasts preserve the patchy chemical modification of igneous grains, in sites associated with crystal plastic strain (Figs 4 & 6). Igneous garnet cores with only subtle misorientation ~~are enclosed by~~ metamorphic rims of higher grossular content; rims are very narrow where the magnitude of lattice misorientation is low (~0–3°), and more extensively developed in areas with abundant 3D defects forming low-angle (~4–10°) boundary networks and sub-grains. Similarly, omphacite cores ~~are enclosed by~~ narrow metamorphic rims ~~of~~ higher jadeite content where lattice misorientation is low, and subtly wider rims in areas with extensive distortion and low-angle boundary development (misorientation steps of ~2°: Figs 5 & 6). The scale and site of the compositional changes in regions of plastic strain ~~in the Breaksea Orthogneiss~~ reflect~~s~~ a dependency of grain-scale metamorphism, on the time-scales involved in this example through intra-crystalline diffusion on the generation of low-angle boundaries (Figs 7 & 8).

The pronounced coupling of grain-scale change and the development of low-angle boundaries could reflect the development of either: (1) enhanced diffusion pathways associated with the clustering of crystalline defects following recovery from strain related to far-field stress; or (2) chemical modification generating lattice volume strain. Distinguishing the role of these mechanisms is dependent on the timing of deformation relative to the observed chemical transformation. In the Breaksea Orthogneiss, the presence of growth zoning in garnet and omphacite neoblasts is consistent with deformation having generally preceded most chemical change. In addition, in lower-strain samples, garnet has grossular-rich overgrowths that lack any accompanying substructure (Fig. 2d). Examples of zoning in plastically-strained garnet and omphacite from Breaksea Sound are inferred to reflect the enhancement of element mobility ~~in relation to~~ crystal substructure. It is envisaged that the activation of pipe diffusion, along the cores of dislocation arrays (low-angle boundaries) contributed to the complex zonal patterns (e.g. Hart, 1957; Love, 1964; Lund et al., 2006; Piazolo et al., 2012, 2016). However, feedback associated with internal volume adjustment and lattice strain recovery may also have ~~subsequently transpired~~ (White & Knipe, 1978; Rutter & Brodie, 1985).

The activation of pipe diffusion in crystal regions of enhanced plastic strain increase the propensity of extensive grain-scale zonation (Fig. 11) (Reddy et al., 2006; Piazolo et al., 2016). The length scale of chemical mo[illegible]ation in distorted lattice volumes with low-angle boundary networks in garnet from the Breaksea Orthogneiss is more than 1.5–2.5-times (d*l*) greater than the length scales associated with zoning from the grain edge lacking lattice distortion (Fig. 8). In omphacite, this association is less pronounced: distorted low-angle boundary networks are associated with only marginally greater (d*l* = 1–1.6-times) length scales of Na and Al zoning compared to that in the undistorted grain rims (Fig. 9). The differing capacity of the low-angle boundaries to act as pathways for element movement in minerals will relate in part to their configuration (e.g. Storey & Prior, 2005). The distinction in style of (1) step-like lattice distortion along low-angle boundaries in garnet, compared to (2) more graduated misorientation in omphacite, is consistent with differing compatibilities of internal strain accommodation by the two minerals during recovery (Figs 3 & 5; Piazolo, Bestman, Prior & Spiers, 2006). The migration of dislocations into low-angle arrays appears to have been more efficient in garnet than in omphacite (e.g. Urai et al., 1986; Piazolo et al., 2006). It is likely that the frequency of 3D interconnection between low-angle boundaries was also greater in garnet. The creation of a low-angle boundary network with recovered sub-grains would contribute to the general effectiveness of mineral substructure to act as element pathways in conjunction with standard diffusion from the grain-edge.

The relative~~ly~~ rate of strain (or recovery) compared to reaction progress and diffusion also ~~becomes~~ relevant in assessing the proficiency of crystal substructure to transform minerals (e.g. Baxter & DePaolo, 2003). It can be assumed, based on empirical theory, that diffusion along dislocation "pipes" proceeds at a rate intermediate to that of intracrystalline- and grain boundary diffusion (Hart, 1957; Ruoff & Balluffi, 1963; Love, 1964; Yardley, 1977). Assessments of metamorphic duration are, however, based primarily on models of grain growth via standard ionic diffusion simply from the grain edge (e.g. Lasaga, 1979; Ague & Carson, 2013; Stowell et al., 2017). Major element relationships preserved in omphacite and garnet in the Breaksea Orthogneiss are consistent with low-angle boundary networks having enhanced the length scales of diffusion in common metamorphic exchange reactions. Less deformed grains that lack interconnected low-angle boundary networks show only limited peripheral chemical modification on account of the slower rates of intra-crystalline diffusion, most likely controlled by poorly linked defects (Fig. 11). Extensive plastic deformation, and recovery, appear~~s~~ to have enhanced element mobility through the development of low-angle boundaries, resulting in heterogeneous zoning during high-*T* metamorphism (see also Piazolo et al., 2016). This influence of crystal plastic strain on the length-scales of major element diffusion would also have the effect of up-s[illegible]ng the 3D extent of element exchange between the rock-forming minerals (and any liquid present) during a given metamorphic event, commonly referred to as the effective equilibrium volume (e.g Stüwe, 1997; Marmo et al., 2002; White, Powell & Baldwin, 2008; Schorn & Diener, 2017). The capacity of minerals to respond to changes in extrinsic variables through major element diffusion, in the example of the Breaksea Orthogneiss, was dependent on the partitioning and related time-scales of D_1 strain during subsolidus cooling.

Assessing the mobility of the trace elements is more difficult, but important due to their usefulness as proxies for reaction progress (e.g. Clarke, White, Lui, Fitzherbert & Pearson, 2007, 2013; Ague & Carson, 2013; Chapman et al., 2015). Although crude in terms of spatial definition, variability in the trace element concentrations in distorted lattice volumes comprising low-angle boundary networks within garnet and omphacite from the Breaksea Orthogneiss are consistent with the enhanced diffusion of these larger ionic elements via such pathways, regardless of their frequency and 3D form (Figs 9 & 10). However, trace element concentrations are strongly focussed despite rock histories involving high-strain, neoblasts typically have lower absolute concentrations of most trace elements in comparison to the porphyroclasts (Figs 9, 10 & S2). Such features are consistent with interpretations involving neoblastic grains inheriting reactant (phenocryst) trace element compositions (Clarke et al., 2013; Chapman et al., 2015). The general absence of an obvious trace element sink in recrystallized samples suggests either; (1) mineral growth was accommodated by the consumption of trace element-poor phases; or (2) the system was open to a scavenging liquid (fluid or melt). The evaluation of these possibilities ideally requires the mapping of element distribution at the micron-scale across broad regions of the rock volume. However, the ~~pseudomorphous~~ growth of garnet and omphacite on plagioclase, involving the incorporation of positive Eu anomalies in the mineral REE patterns, is consistent with a predominately closed reactive volume (Clarke et al., 2013). Widespread (decimetre-scale) metasomatism or extensive melt gain or lost, can also be precluded by the marked similarity of the whole-rock compositions across the gradient in strain (Chapman et al., 2015). The variation in trace element budgets between porphyroclasts and neoblasts in the Breaksea Orthogneiss could largely be accounted for by the incomplete changes in garnet, omphacite and plagioclase mode during metamorphism.

Feedbacks between deformation and metamorphism

Metamorphic changes ~~initiated~~ at the grain-scale by deformation are well known to be mechanically linked into feedback cycles (Brodie & Rutter, 1985; Rutter & Brodie, 1995; Jamtveit, Austrheim & Malthe-Sørenssen, 2000). The Breaksea Orthogneiss presents a clear example whereby the distinctions in the plastic behaviour of the main rock-forming minerals can account for spatially focused metamorphic reaction during strain partitioning (after Williams & Jercinovic, 2012). Core regions of ferromagnesian phenocrysts host perthite inclusions, whereas chemically-distinct K-feldspar and plagioclase neoblasts occur in the foliated rock matrix. Much of the feldspar-rich matrix experienced extensive recrystallization and recovery, with only sparse occurrences of anorthite or perthite in porphyroclasts (Figs 2g & h). It seems likely that diminished transformation in the comparatively stronger ferromagnesian phenocrysts also regulated the overall progress of the plagioclase-consuming reaction (e.g. Rutter & Brodie, 1995; Jamtveit et al., 2000; Williams & Jercinovic, 2012).

Both garnet and omphacite in Breaksea Orthogneiss preserve diverse effects of high-*T* recrystallization. Although typically considered less susceptib~~ility~~ to crystal plastic strain, garnet was plastically deformed and recrystallized consistent with high D_1 strain rates having accompanied the elevated temperature conditions (>750°C) (Kleinschrodt & McGrew, 2000; Prior, Wheeler, Brenker, Harte & Mathews, 2000; Storey & Prior, 2005). Parts of the Breaksea Orthogneiss with abundant plastically deformed garnet are generally restricted to domains of high-garnet mode (Figs 2c & 3a), which also include crystallographic distinct ~~homophase~~ aggregates of omphacite with flaser microstructure achieved by sub-grain rotation recrystallization (Fig. 5: Urai et al., 1986; Svahnberg & Piazolo, 2010). The accommodation of pronounced strain in omphacite aggregates present a stage of microstructure development that could have assisted reaction progress, particularly as the metamorphic conditions were fluid-poor (Chapman et al., 2017). For example, the concurrent attenuation and reduction in grain size of omphacite into flaser structures would help increase the proficiency of reactive volumes with higher densities of grain boundaries (Fig. 6; e.g. Yund & Tullis, 1991). In addition, the flaser microstructures would present suitable sites for the preferential nucleation of garnet coronae, possibly activated by both local chemical potential gradients and attempts to minimise strain energy (Figs 2b, 3 & 4; Stünitz 1998; Satsukawa et al., 2015; Smith, Piazolo, Daczko & Evans, 2015).

Causal dependencies between metamorphism and recrystallization during the D_1 deformation presents a simple explanation for the focussed nature of the reaction relationships. However, intrinsic feedbacks between metamorphism and deformation in rocks like the Breaksea Orthogneiss can potentially be complicated through ongoing dilation or compression (White & Knipe, 1978; Vernon, 1998). Volume changes induced by either phase transformation or deformation are likely to be intimately linked into a feedback cycle that continues to partition strain and reaction. Volume change in the Breaksea Orthogneiss was heterogeneous on a metre to millimetre-scale. The theoretical densification of the monzodioritic protolith at the peak metamorphic conditions (850°C, 1.8 GPa) would result in a negative molar volume change of ~4.34% (=0.9102 cm^3/per mole: after Chapman et al., 2017). The restricted growth of omphacite can account for most of this change, but would appear to have been transiently dependent on deformation (see also Tajčmanová et al., 2014; Wheeler, 2014; Powell et al., 2005).

CONCLUSIONS

A discernible grain-scale dependency between metamorphic reaction and deformation is observed in granulite and eclogite components of the Breaksea Orthogneiss. Crystal plastic deformation in garnet and omphacite localise~~d~~ reaction at the grain scale, but metamorphic change in the feldspathic matrix was more extensive and linked to greater strain. Intra-crystalline element mobility within garnet and omphacite was enhanced, by up to 2[illegible]mes in length scale, along low-angle boundary networks in formerly homogeneous silicates. There was only comparatively limited change along grain margins (high-angle boundaries).

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REFERENCES

Ague, J. J. & Carson, W. D. (2013). Metamorphism as garnet sees it: the kinetics of nucleation, equilibration, and diffusional relaxation. *Elements*, 9, 439–445.

Allibone, A. H., Jongens, R., Turnbull, I. M., Milan, L. A., Daczko, N. R., De Paoli, M. C. & Tulloch, A. J. (2009). Plutonic rocks of western Fiordland, New Zealand: field relations, geochemistry, correlation and nomenclature. New Zealand Journal of Geology and Geophysic*s*, 52, 379–415.

Austrheim, H. (1987). Eclogitization of lower crustal granulites by fluid migration through shear zones. *Earth and Planetary Science Letters*, **81**, 221–232.

Baxter, E. F. & De Paolo, D. J. (2003). Can metamorphic reactions proceed faster than bulk strain? *Contributions to Mineralogy and Petrology*, **146**, 657–670.

Betka, P. M. & Klepeis, K. A. (2013). Three-stage evolution of lower crustal gneiss domes at Breaksea Entrance, Fiordland, New Zealand. *Tectonics*, **32**, 1084–1106.

Bürgmann, R. & Dresen, G. (2008). Rheology of the lower crust and upper mantle: evidence from rock mechanics, geodesy, and field observations. *Annual Reviews of Earth and Planetary Sciences*, **36**, 531–567.

Bradshaw, J. Y. (1989). Origin and metamorphic history of an Early Cretaceous polybaric granulite terrain, Fiordland, southwest New Zealand. *Contributions to Mineralogy and Petrology* **103**, 346–360.

Brenker, F. E., Prior, D. J. & Müller, W. F. (2002). Cation ordering in omphacite and effect on deformation mechanism and lattice preferred orientation (LPO). *Journal of Structural Geology*, **24**, 1991–2005.

Brodie, K. H. & Rutter, E. H. (1985). On the relationships between deformation and metamorphism, with special reference to behaviour of basic rocks. *In,* Thompson, A. B. & Rubie, D. C. (Eds.) *Advances in Physical Geochemistry*. Springer–Verlag, New York, 138–179.

Chapman, T., Clarke, G. L., Daczko, N. R., Piazolo, S. & Rajkumar, A. (2015). Orthopyroxene–omphacite- and garnet–omphacite-bearing magmatic assemblages, Breaksea Orthogneiss, New Zealand: oxidation state controlled by high-*P* oxide fractionation. *Lithos*, **216–217**, 1–16.

Chapman, T., Clarke, G. L. & Daczko, N. R. (2016). Crustal differentiation in a thickened arc — evaluating depth dependencies. *Journal of Petrology*, **57**, 595–620.

Chapman, T., Clarke, G. L., Piazolo, S. & Daczko, N. R. (2017). Evaluating the importance of metamorphism in the foundering of continental crust. *Scientific Reports* **7**, DOI:10.1038/s41598-017-13221-6.

Chapman, T., Clarke, G. L., Piazolo, S. & Daczko, N. R. (submitted). Quantifying the proportions of relict igneous and metamorphic minerals in variably strained orthogneiss. *American Mineralogist*.

Clarke, G. L., Daczko, N. R. & Nocklods, C. (2001). A method for applying matrix corrections to X-ray intensity maps using Bence–Albee algorithm and MATLAB. *Journal of Metamorphic Geology*, **19**, 635–644.

Clarke, G. L., White, R. W., Lui, S., Fitzherbert, J. A. & Pearson, N. J. (2007). Contrasting behaviour of rare earth and major elements during partial melting in granulite facies migmatites, Wuluma Hills, Arunta Block, central Australia. *Journal of Metamorphic Geology*, **25**, 1–18.

Clarke, G. L., Daczko, N. R. & Miescher, D. (2013). Identifying relict igneous garnet and clinopyroxene in eclogite and granulite, Breaksea Orthogneiss, New Zealand. *Journal of Petrology*, **54**, 1921–1938.

Cottrell, A. H. (1953). Theory of dislocations. *Progress in Metal Physics*, **4**, 205–264.

Cyprych, D., Piazolo, S. & Almqvist, B. S. G. (2017). Seismic anisotropy from compositional banding in granulites from deep magmatic arc of Fiordland, New Zealand. *Earth and Planetary Science Letters*, **477**, 156–167.

De Paoli, M. C., Clarke, G. L., Klepeis, K. A., Allibone, A. H. & Turnbull, I. M. (2009). The eclogite–granulite transition: mafic and intermediate assemblages at Breaksea Sound, New Zealand. *Journal of Petrology*, **50**, 2307–2343.

De Paoli, M. C., Clarke, G. L. & Daczko, N. R. (2012). Mineral equilibria modeling of the granulite–eclogite transition: effects of whole-rock composition on metamorphic facies type-assemblages. *Journal of Petrology*, **53**, 949–970.

Hart, E. W. (1957). On the role of dislocations in bulk diffusion. *Acta Metallurgica*, **5**, 597.

Hasalová, P., Schulmann, K., Lexa, O., Štípská, P., Hrouda, F., Ulrich, S., Haloda, J. & Týcová, P. (2008). Origin of migmatites by deformation-enhanced melt infiltration of orthogneiss: a new model based on quantitative microstructural analysis. Journal of Metamorphic Geology, 26, 29–53.

Jamtveit, B., Austrheim, H. & Malthe-Sørenssen, A. (2000). Accelerated hydration of the Earth's deep crust induced by stress perturbations. *Nature*, **408**, 75–78.

Kleinschrodt, R. & McGrew, A. (2000). Garnet plasticity in the lower contiental crust: implications for deformation mechanisms based on microstructures and SEM-electron channeling pattern analysis. *Journal of Structural Geology*, **22**, 795–809.

Klepeis, K. A., Schwartz, J., Stowell, H. & Tulloch, A. J. (2016). Gneiss domes, vertical and horizontal mass transfer, and the initiation of extension in the hot lower-crustal root of a continental arc, Fiordland, New Zealand. *Lithosphere*, **8**, 116–140.

Lasaga, A. C. (1979). Multicomponent exchange and diffusion in silicates. *Geochimica et Cosmochimica Acta*, **43**, 455–469.

Love, G. R. (1964). Dislocation pipe diffusion. *Acta Metallurgica*, **12**, 731–737.

Love, G. & Scott, V. D. (1978). Evaluation of new correction procedure for quantitative electron probe micro analysis. *Journal of Physics*, **11**, 1369–1376.

Legros, M., Dehm, G., Arzt, E. & Balk, T. J. (2008). Observation of giant diffusivity along dislocations cores. *Science*, **319**, 1646–1649.

Lund, M. D., Piazolo, S. & Harley, S. L. (2006). Ultrahigh temperature deformation microstructures in felsic granulites of the Napier Complex, Antarctica. *Tectonophysics*, **427**, 133–151.

Marmo, B. A., Clarke, G. L. & Powell, R. (2002). Fractionation of bulk rock composition due to porphyroblast growth: effects of eclogite facies mineral equilibria, Pam Peninsula, New Caledonia. *Journal of Metamorphic Geology*, **20**, 151–165.

Milan, L. A., Daczko, N. R., Clarke, G. L. & Allibone, A. H. (2016). Complexity of *in situ* U Pb–Hf isotope systematics during arc magma genesis at the roots of a Cretaceous arc, Fiordland, New Zealand. *Lithos*, **264**, 296–314.

Milan, L. A., Daczko, N. R. & Clarke, G. L. (2017). Cordillera Zealandia: A Mesozoic arc flare-up on the palaeo-Pacific Gondwana margin. *Scientific Reports*, DOI: 10.1038/s41598-017-00347-w.

Miranda, E. A. & Klepeis, K. A. (2016). The interplay and effects of deformation and crystallized melt on the rheology of the lower continental crust, Fiordland, New Zealand. *Journal of Structural Geology*, **93**, 91–105.

Piazolo, S., Bestmann, M., Prior, D. J. & Spiers, C. J. (2006). Temperature dependent grain boundary migration in deformed-then-annealed material: observations from experimentally deformed synthetic rocksalt. Tectonophysics, 427, 55–71.

Piazolo, S., Austrheim, H. & Whitehouse, M. (2012). Brittle-ductile microfabrics in naturally deformed zircon: deformation mechanisms and consequences for U–Pb dating. *American Mineralogist*, **97**, 1544–1563.

Piazolo, S., La Fontaine, A., Trimby, P., Harley, S., Yang, L., Armstrong, R. & Cairney, J. (2016). Deformation-induced trace element redistribution in zircon revealed using atom probe tomography. *Nature Communications*, DOI: 10.1038/ncomms10490.

Powell, R. Guiraud, M. & White, R. W. (2005). Truth and beauty in metamorphic phase equilibria: conjugate variables and phase diagrams. *The Canadian Mineralogist*, **43**, 21–33.

Powell, R. & Holland, T. J. B. (2008). On thermometry. *Journal of Metamorphic Geology*, **26**, 155–179.

Powell, R., Evans, K. A., Green, E. C. A. & White, R. W. (2017). On equilibrium in non-hydrostatic systems. *Journal of Metamorphic Geology*, DOI: 10.1111/jmg.12298.

Prior, D. J., Boyle, A. P., Brenker, F., Cheadle, M. C., Day, A., Lopez, G., Peruzzo, L., Potts, G. J., Reddy, S., Spiess, R., Timms, N. E., Trimby, P., Wheeler, J. & Zetterström, L. (1999). The application of electron backscatter diffraction and orientation contrast imaging in the SEM to textural problems in rocks. *American Mineralogist*, **84**, 1741–1759.

Prior, D. J., Wheeler, J., Brenker, F. E., Harte, B. & Mathews, M., 2000. Crystal plasticity of natural garnet: new microstructural evidence. *Geology*, **28**, 1003–1006.

Prior, D. J., Wheeler, J., Peruzzo, L., Spiess, R. & Storey, C. (2002). Some garnet microstructures: an illustration of the potential of orientation maps and misorientation analysis in microstructural studies. *Journal of Structural Geology*, **24**, 999–1011.

Reddy, S. M., Timms, N. E., Trimby, P., Kinny, P. D., Buchan, C. & Blake, K. (2006). Crystal-plastic deformation of zircon: a defect in the assumption of chemical robustness. *Geology*, **34**, 257–260.

Ruoff, A. L. & Balluffi, R. W. (1963). Strain-enhanced diffusion in metals. II. Dislocation and grain-boundary short-circuiting models. *Journal of Applied Physics*, **34**, 1848–1854.

Rutter, E. H. & Brodie, K. H. (1995). Mechanistic interactions between deformation and metamorphism. *Geological Journal*, **30**, 227–240.

Satsukawa, T., Piazolo, S., González-Jiménez, J. M., Colás, V., Griffin, W. L., O'Reilly, S. Y., Gervilla, F., Fanlo, I. & Kerestedjian, T. N. (2015). Fluid-present deformation aids chemical modification of chromite: insights from chromites from Golyamo Kamenyane, SE Bulgaria. *Lithos*, **228–229**, 78–89.

Schorn, S. & Diener, J. F. A. (2017). Details of the gabbro-to-eclogite transition determined from microtextures and calculated chemical potential relationships. *Journal of Metamorphic Geology*, **35**, 55–75.

Smith, J. R., Piazolo, S., Daczko, N. R. & Evans, L. (2015). The effect of pre-tectonic reaction and annealing extent on behaviour during subsequent deformation: Insights from paired shear zones in the lower crust of Fiordland, New Zealand. *Journal of Metamorphic Geology*, **33**, 557–577.

Storey, C. D. & Prior, D. J. (2005). Plastic deformation and recrystallisation of garnet: a mechanism to facilitate diffusion creep. *Journal of Petrology*, **46**, 2593–2613.

Stüwe, K. (19970. Effective bulk composition changes due to cooling: a model predicting complexities in retrograde reaction textures. *Contributions to Mineralogy and Petrology*, **129**, 43–52.

Stünitz, H. (1998). Syndeformational recrystallisation — dynamic or compositionally induced? *Contributions to Mineralogy and Petrology*, **131**, 219–236.

Stowell, H., Schwartz, J. J., Klepeis, K. A., Hout, C., Tulloch, A. J. & Koenig, A. (2017). Sm-Nd ages for granulite and eclogite in the Breaksea Orthogneiss and widespread granulite facies metamorphism in the lower crust, Fiordland magmatic arc, New Zealand. *Lithosphere*, DOI: 10.1130/L662.1.

Svahnberg, H. & Piazolo, S., 2010. The initiation of strain localization in plagioclase-rich rocks: insights from detailed microstructural analyses. *Journal of Structural Geology*, **32**, 1404–1416.

Tajčmanová, L., Podladchikov, Y., Powell, R., Moulas, E., Vrijmoed, J. C. & Connelly, J. A. D. (2014). Grain-scale pressure variations and chemical equilibrium. *Journal of Metamorphic Geology*, **32**, 195–207.

Urai, J. L., Means, W. D. & Lister, G. S. (1986). Dynamic recrystallisation of minerals. In Hobbs, B. E., Heard, H. C. (Eds.). Mineral and rock deformation (laboratory studies). Geophysical monograph of the American Geophysical Union, **36**, pp. 161–200.

Wheeler, J. (2014). Dramatic effects of stress on metamorphic reactions. *Geology*, **42**, 647–650.

White, S. H. & Knipe, R. H. (1978). Transformation- and reaction-enhanced ductility in rocks. *Journal of the Geological Society of London*, **135**, 513–516.

White, R. W., Powell, R. & Baldwin, J. A. (2008). Calculated phase equilibria involving chemical potentials to investigate the textural evolution of metamorphic rocks. *Journal of Metamorphic Geology*, **26**, 181–198.

Williams, M. L. & Jercinovic, M. J. (2012). Tectonic interpretation of metamorphic tectonites: integrating compositional mapping, microstructural analysis and *in situ* monazite dating. *Journal of Metamorphic Geology*, **30**, 739–752.

Williams, M. L., Dumond, G., Mahan, K., Regan, S. & Holland, M. (2014). Garnet-forming reactions in felsic orthogneiss: implications for densification of the lower continental crust. *Earth and Planetary Science Letters*, **405**, 207–219.

Vernon, R. H. (1998). Chemical and volume changes during deformation and prograde metamorphism of sediments In Treloar P. J. & O'Brien P. J. (Eds). *What drives metamorphism and metamorphic reactions?* Geological Society of London Special Publications, **138**, 215–246.

Vernon, R. H., White, R. W. & Clarke, G. L. (2008). False metamorphic events inferred from misinterpretation of microstructural evidence and *P–T* data. *Journal of Metamorphic Geology*, **26**, 437–449.

Vernon, R. H., Collins, W. J. & Cook, N. D. J. (2012). Metamorphism and deformation of mafic and felsic rocks in a magma transfer zone, Stewart Island, New Zealand. *Journal of Metamorphic Geology*, **30**, 473–488.

Yardley, B. W. D. (1977). An emprical study of diffusion in garnet. *American Mineralogists*, **62**, 793–800.

Yund, R. A. & Tullis, J. (1991). Compositional changes of minerals associated with dynamic recrystallisation. *Contributions to Mineralogy and Petrology*, **108**, 346–355.

FIGURE CAPTIONS

Figure 1 Simplified geological map of the Breaksea Sound area between northern Resolution Island and Coal River (after Chapman et al., 2017). Circles represent sample locations. Abbreviations are Resolution Island Shear Zone and Straight River Shear Zone. Inset shows location of the field area in relation to the South Island geology.

Figure 2a Large igneous garnet (Grt_i) containing facetted inclusions of omphacite, antiperthite, plagioclase and rutile. Antiperthite inclusions are intergrown with K-feldspar. The garnet core is defined by rutile exsolution needles (arrow). **b** Highly strained mafic grain clusters defined by ribbons (arrow) or attenuated omphacite (Omp_m) and garnet neoblasts (Grt_m) that are intergrown with quartz and rutile. **c** Recrystallisation transition from large elongated igneous garnet (Grt_i) with abundant rutile exsolution to garnet neoblasts (Grt_m) with vermicular inclusions on the each of grain cluster. **d** Igneous garnet core (Grt_i) surrounded by optically distinct metamorphic overgrowth defined by lobate boundaries (labelled Grt_m). **e–f** Large igneous omphacite (Omp_i) containing cores with titano-haematite lamellae (Ti-Hem) and facetted plagioclase inclusions (Pl). Surrounding the porphyroclasts are small aggregates of homophase omphacite defining flaser tails (Omp_m). **g** Granoblastic feldspar-rich matrix displaying 120° triple (arrow) and albite deformation twins (grain labelled Pl). **h** Graphic intergrowths of plagioclase and K-feldspar within the feldspar-rich matrix.

Figure 3a EBSD misorientation map for a garnet recrystallisation microstructure (shown in Fig. 2c) of elongate igneous garnet (white core) transitioning to garnet neoblasts (right). The false colour displays the magnitude of crystallographic distortion (°) relative to an arbitrary point (cross) of the same mineral within the analysis region. Inset, high resolution misorientation map of high-strain region in garnet (shown in red) with prominent low-angle boundaries. **b** Lattice dispersion pattern from boxed area marked in (a); note the clear small circle dispersion of most axes, except <100> which represents the rotation axis. **c–d** Misorientation profile showing gradual lattice distortion and low-angle boundaries in regions (arrows) transition from igneous garnet to metamorphic overgrowths, line locations and colours correspond to misorientation map (a).

Figure 4 Matrix corrected X-ray maps of Mg (a), Fe (b) and Ca (c) in garnet. Only analyses of garnet are shown in the maps (wt % Oxide) for the purpose of showing the pronounced patchy zonation corresponding to highly distorted crystal regions (d).

Figure 5a EBSD misorientation map for a omphacite flaser microstructure, across elongated porphyroclast and homophase neoblastic aggregates. The false colour displays the magnitude of crystallographic distortion (°) relative to an arbitrary point (cross) of the same mineral within the analysis region. Inset, high resolution misorientation map of low-angle boundary domain in omphacite (shown in red). **b** Lattice dispersion pattern from boxed area marked in (a); note the clear small circle dispersion of most axes, except [001] and [110] which represent the rotation axes. **c–d** Misorientation profile showing gradual lattice distortion and low-angle boundaries (arrows) in porphyroclast domains and neoblasts, line locations and colours correspond to misorientation map.

Figure 6 Matrix corrected X-ray maps of Al (a), Na (b), Mg (c) and Ca (d) in omphacite (Fig. 4). Only analyses of omphacite are shown in the maps (wt % Oxide) for the purpose of showing the pronounced patchy zonation. The misorientation map displaying crystal plastic strain of this region is shown in Figure 5a.

Figure 7 Histogram of mean distance calculations of chemical zonation, (a) Ca and (b) Mg, associated with cores, highly distorted regions (abundant low-angle boundary networks, >1.5° misorientation/μm^2) and low distortion rims (<1.5° misorientation/μm^2) in garnet. Error bars represent 1σ and d*l* is the ratio of distance between highly distorted regions and low distortion rims.

Figure 8 Histogram of distance calculations of zoning, (a) Ca, (b) Na and (c) Al), associated with cores, highly distorted regions (abundant low-angle boundary networks, >1.5° misorientation/μm^2) and low distortion rims (<1.5° misorientation/μm^2) in clinopyroxene. Error bars represent 1σ and d*l* is the ratio of distance between highly distorted regions and low distortion rims.

Figure 9 Bivariate plots (*versus* Y) of the trace element concentrations in garnet across distinct substructural domains: (a) Cr, (b) Ti, (c) Zr and (d) Ni. Error bars represent 1σ relative standard deviation on each analysis.

Figure 10 Bivariate plots (*versus* Ti) of the trace element concentrations in omphacite across distinct substructural and microstructural domains: (a) Sr, (b) Cr, (c) Ni and (d) Nd. Error bars represent 1σ relative standard deviation on each analysis.

Figure 11 Schematic diagram of zoning style associated with the generation of 3D low-angle boundary networks during crystal plastic strain (b) versus standard flux diffusion in homogeneous garnet (a). Both mechanisms occur concurrently within deformed crystals of the Breaksea Orthogneiss.

Supplementary Table 1 Trace element mineral chemistry (LA-ICPMS) of garnet and omphacite.

Supplementary Figure 1 Summary of mineral misorientation and elemental correlation analysis for garnet and omphacite. The false colour EBSD maps display the magnitude of crystallographic distortion (°) relative to an arbitrary point (cross) of the same mineral within the analysis region. Elemental analyses of garnet or omphacite in (wt % O) show patchy zonation corresponding to regions of crystal plastic strain. Euclidean distance maps associate the extent of zonation in garnet and omphacite to the crystalline regions with (1) high distortion and abundant low-angle boundaries and (2) low lattice distortion rims (marked).

Supplementary Figure 2 Gd_N/Yb_N *versus* Eu* ($=Eu_N/\sqrt{Sm_N Gd_N}$) diagram of garnet substructural composition (cf. Clarke et al., 2013).

Supplementary Figure 3 Bivariate plots (*versus* Ti) of the trace element concentrations in omphacite across distinct substructural and microstructural domains: (a) Mn and (b) Zr. Error bars represent 1σ relative standard deviation on each analysis.