

Growth zoning of garnet porphyroblasts: Grain boundary and microtopographic controls

Tim J. Dempster | Sarah Coleman | Ross Kennedy | Peter Chung |
Roderick W. Brown

School of Geographical and Earth Sciences,
University of Glasgow, Glasgow, UK

Correspondence

Tim J. Dempster, School of Geographical
and Earth Sciences, University of Glasgow,
Glasgow, UK.

Email: tim.dempster@glasgow.ac.uk

Abstract

Chemical zoning in the outer few 10s of microns of garnet porphyroblasts has been investigated to assess the scale of chemical equilibrium with matrix minerals in a pelitic schist. Garnet porphyroblasts from the Late Proterozoic amphibolite facies regional metamorphic mica schists from Glen Roy in the Scottish Highlands contain typical prograde growth zoning patterns. Edge compositions have been measured via a combination of analysis of traverses across the planar edges of porphyroblast surfaces coupled to X-ray mapping of small areas within polished thin sections at the immediate edge of the porphyroblasts. These approaches reveal local variation in garnet composition, especially of grossular (Ca) and almandine (Fe) components, with a range at the edge from <7 mol.% grs to >16 mol.% grs, across distances of less than 50 μm . This small-scale patchy compositional zoning is as much variation as the core–rim compositional zoning across the whole of a 3 mm porphyroblast. Ca and Fe heterogeneity occurs on a scale suggesting a combination of inefficient diffusive exchange across grain boundaries during prograde growth and the evolving microtopography of the porphyroblast surface control garnet composition. The latter creates haloes of compositional zoning adjacent to some inclusions, which typically extend from the inclusion towards the porphyroblast edge during further growth. The lack of a consistent equilibrium composition at the garnet edge is also apparent in the internal zoning of the porphyroblast and so processes occurring during entrapment of some mineral inclusions have a profound influence on the overall chemical zoning. Garnet compositions and associated zoning patterns are widely used by petrologists to reconstruct P – T – t paths for crustal rocks. The evidence of extremely localized (10–50 μm scale) equilibrium during growth further undermines these approaches.

KEYWORDS

garnet, grain boundaries, local equilibrium, prograde growth zoning, surface microtopography

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2020 The Authors. *Journal of Metamorphic Geology* published by John Wiley & Sons Ltd

1 | INTRODUCTION

Metamorphism involves the textural and mineralogical re-adjustment of rocks to changing environmental conditions and so is a process inherently dependent on the ability of individual minerals to equilibrate. Garnet is perhaps the most informative of the common metamorphic minerals because of it can preserve changing chemistry during growth and hence capture information on the evolving pressure–temperature conditions (Caddick, Konopásek, & Thompson, 2010; Kohn, 2014; Robyr, Darbellay, & Baumgartner, 2014; Spear, Kohn, Florence, & Menard, 1990; Tinkham & Ghent, 2005; Thompson, Tracy, Lyttle, & Thompson, 1977). As a consequence, chemical zoning profiles across porphyroblasts through the core of the mineral are typically analysed by metamorphic petrologists, used to infer P – T – t paths and linked to suggested tectonic evolution (e.g. Dempster & Harte, 1986; Gropo, Rolfo, & Lombardo, 2009; Selverstone, Spear, Franz, & Morteani, 1984; Spear, 1993; Vance & Mahar, 1998). A variety of different types of zoning have been reported in garnets ranging from simple concentric patterns to flattened profiles, oscillatory zoning and zoning linked to discrete fractures and inclusions (e.g. Hames & Menard, 1993; Hirsch, Prior, & Carlson, 2003; Hollister, 1966; Kohn, 2014; Schumacher, Rötzer, & Maresch, 1999; Stowell, Zuluaga, Boyle, & Bulman, 2011; Whitney, Mechum, Dilek, & Kuehner, 1996). Interpretations derived from the compositional zoning of garnet are central to the current understanding of conditions and thermal evolution in the deep crust and as a result these types of petrological studies are widespread.

A crucial assumption associated with the use of garnet compositions to determine the metamorphic conditions, is that garnet growth occurs in equilibrium with the mineral assemblage and chemistry of the matrix minerals. The scale of this equilibrium is open to question, as many minerals, most notably garnet, are unable to equilibrate without the aid of factors such as deformation and fluid presence (e.g. Carlson, Pattison, & Caddick, 2015; Dempster, 1992; Dempster, Gilmour, & Chung, 2019). A test of this assumption is that the porphyroblast edge should be a consistent composition irrespective of the mineralogy of the immediately adjacent matrix. Chemical zoning profiles and X-ray compositional maps on the scale of whole garnet porphyroblasts often reveal apparently simple concentric zoning patterns (Hollister, 1966; Kohn, 2014), which seem to confirm models of progressive equilibrium growth. However many studies report apparent irregularities in the zoning characteristics that are not obviously linked to equilibrium processes on the scale of the individual porphyroblast (Carlson, Hixon, Gerber, & Bodnar, 2015; Chernoff & Carlson, 1997; Hirsch et al., 2003; O'Brien, 1999), especially those associated with trace elements such as Cr and Y (Lanzirotti, 1995; Martin, 2009; Pyle & Spear, 2003; Yang & Rivers, 2001). Here we investigate

major element zoning in garnet porphyroblasts from the Barrovian regional metamorphic rocks of western Scotland to address whether garnet porphyroblast edges represent consistent equilibrium compositions and the extent to which internal zoning within the garnet is influenced by processes at the growing edge.

Recently developed analytical techniques more readily allow the analysis of garnet porphyroblast edges, and have demonstrated the sluggish nature of grain boundary diffusion during retrograde histories (Dempster, Symon, & Chung, 2017). This raises important questions about the ability of the matrix mineralogy to maintain equilibrium (Ague & Carlson, 2013) and here we apply these same techniques to the investigation of kinetic restrictions on prograde garnet growth.

2 | GEOLOGICAL SETTING

The Late Proterozoic Dalradian Leven Schists (Harris, Haselock, Kennedy, & Mendum, 1994) from Glen Roy in the Scottish Highlands have experienced Ordovician amphibolite facies regional metamorphism during the Caledonian orogeny at *c.* 470 Ma (Dempster et al., 2002; Oliver, Chen, Buchwaldt, & Hegner, 2000). These pelitic schists contain large (3 mm) garnet porphyroblasts, together with biotite, strongly aligned muscovite and granular quartz and plagioclase in the matrix (Dempster, La Piazza, Taylor, Beaudoin, & Chung, 2017; Phillips et al., 1994). Garnet porphyroblasts are typically evenly spaced within the schists. They contain abundant aligned quartz inclusions that, together with less common ilmenite, indicates syntectonic growth with respect to the external muscovite fabric (Figure 1a). Margins of the garnet porphyroblasts are either planar, particularly where the porphyroblast is relatively free from inclusions, or appear to be irregular with partially enclosed quartz (Figure 1a). The garnet mica schists are locally interbedded with thin originally calcareous layers now enriched in plagioclase at the expense of muscovite.

This study was undertaken on two samples previously analysed and described by Dempster, La Piazza, et al. (2017). The majority of observations and analysis was performed on sample GR05. Some garnet surface analysis was also done on an immediately adjacent pelite GR03. Both samples contain a similar assemblage with ~7% to 8% garnet, although GR03 contains trace amounts (0.6%) of staurolite at the garnet margins and some originally calcareous, plagioclase-rich layers. The development of staurolite in a few schists at this locality is linked to breakdown of garnet via a coupled dissolution–reprecipitation reaction (Dempster, La Piazza, et al., 2017). This locally results in the patchy development of a fluid inclusion-rich ‘cloudy’ garnet (cf. Martin et al., 2011). Cloudy garnet is rarely present in sample GR05, which also lacks staurolite. Typically the schist lacks evidence of

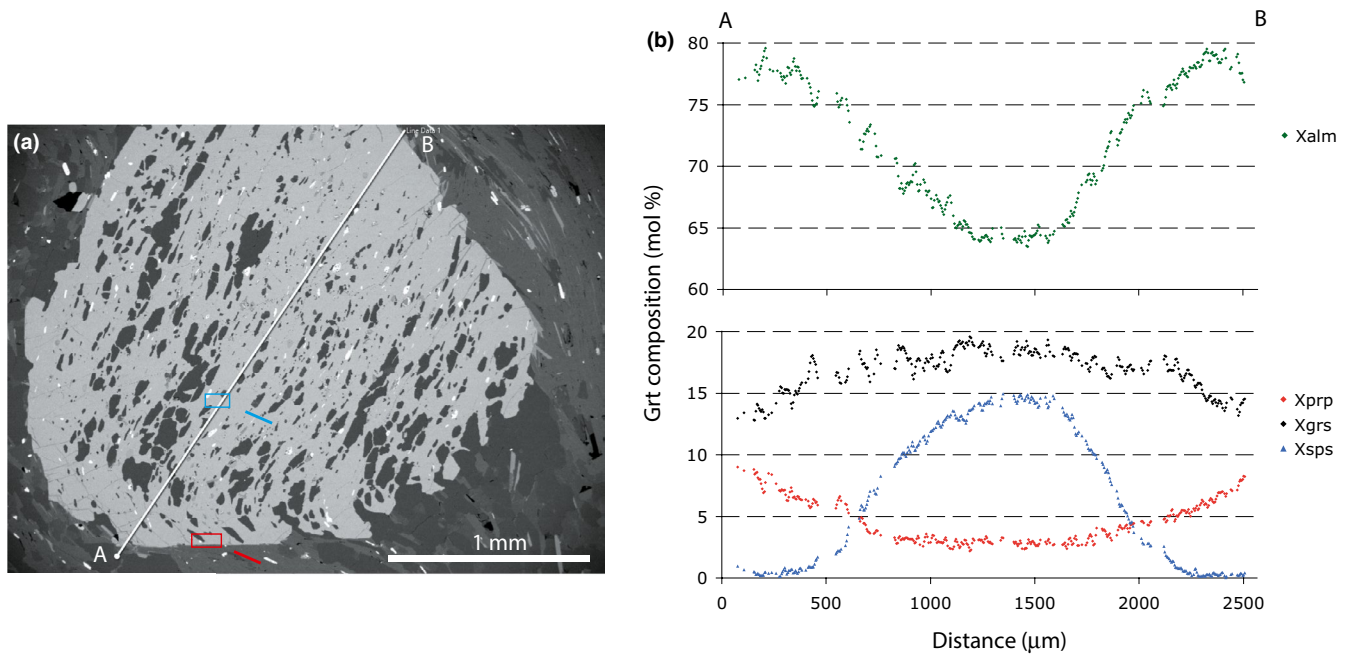


FIGURE 1 (a) Backscattered electron image of garnet porphyroblast (grt1) showing aligned quartz (dark BSE) and ilmenite (bright BSE) inclusions in syntectonic growth geometry with regards to the alignment of muscovite in the adjacent matrix (Sample GR05). Line of traverse A–B shown. Red box marked with arrow depicts the area mapped in detail in Figure 6. Blue box marked with arrow depicts the area mapped in detail in Figure 8. (b) Compositional zoning profile of garnet along line A–B showing molecular proportions of end-members alm (Fe), grs (Ca), prp (Mg) and sps (Mn). Compositional analyses (grt1) are presented in Supplementary publication. Mineral abbreviations follow Whitney and Evans (2010) throughout

retrogression, although in all samples trace amounts of secondary chlorite may be present at the immediate edge of some garnet porphyroblasts. Based on the mineral assemblages present in the area, peak metamorphic temperature estimates of $\sim 550^{\circ}\text{C}$ appear probable (Phillips et al., 1994; Richardson & Powell, 1976). However, there is a lack of metamorphic equilibrium in these rocks that does not preclude higher temperatures having been experienced (Dempster, La Piazza, et al. 2017, 2019). Garnet porphyroblasts are zoned with prominent Mn-rich cores to porphyroblasts (Dempster, La Piazza, et al., 2017), which indicates that equilibration via volume diffusion is ineffective on the scale of single porphyroblasts (Dempster, 1985; Yardley, 1977). Hence long timescales at high temperatures in excess of 650°C are unlikely (Mueller, Watson, & Harrison, 2010; Viète, Hermann, Lister, & Stenhouse, 2011). Pressures of peak regional metamorphism in this area have been estimated at 0.7–0.8 GPa (Phillips et al., 1994).

3 | METHODS

Surface analysis was performed following methods of Dempster, Symon, et al. (2017) using snapped rock slices. Exposed garnet porphyroblast surfaces with flat crystal faces were selected and rotated prior to analysis to be perpendicular to the electron beam. Topographic features on the garnet

were matched with those on the adjacent corresponding matrix surfaces, such that the positions of matrix mineral grain boundaries can be precisely located on the garnet surface. X-ray mapping and chemical traverses of both surfaces and the standard polished thin sections were acquired using a Carl-Zeiss Sigma VP electron microscope operated at 20 kV, with Oxford Instruments X-Max 80 energy dispersive spectrometry (EDS) using a take-off angle of 35° and processed using Aztec Software 3.0. Although EDS analysis yields greater uncertainty in absolute mineral compositions than wavelength spectrometry (Reed, 2005), EDS provides a reliable indication of relative compositions crucial for the assessment of chemical zoning within garnet. Routinely between 100 and 500 analysis points were made for each traverse with data then smoothed through a rolling average over distances corresponding to ~ 1 to $2\ \mu\text{m}$ to eliminate any analytical noise. A spacing between analytical points of $\sim 5\ \mu\text{m}$ was used for the traverse across the whole porphyroblast. Repeat analysis of single spots close to a garnet porphyroblast rim reveals that typical uncertainties associated with each X_{grs} and X_{sps} measurement along individual traverses are ± 0.14 mol.% and those associated with X_{prp} and X_{alm} are ± 0.26 mol.%. Compositional data from the garnet surfaces were filtered based on matching ideal garnet compositions, to exclude any inclusions analysed, or those analytical points located close to chlorite veins. As reported by Dempster, Symon, et al. (2017), repeat analysis of the same traverse in different

orientations relative to the EDS detector typically shows no change in the compositions that could be explained by topography alone. However all analytical points within a few microns of large topographic steps were removed from the data set so as to ensure that potential topographic influence (Reed, 2005) was minimized. Relative to garnet analysed from polished thin sections some skewing of compositional data towards heavier elements is observed in some of the surface analyses with typical X_{alm} and X_{sps} contents elevated by ~2 mol.%. However, generally relative concentrations of end-member components are consistent between the two types of analyses. Compositional data from closely spaced traverses and some isolated area analysis were combined to create contour maps of small areas. The filtered compositional analyses, prior to smoothing, used to construct these traverses and maps (>8,000 individual analyses) are presented in the Supplementary file that accompanies this publication. The almandine and grossular maps were produced by interpolation of the point values onto a regular $1 \times 1 \mu\text{m}$ grid using the adjustable tension continuous curvature spline technique provided as part of the Generic Mapping Tools library (Wessel & Luis, 2017). Tension was set to 0.25 and spatial aliasing and elimination of redundant data was minimized by using only the median value within each $1 \times 1 \mu\text{m}$ cell (if there were multiple data in a grid cell). Contours are smoothed using a Gaussian filter of width $5 \mu\text{m}$. Areas selected for detailed compositional mapping from close to planar edges of porphyroblasts, lack elevated Mn contents. Outlines of inclusions and garnet porphyroblast edges were then superimposed on the resulting geochemical maps. This superposition may create artefacts in the contouring that are unrelated to the inclusion edge. The four analysed areas are from two adjacent porphyroblasts in GR05, totalling ($<0.05 \text{ mm}^2$) and represent: one area at the edge of garnet adjacent to a high strain cleavage lithon dominated by aligned muscovite; one area at the edge of garnet close to a quartz- and plagioclase-dominated pressure shadow; one area at the edge near matrix with a mixture between quartz and muscovite; and, one area from a more central part of a porphyroblast.

4 | RESULTS

4.1 | Porphyroblast-scale compositional zoning

Compositional zoning profiles taken through the centre of individual large porphyroblasts display classical bell-shaped Mn profiles (Harte & Henley, 1966; Hollister, 1966; Kohn, 2014). A gradual decrease in the Ca content from ~19 mol.% grossular (grs) component in the core to ~13 mol.% grs in the margins occurs, and a progressive increase in Mg content and Mg/Fe towards the rim (Figure 1b). Mn contents are

typically very low (<1 mol.%) at the edge of porphyroblasts but tend to be locally variable in absolute levels (Figure 1b). Despite the generally higher concentrations, Ca typically has rather more irregular variation in the absolute content than either Mg or Mn, with local short wavelength variations of at least 2–3 mol.% grs throughout the compositional profile (Figure 1b). The Mg and Mn show smooth variation from core to rim. Fe zoning typically mirrors the combination of the other divalent cations (Figure 1).

4.2 | Garnet surface microtopography

Electron images of garnet porphyroblasts in the snapped samples reveal numerous flat terraces, with widths of between a few microns and up to hundreds of microns across (Figure 2a). These terraces are separated by multiple linear sets of parallel-aligned steps (Figure 2a). Such regular steps characterize all of the garnet porphyroblast surfaces, with the notable exception of those that have abundant secondary chlorite at their margins. In such instances the garnet locally has a smooth, gently curved topography, lacking the detailed microtopography (Figure 2b). In thin section view, most garnet porphyroblasts have an equant smooth shape with some approximately planar surfaces and some apparently irregular margins near inclusion-rich domains (Figure 1a). However snapped samples reveal that most garnet surfaces are dominated by many perfectly flat crystal edges, even those with abundant partial inclusions (Figures 2a,c and 3a). In addition to the aligned steps, more rarely, imprints of matrix phases are present forming a shallow depression on the garnet surface. This is most commonly observed when biotite is the immediately adjacent matrix phase (Figure 2c). Other than this, the regular stepped topography of the garnet crystal surface seems to be independent of the location of grain boundaries in the adjacent matrix (Figure 3b). Sets of parallel steps may define small rhomboid cavities, which create embayments in the garnet surface mirrored perfectly by the matrix edge topography. Matrix quartz, plagioclase and more rarely biotite typically occupy the central low point of such cavities, and some have grain boundaries between these matrix phases striking across the planar steps (Figures 2c and 3a,b). A few of the flat terrace areas of the garnet surface have an additional smaller-scale stepped topography characterized by small rhomboid depressions (Figure 4a). This is most commonly observed where the garnet porphyroblast edge is adjacent to plagioclase in the matrix. Other surfaces adjacent to plagioclase may have a less regular second-order pitted topography (Figure 3a). Such pits are typically only a few microns in diameter and have both an irregular shape and distribution. Chlorite-filled fractures of a few microns width also cut across some of the garnet surfaces (Figures 2c and 3a).

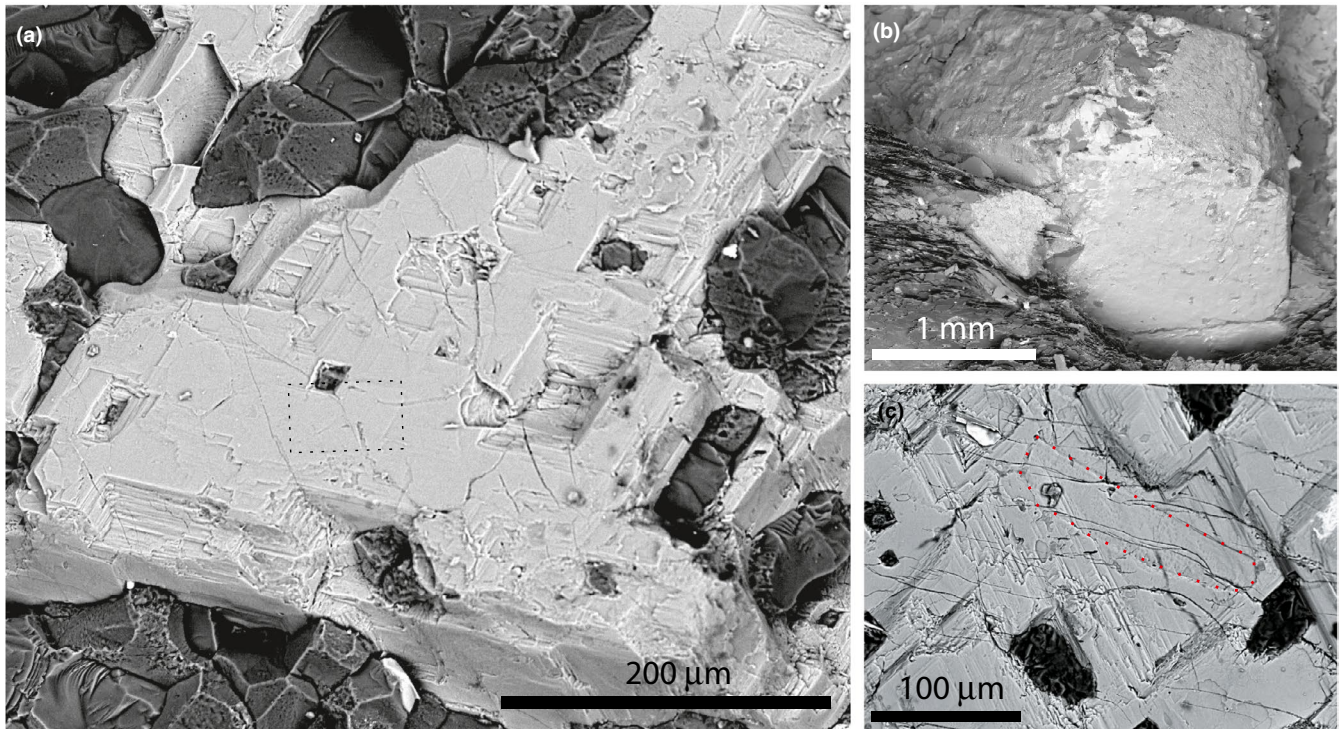


FIGURE 2 Backscattered electron images of garnet porphyroblast surfaces. (a) Typically garnet surface showing flat terraces with parallel steps at their margins and rhomboid shaped cavities with dark quartz in the centre. Matrix quartz and plagioclase (dark BSE signal) show granoblastic grain boundaries. Area of traverse shown in Figure 4 marked by dotted box (Sample GR05). (b) Smooth gently curved garnet porphyroblast surface adjacent to retrograde matrix chlorite. Contrast with upper left surface of the porphyroblast which has a typical stepped surface (Sample GR05). (c) Garnet surface showing fractured, stepped topography and central flat embayment (outline in red) that coincides exactly with the position of a biotite in the immediately adjacent matrix (Sample GR03)

The complex topographic variation shown by the snapped sample preparation methods is not immediately obvious in many of the thin section views, however small-scale steps, typically 1–2 μm but up to 5 μm in width, in the garnet edge are present on some of the porphyroblast grain boundaries. These occur on scales of a few microns both associated with grain boundaries, such as embayments adjacent to biotite, and steps that are not currently linked to adjacent matrix mineral boundaries.

4.3 | Garnet surface chemistry

Garnet porphyroblast surfaces preserve compositional variations that are of similar magnitude to those recorded in the core–rim traverses (Figures 1 and 3). Ca composition of the porphyroblast edge ranges from 8 to 12 mol.% grs (Figure 3d). Mn contents (X_{sps}) typically show <1 mol.% variation along a single porphyroblast face (Figure 3c,d) but may record differences of a few mol.% sps content between porphyroblasts in a single sample. Almandine (Fe) (X_{alm}) contents typically mirror the X_{grs} variation and pyrope (Mg) (X_{prp}) typically shows lower amplitude (<2 mol.% prp), longer wavelength variations than either the Ca and Fe variation (Figure 3). In

contrast to the core–rim compositional profiles, the high amplitude variations in Ca content across the garnet surface typically show the smoothest, apparently least noisy, variation of the divalent cations (Figure 4b). The wavelength of the compositional variation varies with some sharp changes of >2 mol.% over distances less than 20 μm , and some gradual changes with wavelengths up to 100 μm (Figure 3d).

Many of the abrupt changes in grossular (Ca) content coincide with grain boundaries between adjacent matrix minerals (Figures 3d and 4b). In other instances compositional variation coincides broadly with the location of topographic steps in the garnet surface, such as present towards the left hand end of the profiles shown in Figures 3d and 4b. The exact spatial correlation is hard to constrain because of a combination of the width of the electron beam and a cautious approach to filtering data associated with topography of the surface. Local low Ca, high Fe contents broadly match the location of topographic steps with short wavelength, high amplitude variations on the garnet surface (Figure 3c,d). Such zones linked to abundant topographic steps have amplitudes of 1–2 mol.% X_{grs} and X_{alm} relative to ‘background’ levels. The wavelengths range from a few microns up to 50 μm , well in excess of any topographic influence on the electron beam analysis associated with an irregular surface and the take-off angle. There appears to be much

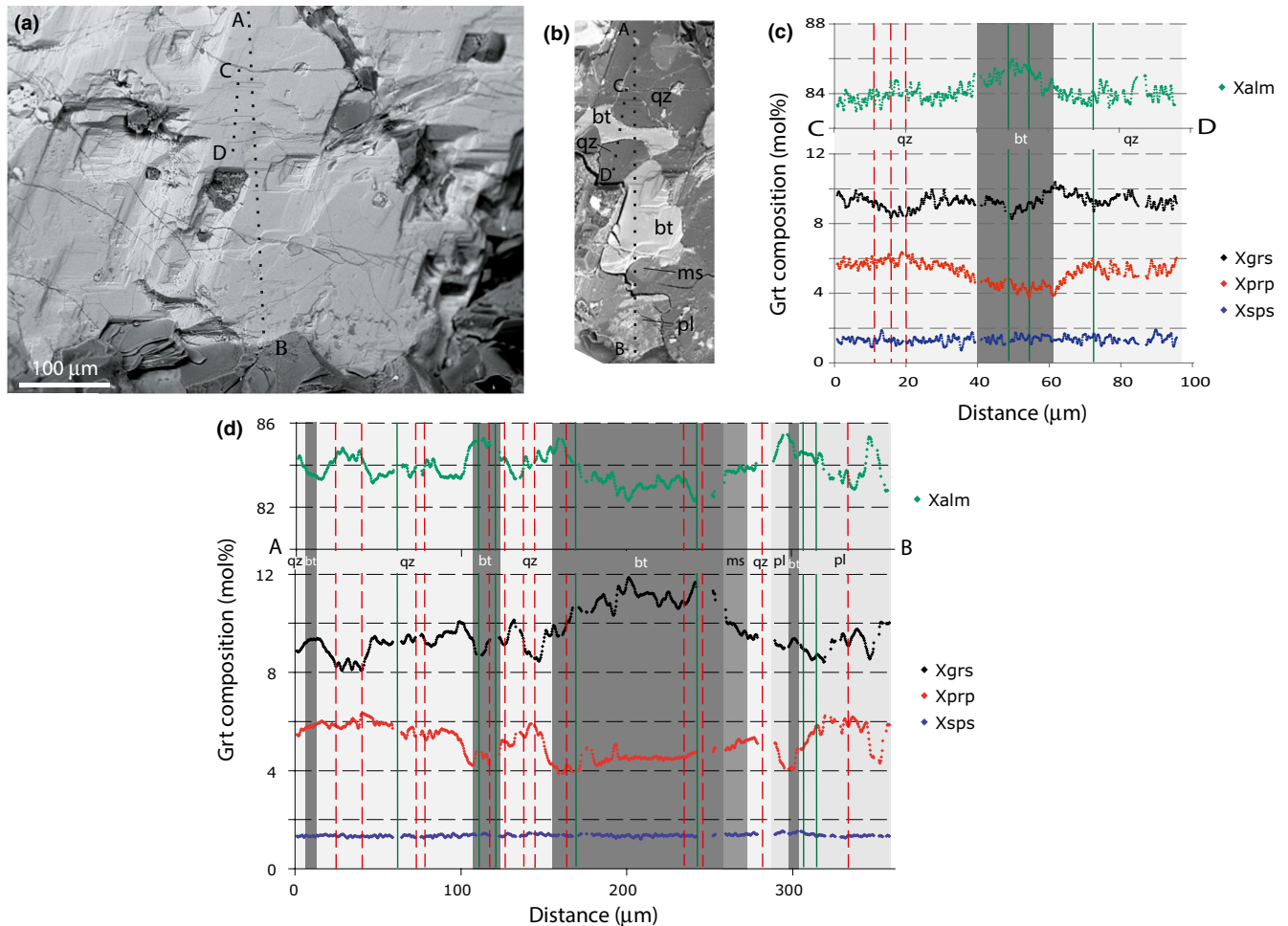


FIGURE 3 (a) Backscattered electron image of a garnet porphyroblast surface (Sample GR05) showing numerous flat terraces. Dotted lines mark analysed traverses, A–B and C–D. (b) Backscattered electron image of matrix surface from adjacent to the porphyroblast surface. Image has been flipped about a vertical axis to allow geometry to be more readily compared to the garnet surface shown in (a). (c) Compositional zoning profile of garnet along line C–D showing molecular proportions of end-members alm (Fe), grs (Ca), prp (Mg) and sps (Mn). Positions and types of adjacent matrix minerals shown by shading in the background of the plot, green vertical lines mark positions of chlorite-filled fractures and dashed red lines mark obvious topographic steps on the porphyroblast surface. (d) Compositional zoning profile of garnet along line A–B showing molecular proportions of end-members alm (Fe), grs (Ca), prp (Mg) and sps (Mn)

less variation in Mg that can be linked to surface topography and changes in the latter are more obviously associated with the nature of the adjacent matrix phase (Figure 3d).

Garnet surfaces adjacent to matrix biotite typically have low X_{prp} , low X_{alm} and high X_{grs} contents, relative to the garnet adjacent to quartz or plagioclase (Figure 3c,d). Garnet porphyroblast surfaces adjacent to muscovite generally have lower X_{grs} and higher X_{prp} than those adjacent to biotite. Garnet adjacent to plagioclase may be particularly variable, in comparison to that next to quartz, with a series of short wavelength, high amplitude ~2 mol.% changes in Ca and Fe contents (Figure 4b). Typically X_{prp} shows relatively consistent variation in comparison to X_{grs} (Figure 4b). X_{prp} compositions are typically ~2 mol.% lower adjacent to grain boundaries with matrix biotite (Figure 3c,d). The variations in X_{prp} of garnet surfaces across grain boundary junctions in the matrix show generally gently curving transitions over

distances of a few 10s of microns, especially towards lower X_{prp} adjacent to matrix biotite. In contrast Ca variation shows shorter wavelength variation that in some instances may be linked to grain boundaries (Figure 4b) but also in other examples are apparently unrelated to the present location of triple junctions on the garnet surface (Figure 3c).

There is no obvious link between the garnet chemistry and the location of the small chlorite-filled fractures.

4.4 | Patchy compositional zoning

Compositional maps, and traverses acquired adjacent to, and parallel with, relatively planar porphyroblast edges, show a variety of different zoning characteristics. The variation occurs both perpendicular to, and parallel with, the porphyroblast edge (Figures 5b and 6a). All three of the porphyroblast edges

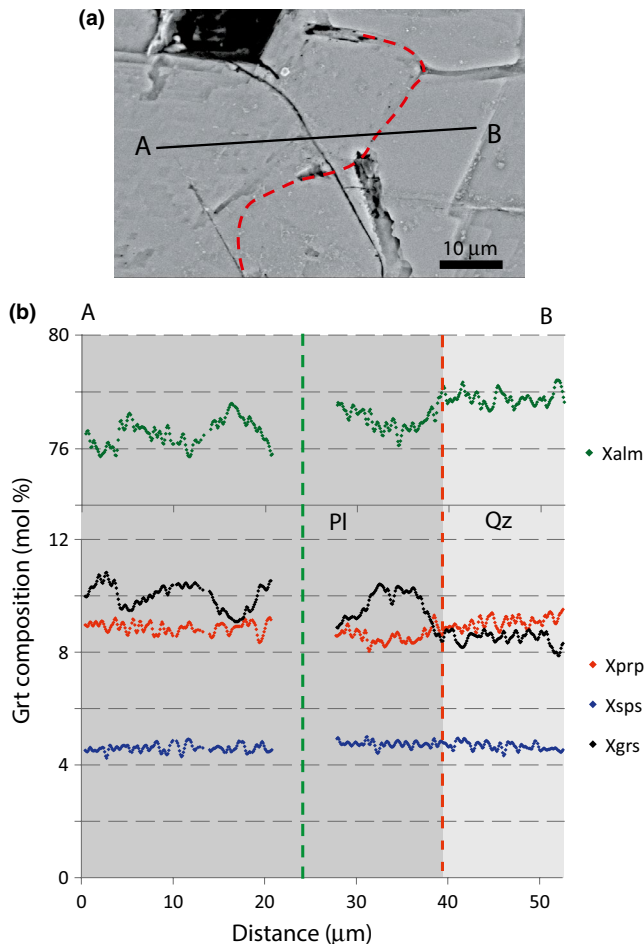


FIGURE 4 (a) Backscattered electron image of a garnet porphyroblast surface (Sample GR03) from area shown in Figure 2a. Line of analysed traverse A-B is marked (black line), together with the position of a plagioclase–quartz grain boundary in the matrix adjacent to the garnet (dashed red line). Garnet to the left of the image is adjacent to plagioclase and shows shallow rhomboid depressions in the surface. (b) Compositional zoning profile of garnet along line A-B showing molecular proportions of end-members alm (Fe), grs (Ca), prp (Mg) and sps (Mn). Positions of matrix grain boundary between quartz and plagioclase shown by shading in the background of the plot and the red dashed line. The green dashed vertical line marks position of fracture

analysed show similar styles of compositional zoning irrespective of the position of the edge and structure of the adjacent matrix (Figures 5–7). These also share characteristics with features of the porphyroblast surface chemistry (Figure 3) and patchy zoning in the garnet interior (Figure 8). Three dominant types of localized zoning are present.

4.4.1 | Local zoning parallel to the porphyroblast edge

Typically garnet margins feature lower average Ca contents at the rims (Figures 5b,e and 7), and slightly lower

Mg (Figure 5e), with a minor reduction in Mg/Fe in the outer 5 µm. A few porphyroblasts have minor increases in Mn content localized at the immediate edge of the porphyroblast (Figure 5e). The Mn variation ranges from an average of ~1 mol.% X_{sps} at the rim to <0.4 mol.% 20 µm away from the garnet edge. Compositional zones parallel to the porphyroblast edge are least developed in the mapped area adjacent to the muscovite-rich cleavage folia (Figure 6a).

4.4.2 | Broad zoning along the porphyroblast edge

In contrast to some aspects of the surface composition (Figure 3), typically there appears to be little direct correlation between the nature of the matrix mineralogy and the zoning of the garnet in the analysed areas (Figure 7a–c). The exception to this is where biotite is adjacent to the porphyroblast (Figure 7). In this instance, the matrix biotite physically extends into the edge of the porphyroblast (Figure 7c) and a broad low Mg zone of garnet of <0.5 mol.% prp lower than background contents occurs at the immediate margin. This geochemical feature does not extend more than 10 µm into the garnet, where Mg profiles appear to be flatter (Figure 7d).

Some of the contoured maps do reveal local broad highs and lows in Ca composition along the garnet edge with wavelengths of 50–100 µm (Figure 6a,c). The high Ca contents are matched by low Fe. These broad scale variations have an amplitude of ~2–3 mol.% grs and appear to be of a similar scale to those observed in the garnet surface traverses (Figures 3d and 4b), although they do not currently correlate with either the nature of the adjacent matrix phases or the grain boundaries between them.

4.4.3 | Inclusion-related patchy zoning

All of the mapped areas contain multiple small-scale (~10–20 µm wavelength), high amplitude (up to 10 mol.%) patchy variation in particular for both grossular and almandine contents (Figures 5–7). Patchy variation in both Mn and Mg is also present but with both of these cations it is typically low amplitude and long wavelength by comparison (Figures 6c and 7d). Similar short wavelength Ca and Fe variations are present in the internal parts of the porphyroblasts (Figure 8a). These are of lower amplitude and no associated Mn or Mg variation is observed (Figure 8b). As such they appear to be a common feature of the Ca–Fe zoning in garnet rather than isolated edge-related ‘anomalies’. Many of the patchy zones may be spatially linked to the presence of mineral inclusions within

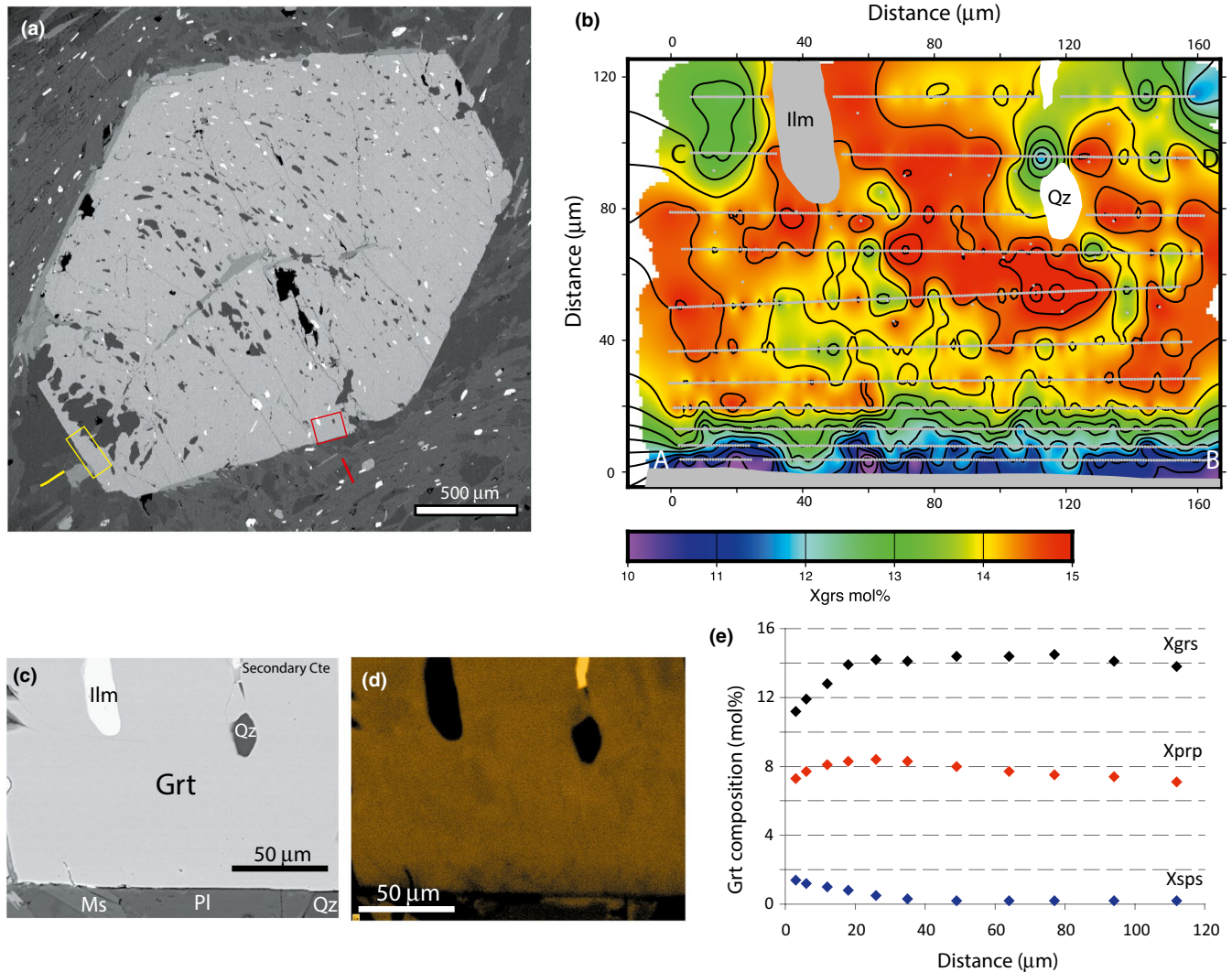


FIGURE 5 (a) Backscattered electron image of garnet porphyroblast in GR05 showing the location of ARC-GIS generated zoning maps shown in (b) red and Figure 7 (yellow). Compositional data from traverses used to construct this map (grt2) are presented in Supplementary Publication. (b) Contoured map of X_{grs} constructed from parallel traverses coupled to individual point/area analyses from part of the garnet shown in (a). (c) Backscattered electron image showing detail of area mapped with adjacent matrix phases marked. (d) Ca distribution map of the same area. (e) Compositional zoning profile of the edge of the garnet based on average X_{grs} , X_{prp} and X_{sps} contents of each traverse shown in (b)

the garnet (Figure 7a and 8a) and appear to be at a similar scale (i.e. 10s of microns) and general orientation to the inclusions (Figure 6a,b). Others appear unrelated to inclusions (Figure 6a) at least in the plane of the thin section and equally many inclusions lack associated zones (Figure 5b). The patchy zones are aligned at a high angle to the orientation of the porphyroblast boundary irrespective of its position relative to the rock cleavage (Figures 6a and 7a,b). The most striking compositional variation at the mapped edge of garnet occurs adjacent to the muscovite-rich cleavage folia (Figure 6a).

The extent of the Ca variation across these short wavelength patchy zones is locally greater than the variation shown in traverses across the whole porphyroblast (Figures 1, 6a,c and 7b,d). Short wavelength Ca zoning may also be

observed in the whole porphyroblast traverse but these are poorly defined with a 5 μm spacing between analysis points (Figure 1b). These patchy zones are of similar amplitude to the short wavelength zones documented in the garnet surface analysis (Figures 3 and 4) and are marked by an overall increase in Mg/Fe relative to the adjacent high Ca garnet. The contoured maps (e.g. Figure 5b) constructed from parallel traverses show the same general overall patterns as Ca X-ray EDS maps (Figure 5d).

There may be a general symmetry in zoning adjacent to inclusions, along a porphyroblast edge-parallel axis (Figures 6a and 8a), although typically zones extend much further, for several 10s of microns, towards the outer edge of the garnet. These extend to a distance well beyond any possible extension of the inclusion margin itself given the

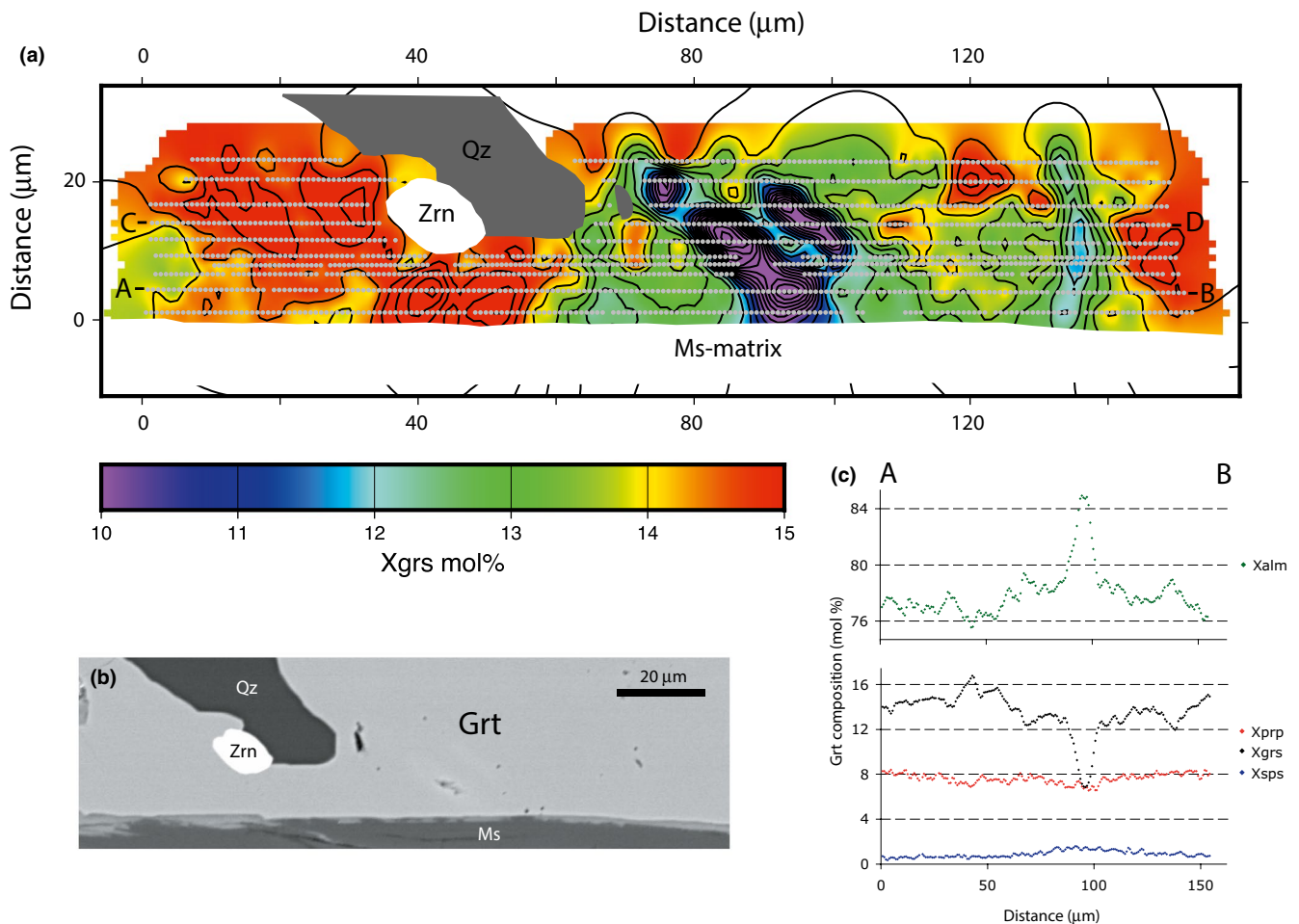


FIGURE 6 (a) Contoured map of X_{grs} constructed from parallel traverse data from the garnet (GR05) area highlighted in red on Figure 1a. Compositional data from traverses used to construct this map (grt3) are presented in Supplementary Publication. (b) Backscattered electron image showing detail of the same area of the garnet porphyroblast. (c) Compositional zoning profile of garnet along individual traverse A–B showing molecular proportions of end-members alm (Fe), grs (Ca), prp (Mg) and sps (Mn)

lack of ‘contamination’ of the garnet analyses over relatively large areas (see Supplementary information). There is a lack of zoning on the opposite ‘internal’ edge of such inclusions (Figure 8a). 10–20 μm wide Ca-poor zones are observed immediately adjacent to all of the dominant minerals that form the inclusion population; plagioclase, quartz and ilmenite; despite the lack of many of the key cations in these inclusions. Each of these inclusion types may show no adjacent zoning (Figures 5b and 6a).

Where such Ca-poor zones are present adjacent to inclusions they may continue towards the edge of the porphyroblast as a low Ca, high Fe ‘channel’ within the garnet (Figure 7b). These patchy zones may continue as a channel to the porphyroblast margin, however, in most they ‘close off’ a few 10s of microns away from the inclusion (Figures 6a and 8a). The channel shown in Figure 7b does not align with present grain boundaries in the immediately adjacent matrix, but appears to match the location of a small step in the porphyroblast edge. Although the prominent

channel zones are most obviously marked by Fe and Ca variation, minor changes in the Mg and Mn contents also occur in these zones close to the porphyroblast edge. High Mn contents, up to 0.5 mol.% spessartine above ‘background’, of similar levels to the slightly elevated contents at the garnet rim are associated with the high Fe patches and channels (Figures 5e, 6c and 7d). Such Mn anomalies are typically much less prominent and appear to be broader than that of Fe (Figures 6c and 7d).

5 | INTERPRETATION

Overall smooth large-scale compositional zoning profiles in the garnet porphyroblasts are consistent with continuous prograde growth (Kohn, 2014) and progressive depletion in Mn in the matrix (Hollister, 1966) and/or changing Mn partitioning (Dempster et al., 2019). The presence of small volumes of marginal chlorite may be associated

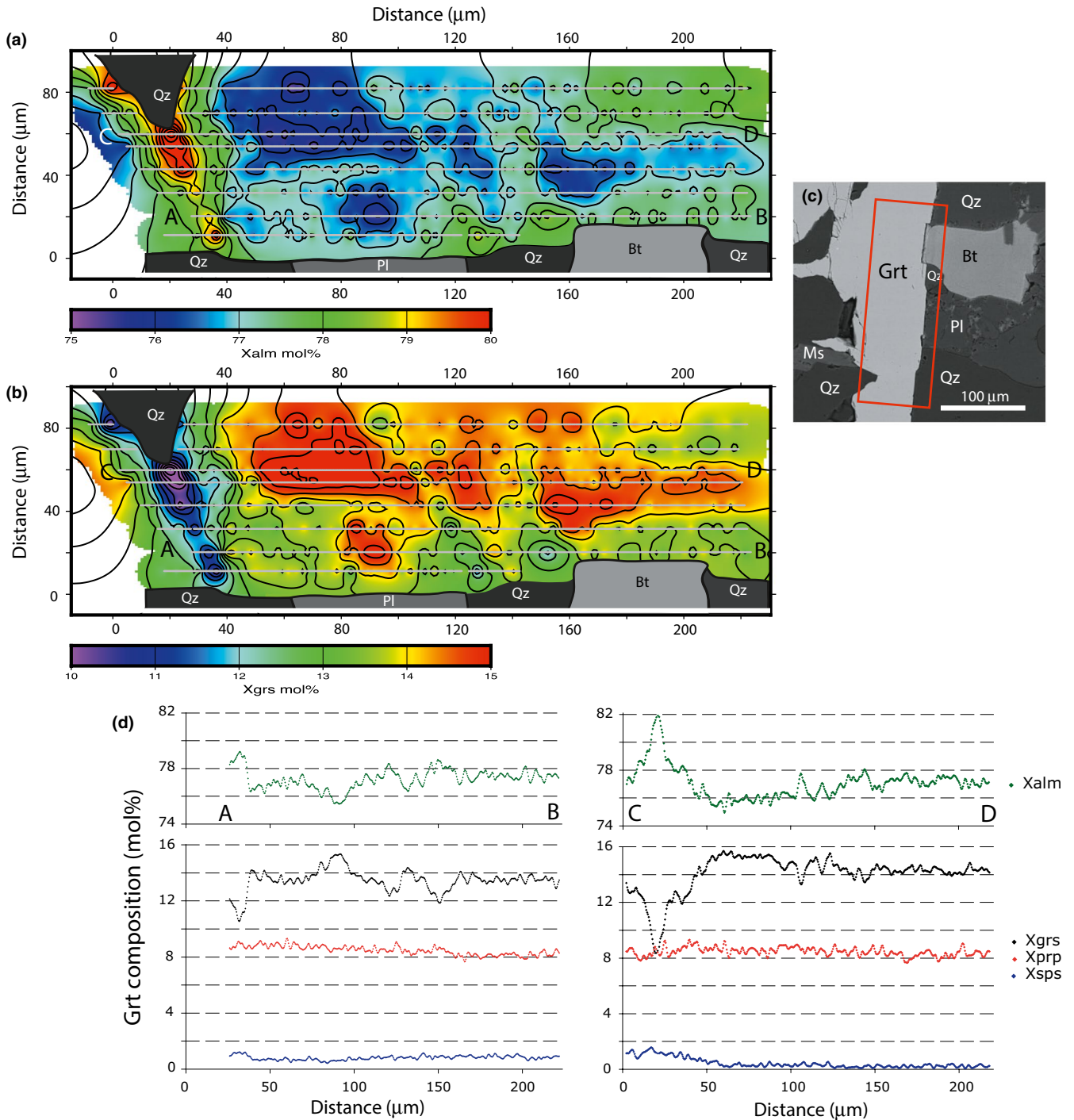


FIGURE 7 Contoured map of X_{alm} constructed from parallel traverse data from the area of the garnet porphyroblast highlighted in yellow on Figure 5a. Individual traverses marked by grey lines. Compositional data from traverses used to construct this map (grt4) are presented in Supplementary Publication. (b) Contoured map of X_{grs} from the same area. (c) Backscattered electron image showing the area of the garnet porphyroblast edge that was analysed. The position within the larger porphyroblast is shown in Figure 5a. (d) Compositional zoning profiles of garnet along individual traverses A–B and C–D, showing molecular proportions of end-members alm (Fe), grs (Ca), prp (Mg) and sps (Mn)

with some local retrograde modification of garnet and may be linked to slightly elevated Mn contents of the porphyroblast rims (de Béthune, Laduron, & Bocquet, 1975). The smooth topography associated with garnet porphyroblast surfaces immediately adjacent to secondary chlorite is also compatible with minor garnet dissolution.

5.1 | Diffusive modification of growth zoning

All garnet will be subject to diffusive modification of zoning after crystallization, this will involve elements of both

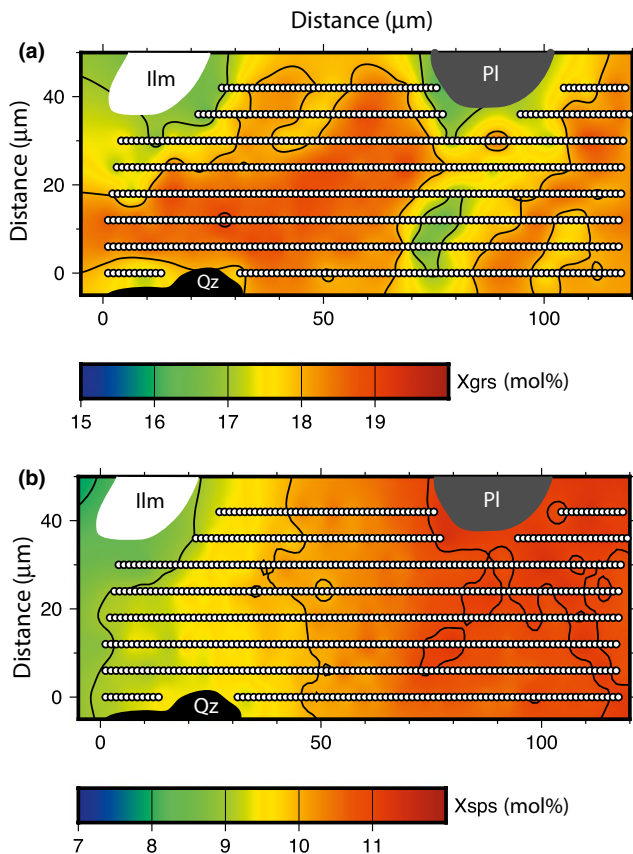


FIGURE 8 (a) Contoured map of X_{grs} constructed from parallel traverse data from the area of the garnet porphyroblast highlighted in blue on Figure 1a. Individual traverses marked by lines. Compositional data from traverses used to construct this map (grt5) are presented in Supplementary Publication. (b) Contoured map of X_{sps} from the same area

prograde and retrograde modification (Borinski et al., 2012; Dempster, 1985; Mueller et al., 2010; Pattison & Bégin, 1994; Tracy, Robinson, & Thompson, 1976; Tuccillo, Essene, & van der Pluijm, 1990). The preservation of the typical porphyroblast-scale zoning indicates that high- T modification through volume diffusion is ineffective in these metamorphic conditions (e.g. Kohn, 2014). In such circumstances the effects of volume diffusion will be most obviously manifested by retrograde localized lower Mg/Fe zones in garnet immediately adjacent to all biotite at the porphyroblast edge (e.g. Tracy et al., 1976). Although diffusive exchange between some inclusions and the host porphyroblast is possible it would not account for patchy Fe–Ca zoning in garnet adjacent to isolated inclusions of any of the dominant inclusion types: quartz; plagioclase; or ilmenite. Equally the asymmetric geometry of the patchy zones associated with inclusions is incompatible with an origin of diffusive exchange. Hence these zones are unrelated to either diffusive exchange with the matrix across a simple planar interface (Pattison & Bégin, 1994; Tracy et al., 1976) or an exchange with inclusions, as not all inclusions of similar type or the equivalent

matrix phases have similar compositional zoning in the adjacent garnet. Consequently late diffusive exchange cannot explain the patchy geometry of the local high amplitude Ca and Fe zoning.

Garnet from this study does show some localized minor reduction in Mg/Fe adjacent to matrix biotite and this suggests some low- T grain boundary diffusive exchange occurs both along and across the garnet boundary (Dempster, Symon, et al., 2017). The extent of this local exchange internally within the garnet occurs over $\sim 20 \mu\text{m}$ and is of limited amplitude (2 mol.% prp) in comparison to the scale of grain boundary diffusion exchange that created 6 mol.% pyrope variations on the surfaces of garnet porphyroblasts in Dalradian schists to the east (Dempster, Symon, et al., 2017). This together with the localized short wavelength, high amplitude Ca and Fe zoning within the porphyroblast (Figure 7) that lacks a consistent geometry with respect to either matrix mineralogy or inclusions indicates that retrograde volume diffusion in isolation has rather limited effect on these garnets, particularly for Ca and Fe. This may be due to relatively low temperatures or short timescales (Mueller et al., 2010, 2015). Volume diffusion may be responsible for some smoothing of the original growth zoning. Hence the original geometry of zones may be partially masked as a consequence of slight smoothing by late diffusion of cations (Mueller et al., 2010). This is most evident for Mg and Mn given the broader zoning associated with these cations (e.g. Figures 6c and 8b) and supports suggestions of faster intracrystalline diffusion of Mn and Mg relative to other cations (Carlson, 2006; Chernoff & Carlson, 1997; Vielzeuf, Baronnet, Perchuk, Laporte, & Baker, 2007).

5.2 | Patchy zoning

Several studies have reported patchy zoning of elements on the scale of whole garnet porphyroblasts, including Mn (e.g. Hirsch et al., 2003), Ca (e.g. Chernoff & Carlson, 1997) and trace elements (e.g. Martin, 2009). This has been variously attributed to solubility-limited transport, interface controls, diffusional impediments, zonation of reactants and fluid-driven zoning (Ague & Carlson, 2013). Local retrograde exchange with plagioclase inclusions (Whitney, 1991) and fluid-induced dissolution–reprecipitation processes associated with fractures and localized reaction (Dempster, La Piazza, et al., 2017; Hames & Menard, 1993) have also been shown to create heterogeneity in the internal zoning. Very few studies have investigated chemical zoning at garnet edges in detail.

Two dominant types of patchy Ca–Fe zoning are evident from both the surface analysis and the detailed mapping of small areas. Compositional heterogeneity is present in broad zones of $\sim 100 \mu\text{m}$ scale, consistent with the typical grain size of matrix phases. There is also intense patchy zoning on a

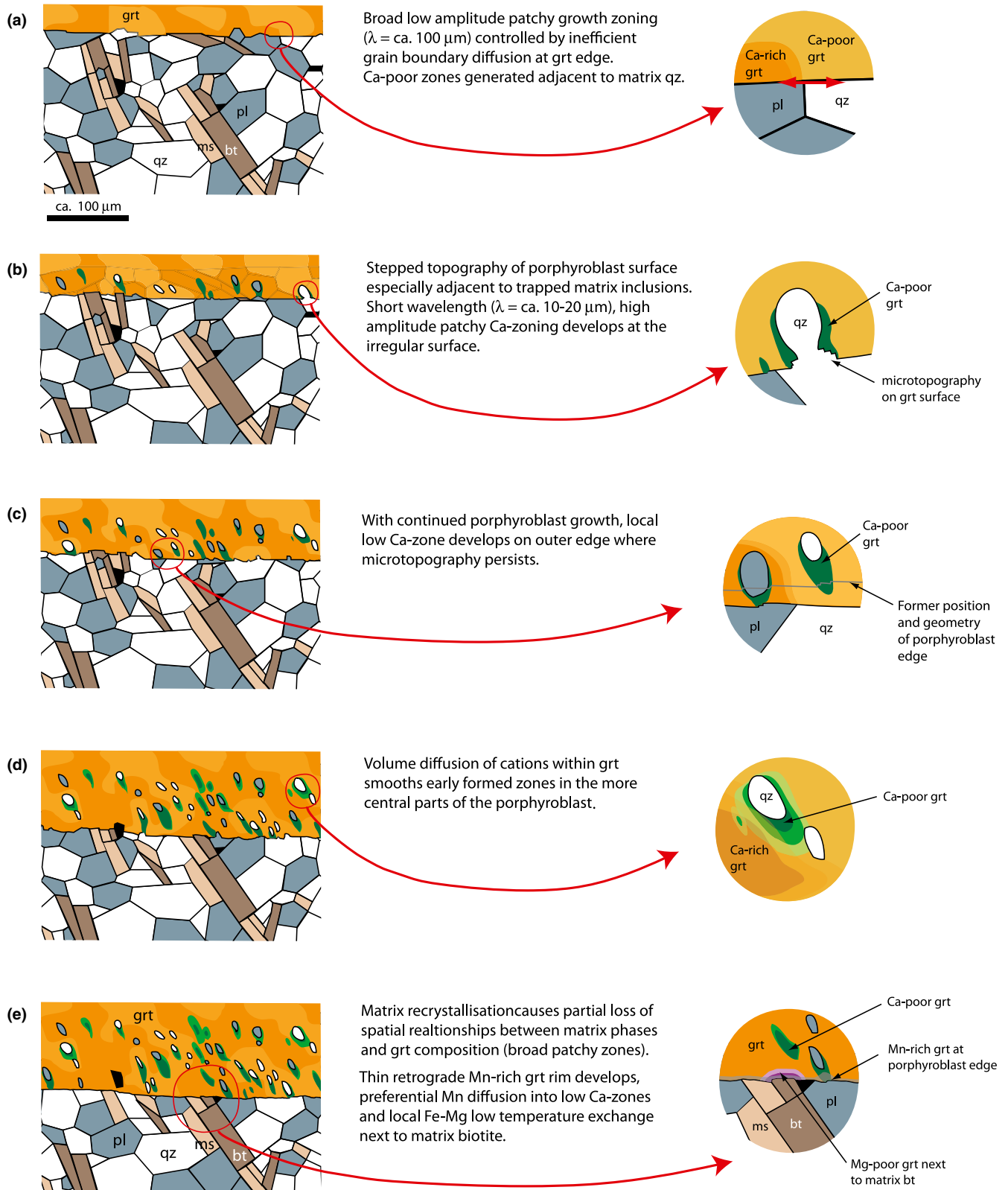


FIGURE 9 Model showing the development of compositional zoning (sequence a–e) at the leading edge of a garnet porphyroblast. Low Ca, high Fe zones develop linked to adjacent quartz in the matrix and with progressive overgrowth and trapping matrix phases, and the associated formation of microtopography on garnet surface (sequence a–d). Late diffusion of Mn into garnet edge (step e) preferentially occurs in Low Ca, high Fe zones

smaller 10–20 μm scale, spatially linked to mineral inclusions in the garnet and generally compatible with the scale of those inclusions.

The former appears to relate to the scale and nature of the matrix minerals with the implication of heterogeneity resulting from sluggish grain boundary diffusion in the matrix (Dempster, Symon, et al. 2017). The spatial link between the broad edge zoning and the adjacent phases appears to be preserved in some instances (Figure 3b) but lost in others (Figure 6a), presumably as a consequence of recrystallization within the matrix after the garnet has grown. Similar patterns of zoning have been reported in studies of trace element zoning of garnets linked to slow diffusion in the matrix (e.g. Martin, 2009; Yang & Rivers, 2001). There have been few such reports of the major cation zoning being influenced by these processes.

The second type of patchy Ca–Fe zoning is linked to the presence of some, but not all, inclusions. However, diffusive modification cannot explain either the chemistry or the geometry of these zones. Therefore the zoning must be developed during entrapment of some inclusions and as such should result from processes at the growing garnet porphyroblast edge. The local compositional zoning at the porphyroblast surface may be traced between the interior of the porphyroblast and the garnet edge. In addition very similar patchy zoning is present in the central areas of the porphyroblast. As a consequence the edge-related heterogeneity has a major influence on the internal zoning (Figure 9).

A general model involving growth zoning coupled to very localized equilibrium at the garnet edge, followed by some minor smoothing through volume diffusion, seems a most likely explanation of the zoning characteristics of these garnets (Figure 9). An exchange facilitated by late structures, such as annealed fractures, could have originally provided channels of enhanced mobility within garnet (Whitney et al., 2000). However, it would be predicted that such zoning would be related to continuous planar features. Some short channel-like geometries are preserved (Figure 7a,b), but many of the high amplitude zoning complexities are represented by isolated geochemical anomalies (Figures 5b and 6a).

The patchy zoning appears to have a more truncated nature on the studied garnet edge adjacent to the muscovite-rich cleavage domain (Figure 6). The simple concentric elements of growth zoning displayed by other maps (Figures 5 and 7) are less well developed in this area. This may reflect an element of solution transfer or restricted later growth at this interface in comparison to other structural sites around the porphyroblast (Bell & Cuff, 1989). Although slight increases in Mn content of garnet rims are typically interpreted as retrograde dissolution (de Béthune et al., 1975), these garnets show only limited textural evidence of retrograde dissolution. The slightly elevated Mn contents of these rims could equally reflect prograde solution transfer processes during active deformation.

5.3 | Origin of patchy growth zoning

Porphyroblast edge compositional zoning provides key information on geochemical transport processes within the pelitic matrix and the nature of equilibration at the edge of a growing porphyroblast. There appear to be two perhaps related controls on the zoning at the garnet edge:

1. Position of grain boundaries or the position of former grain boundaries in the adjacent matrix; and,
2. Topographic steps in crystal edges.

These processes may be linked through the processes occurring during the entrapment of inclusions and all stages of porphyroblast growth.

There is increasing recognition that slow grain boundary diffusion may control the supply of essential components to the growing edge of minerals (Carlson, Hixon, et al., 2015; Carlson, Pattison, et al., 2015; Dempster, Symon, et al., 2017; Dohmen & Chakroborty, 2003; Hirsch et al., 2003). Some of the longer wavelength variations in garnet composition appear to reflect the nature of the adjoining matrix phase, that is, the location of grain boundaries in the matrix (Figure 3c,d). Generally low grossular and high almandine contents of garnet adjacent to quartz relative to biotite and plagioclase (Figures 3d, 4b, 9) are testament to the importance of grain boundary type. As such this link between garnet chemistry and matrix mineralogy suggests that the matrix may have a control on the growth zoning of the whole porphyroblast (Figure 9). This localized 100 μm scale equilibrium between garnet and matrix phases will reflect sluggish rates of diffusive exchange along the porphyroblast-matrix interface (Dempster, Symon, et al. 2017). However in many instances matrix grain boundary locations currently lack associated geochemical anomalies within adjacent garnet. This could be caused by recrystallization of the matrix minerals after garnet growth and loss of such textural links (Figure 9e).

Grain boundaries do partly control the topography of the garnet surface, this is most obvious from the imprints associated with matrix biotite (Figure 7c). The reason why biotite restricts the growth of garnet is uncertain as it contains many of the key elements required for garnet growth. However the strong crystal form of biotite in comparison to some matrix phases may inhibit matrix recrystallization, especially in areas away from the cleavage domain. Hence matrix imprints on the garnet surface (Figure 2c) may be more readily created here. Further work would be required to know whether biotite in such structural positions is more prone to creating an edge-related geochemical anomaly in the garnet zoning.

Local variations in the garnet geochemistry are also linked to the topography of the surface. These appear to be linked to shorter wavelength variations than the scale of features linked to matrix mineralogy (Figure 3d). This suggests that ‘defects

or irregularities' in the crystal surface exert a strong control on the chemistry of the garnet (Figure 9). Microtopography of surfaces is known to influence the chemistry of growing minerals with steps being more reactive and chemically responsive than the immediately adjacent flat terrace features (Hochella, 1990, 1995). Given the link between garnet chemistry and matrix mineralogy and the zoning that is preserved around some inclusions, it is suggested that steps and associated chemical zones on the garnet surface may initially develop around partially enclosed inclusions during garnet growth (Figure 9). However, many inclusions lack associated zoning and as such it is likely that the patchy zones do not represent a chemical interaction between the inclusion phase and the garnet but instead represent a structural control that is not associated with all inclusions. These will then persist as crystallographic discontinuities after an inclusion has been overgrown so that channels of low Ca and high Fe run from the edge of the inclusion to the stepped edge of the porphyroblast (Figures 7b and 9). With continued growth crystal growth steps may be eliminated and consequently such channel-like features may evolve into isolated features of the internal zoning (Figure 9).

The importance of mineral inclusions in influencing the internal zoning of porphyroblasts has only rarely been emphasized (Hames & Menard, 1993; O'Brien, 1999; Vernon, 2004). However, published garnet porphyroblast zoning maps, reveal a seemingly common association between abundant inclusions and a variety of irregularities in simple concentric zoning patterns (e.g. Gasco, Gattiglio, & Borghi, 2011; Hirsch et al., 2003; Wilber & Ague, 2006; Yang & Rivers, 2001). That not all inclusions are associated with a high Fe, low Ca halo suggests that the nature of the individual inclusion–garnet interface may be an important control on garnet composition. Localized distribution of fluids on the interface between the matrix and the growing porphyroblast may potentially also partly influence the garnet geochemistry and has been suggested to control the contrasting shape of mineral inclusions relative to their equivalent matrix phase (Vernon, 1999). As such this could also provide a link between inclusion location and garnet composition.

Such geochemical 'anomalies' may extend well beyond the immediate location of the step in the garnet surface (Figures 6 and 7). This could be due to a number of factors: in part an analytical artefact, a consequence of the width of the area activated by the electron beam; in part a consequence of volume diffusion smoothing out the geochemical discontinuities; and, in part perhaps the evolving geometry of surface microtopography during porphyroblast growth (Figure 9). The effects of microtopography are most evident in the zoning of Ca and Fe that result. However, small increases in the Mn content along the low Ca and high Fe channels are also present. These Mn contents are directly comparable to the slightly elevated Mn contents at the garnet rim (Figure 9).

This may represent evidence of enhanced diffusion of Mn linked to the different chemistry of the garnet in the channel area (Ganguly, 2010; Ganguly, Cheng, & Chakraborty, 1998). The broader Mn anomalies parallel to the garnet surface associated with these channels (Figure 8e) may also be a result of enhanced Mn-diffusion relative to Ca and Fe (Carlson, 2002, 2006). The lack of any Mn zoning associated the patchy Ca–Fe zones in the more central areas of the porphyroblast may also be an indication of more effective volume diffusion for Mn in the longer lived core areas of porphyroblasts.

5.4 | Implications of local compositional zoning at the garnet edge

Crucially garnet porphyroblasts do not have a consistent composition in equilibrium with the general matrix but edge-parallel zoning reflects the nature of the grain boundary itself. Kinetically limited transport of trace elements within the matrix has been previously reported to influence garnet zoning (e.g. Martin, 2009; Yang & Rivers, 2001). This creates short length scales over which equilibrium occurs (Kohn, 2014). These types of processes also influence major element zoning in garnet and this has obvious implications for the appropriate choice of equilibrium mineral compositions in thermodynamic approaches to the determination of metamorphic conditions. This prograde growth zoning reflects a combination of slow grain boundary diffusion and variation in partition coefficients linked to both the adjacent mineralogy and the topography of the garnet surface. The restricted cation mobility along the porphyroblast edge suggests that fluids were not pervasively present during garnet growth. Although the supply of Al may control garnet growth (Carlson, 1999), the mobility of the divalent cations is crucial in determining garnet chemistry. Disequilibrium processes are increasingly recognized in metamorphic rocks (Carlson, 2002; Carlson, Hixon, et al., 2015; Carlson, Pattison, et al., 2015; Dempster, La Piazza, et al., 2017, 2019; Waters & Lovegrove, 2002) and challenge aspects of thermodynamic equilibrium explanations for petrologic processes. In these rocks, the zoning of garnet at the porphyroblast edge can be linked to the internal growth zoning of the garnet and so has strongly influenced the porphyroblast interior. The 10–100 μm scale of these chemical variations has obvious implications for any use of major element chemistry of garnet to determine metamorphic conditions or P – T paths based on equilibrium thermodynamic approaches (e.g. Holland & Powell, 1998), particularly those geobarometry approaches methods based on the Ca content of garnet (e.g. Holdaway, 2001). Such grain edge-induced irregularities will be progressively smoothed and may ultimately be lost through the influence of volume diffusion (Kohn, 2014; Mueller et al., 2010). It is notable that Ca variation that is

reported in many investigations of garnet zoning is often rather noisy (Carlson, Hixon, et al., 2015; Carlson, Pattison, et al., 2015; Martin, 2009; Moore, Carlson, & Hesse, 2013). In some instances this could reflect the presence of small-scale oscillatory type zoning (Schumacher et al., 1999), however, the scale of local controls at the growing porphyroblast edge may be dominant. Different cations within garnet record different behaviour both during prograde growth and subsequent diffusive re-equilibration (Carlson, 2002). Thus Mn and Mg appear to be most prone to diffusive smoothing and late modification, while Ca and/or Fe are subject to most kinetic restrictions and struggle to maintain a uniform equilibrium composition during porphyroblast growth in these amphibolite facies conditions. The resulting patchy zoning of Ca and Fe may then be a factor controlling the later modification of garnet via coupled dissolution–reprecipitation processes (Dempster et al., 2019).

The geochemical heterogeneity parallel to the growth surfaces occurs on a 10–100 µm scale rarely reported given the propensity for the analysis of zoning in coloured images on the scale of whole garnet porphyroblasts (e.g. Caddick & Kohn, 2013). However, the amplitude of the variation observed does give cause to question, which, if any of the edge compositions of garnet represent a composition in equilibrium with the matrix.

6 | CONCLUSIONS

- Garnet compositions at the porphyroblast edge are not constant reflecting extremely localized equilibrium during prograde growth. Patchy zoning of Ca and Fe occurs and is associated with the entrapment of mineral inclusions in the garnet.
- Magnitudes of local chemical variation at the garnet edge are equivalent to those of chemical zoning developed from core to rim during prograde growth.
- Prograde zoning at the garnet edge is caused by a combination of slow diffusion along grain boundaries and the microtopography of the garnet surface. The topography of the garnet edge in part may develop in response to the entrapment of mineral inclusions within the porphyroblast.
- Surface compositional variation feeds through to strongly influence the major element internal growth zoning characteristics of garnet.
- Equilibrium thermodynamic approaches that estimate conditions of metamorphism based on garnet compositions may be fraught with difficulty because of a lack of well-constrained equilibrium compositions.

ACKNOWLEDGEMENTS

Robert McDonald and Mark Wildman are thanked for technical assistance.

ORCID

Tim J. Dempster  <https://orcid.org/0000-0002-2334-7977>
 Roderick W. Brown  <https://orcid.org/0000-0002-0763-3711>

REFERENCES

- Ague, J. J., & Carlson, W. D. (2013). Metamorphism as garnet sees it: The kinetics of nucleation and growth, equilibration, and diffusional relaxation. *Elements*, 9, 439–445.
- Bell, T. H., & Cuff, C. (1989). Dissolution, solution transfer, diffusion versus fluid flow and volume loss during deformation/metamorphism. *Journal of Metamorphic Geology*, 7, 425–447.
- Borinski, S. A., Hoppe, U., Chakraborty, S., Ganguly, J., & Bhowmik, S. K. (2012). Multicomponent diffusion in garnets I: General theoretical considerations and experimental data for Fe-Mg systems. *Contributions to Mineralogy and Petrology*, 164, 571–586.
- Caddick, M. J., & Kohn, M. J. (2013). Garnet: Witness to the evolution of destructive plate boundaries. *Elements*, 9, 427–432.
- Caddick, M. J., Konopásek, J., & Thompson, A. B. (2010). Preservation of garnet growth zoning and the duration of prograde metamorphism. *Journal of Petrology*, 51, 2327–2347.
- Carlson, W. D. (1999). The case against Ostwald ripening of porphyroblasts. *Canadian Mineralogist*, 37, 403–413.
- Carlson, W. D. (2002). Scales of disequilibrium and rates of equilibration during metamorphism. *American Mineralogist*, 87, 185–204.
- Carlson, W. D. (2006). Rates of Fe, Mg, Mn, and Ca diffusion in garnet. *American Mineralogist*, 91, 1–11.
- Carlson, W. D., Hixon, J. D., Garber, J. M., & Bodnar, R. J. (2015). Controls on metamorphic equilibration: The importance of intergranular solubilities mediated by fluid composition. *Journal of Metamorphic Geology*, 33, 123–146.
- Carlson, W. D., Pattison, D. R. M., & Caddick, M. J. (2015). Beyond the equilibrium paradigm: How consideration of kinetics enhances metamorphic interpretation. *American Mineralogist*, 100, 1659–1667.
- Chernoff, C. B., & Carlson, W. D. (1997). Disequilibrium for Ca during growth of pelitic garnet. *Journal of Metamorphic Geology*, 15, 421–438.
- de Béthune, P., Laduron, D., & Bocquet, J. (1975). Diffusion processes in resorbed garnets. *Contributions to Mineralogy and Petrology*, 50, 197–204.
- Dempster, T. J. (1985). Garnet zoning and metamorphism of the Barrovian Type Area, Scotland. *Contributions to Mineralogy and Petrology*, 89, 30–38.
- Dempster, T. J. (1992). Zoning and recrystallization of phengitic micas: Implications for metamorphic equilibration. *Contributions to Mineralogy and Petrology*, 109, 526–537.
- Dempster, T. J., & Harte, B. (1986). Polymetamorphism in the Dalradian of the central Scottish Highlands. *Geological Magazine*, 123, 95–104.
- Dempster, T. J., Gilmour, M. I., & Chung, P. (2019). The partial equilibration of garnet porphyroblasts in pelitic schists and its control on prograde metamorphism, Glen Roy, Scotland. *Journal of Metamorphic Geology*, 37, 383–399.
- Dempster, T. J., La Piazza, J., Taylor, A., Beaudoin, N., & Chung, P. (2017). Chemical and textural equilibration of garnet during amphibolite facies metamorphism: The influence of coupled dissolution–reprecipitation. *Journal of Metamorphic Geology*, 36, 1–20.
- Dempster, T. J., Rogers, G., Tanner, P. W. G., Bluck, B. J., Muir, R. J., Redwood, S. D., Ireland, T. R., & Paterson, B. A. (2002). Timing

- of deposition, orogenesis and glaciation within the Dalradian rocks of Scotland: Constraints from U-Pb ages. *Journal of the Geological Society, London*, 159, 83–94.
- Dempster, T. J., Symon, S., & Chung, P. (2017). Intergranular diffusion rates from the analysis of garnet surfaces: Implications for metamorphic equilibration. *Journal of Metamorphic Geology*, 35, 585–600.
- Dohmen, R., & Chakraborty, S. (2003). Mechanism and kinetics of element and isotopic exchange mediated by a fluid phase. *American Mineralogist*, 88, 1251–1270.
- Ganguly, J. (2010). Cation diffusion kinetics in aluminosilicate garnets and geological applications. *Reviews in Mineralogy and Geochemistry*, 72, 559–601.
- Ganguly, J., Cheng, W., & Chakraborty, S. (1998). Cation diffusion in aluminosilicate garnets: Experimental determination in pyrope-almandine diffusion couples. *Contributions to Mineralogy and Petrology*, 131, 171–180.
- Gasco, I., Gattiglio, M., & Borghi, A. (2011). Lithostratigraphic setting and P-T metamorphic evolution for the Dora Maira Massif along the Peidmont Zone boundary (middle Susa Valley, NW Alps). *International Journal of Earth Sciences*, 100, 1065–1085.
- Groppo, C., Rolfo, F., & Lombardo, B. (2009). P-T evolution across the Main Central Thrust Zone (Eastern Nepal): Hidden discontinuities revealed by petrology. *Journal of Petrology*, 50, 1149–1180.
- Hames, W. E., & Menard, T. (1993). Fluid-assisted modification of garnet composition along rims, cracks, and mineral inclusion boundaries in samples of amphibolite facies schists. *American Mineralogist*, 78, 338–344.
- Harris, A. L., Haselock, P. J., Kennedy, M. J., & Mendum, J. R. (1994). The Dalradian Supergroup in Scotland, Shetland and Ireland. In A. L. Harris & W. Gibbons (Eds.) *A revised correlation of Precambrian rocks in the British Isles*. Geological Society, London, *Special Report*, 22, 33–53.
- Harte, B., & Henley, K. J. (1966). Occurrence of compositional zoned almanditic garnets in regionally metamorphosed rocks. *Nature*, 210, 689–692.
- Hirsch, D. M., Prior, D. J., & Carlson, W. D. (2003). An overgrowth model to explain multiple, dispersed high-Mn regions in the cores of garnet porphyroblasts. *American Mineralogist*, 88, 131–141.
- Hochella, M. F. Jr (1995). Mineral surfaces: Their characterization and their chemical, physical and reactive nature. In: D. J. Vaughan & R. A. D. Patrick. *Mineral surfaces* (pp. 17–60). London, UK: Chapman & Hall.
- Hochella, M. F. Jr (1990). Atomic structure, microtopography, composition, and reactivity of mineral surfaces. *Reviews in Mineralogy*, 23, 87–132.
- Holdaway, M. J. (2001). Recalibration of the GASP geobarometer in light of recent garnet and plagioclase activity models and versions of the garnet-biotite geothermometer. *American Mineralogist*, 86, 1117–1129.
- Holland, T. J. B., & Powell, R. (1988). An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16, 309–343.
- Hollister, L. S. (1966). Garnet zoning: An interpretation based on the Rayleigh fractionation model. *Science*, 154, 1647–1651.
- Kohn, M. J. (2014). Geochemical zoning in metamorphic minerals. *Treatise on Geochemistry*, 4, 249–280.
- Lanzirotti, A. (1995). Yttrium zoning in metamorphic garnets. *Geochimica et Cosmochimica Acta*, 59, 4105–4110.
- Martin, A. J. (2009). Sub-millimeter heterogeneity of Yttrium and Chromium during growth of semi-pelitic garnet. *Journal of Petrology*, 50, 1713–1727.
- Martin, L. A. J., Ballèvre, M., Boulvais, P., Halfpenny, A., Vanderhaeghe, O., Duchêne, S., & Delouie, E. (2011). Garnet re-equilibration by coupled dissolution-reprecipitation: Evidence from textural, major element and oxygen isotope zoning of ‘cloudy’ garnet. *Journal of Metamorphic Geology*, 29, 213–231.
- Moore, S. J., Carlson, W. D., & Hesse, M. A. (2013). Origin of yttrium and rare earth element distributions in metamorphic garnet. *Journal of Metamorphic Geology*, 31, 663–689.
- Mueller, T., Massonne, H.-J., & Willner, A. P. (2015). Timescales of exhumation and cooling inferred by kinetic modeling: An example using lamellar garnet pyroxenite from Variscan Granulitgeirge, Germany. *American Mineralogist*, 100, 747–759.
- Mueller, T., Watson, E. B., & Harrison, T. M. (2010). Application of diffusion data to high temperature earth systems. *Reviews in Mineralogy and Geochemistry*, 72, 997–1038.
- O’Brien, P. J. (1999). Asymmetric zoning profiles in garnet from HP-HT granulite and implications for volume and grain-boundary diffusion. *Mineralogical Magazine*, 63, 227–238.
- Oliver, G. J. H., Chen, F., Buchwaldt, R., & Hegner, E. (2000). Fast tectonometamorphism and exhumation in the type area of Barrovian and Buchan zones. *Geology*, 28, 459–462.
- Pattison, D. R. M., & Bégin, N. J. (1994). Zoning patterns in orthopyroxene and garnet in granulites: Implications for geothermometry. *Journal of Metamorphic Geology*, 12, 387–410.
- Phillips, E. R., Key, R. M., Clark, G. C., May, F., Glover, B. W., & Chacksfield, B. C. (1994). Tectonothermal evolution of the Neoproterozoic Grampian and Appin groups, southwestern Monadhliath Mountains, Scotland. *Journal of the Geological Society London*, 151, 971–986.
- Pyle, J. M., & Spear, F. S. (2003). Yttrium zoning in garnet: Coupling of major and accessory phases during metamorphic reactions. *American Mineralogist*, 88, 708.
- Reed, S. J. B. (2005). *Electron microprobe analysis and scanning electron microscopy in geology*. Cambridge, UK: Cambridge University Press. 188 pp.
- Richardson, S. W., & Powell, R. (1976). Thermal causes of the Dalradian metamorphism in the central Highlands of Scotland. *Scottish Journal of Geology*, 12, 237–268.
- Robyr, M., Darbellay, B., & Baumgartner, L. P. (2014). Matrix-dependent garnet growth in polymetamorphic rocks of the Sesia zone, Italian Alps. *Journal of Metamorphic Geology*, 32, 3–24.
- Schumacher, R., Rötzler, K., & Maresch, W. V. (1999). Subtle oscillatory zoning in garnet from regional metamorphic phyllites and mica schists, Western Erzgebirge, Germany. *The Canadian Mineralogist*, 37, 381–402.
- Selverstone, J., Spear, F. S., Franz, G., & Morteani, G. (1984). High pressure metamorphism in the SW Tauern Window, Austria: P-T paths from hornblende-kyanite-staurolite schists. *Journal of Petrology*, 25, 501–531.
- Spear, F. S. (1993). *Metamorphic phase equilibria and pressure – temperature – time paths*. Washington, DC: Mineralogical Society of America. 799 pp.
- Spear, F. S., Kohn, M. J., Florence, F. P., & Menard, T. (1990). A model for garnet and plagioclase growth in pelitic schists: Implications for thermobarometry and P-T path determinations. *Journal of Metamorphic Geology*, 8, 683–696.

- Stowell, H., Zuluaga, C., Boyle, A., & Bulman, G. (2011). Garnet sector and oscillatory zoning linked with changes in crystal morphology during rapid growth, North Cascades, Washington. *American Mineralogist*, *96*, 1354–1362.
- Thompson, A. B., Tracy, R. J., Lyttle, P. T., & Thompson, J. B. Jr (1977). Prograde reaction histories deduced from compositional zonation and mineral inclusions in garnet from the Gassetts Schist, Vermont. *American Journal of Science*, *277*, 1152–1167.
- Tinkham, D. K., & Ghent, E. H. (2005). Estimating P-T conditions of garnet growth with isochemical phase-diagram sections and the problem of effective bulk-composition. *The Canadian Mineralogist*, *43*, 35–50.
- Tracy, R. J., Robinson, P., & Thompson, A. B. (1976). Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts. *American Mineralogist*, *61*, 762–775.
- Tuccillo, M. E., Essene, E. J., & van der Pluijm, B. A. (1990). Growth and retrograde zoning in garnets from high-grade metapelites: Implications for pressure-temperature paths. *Geology*, *18*, 839–842.
- Vance, D., & Mahar, E. (1998). Pressure-temperature paths from pseudosections and zoned garnets: Potential, limitations and examples from the Zaskar Himalaya, NW India. *Contributions to Mineralogy and Petrology*, *132*, 225–245.
- Vernon, R. H. (1999). Quartz and feldspar microstructures in metamorphic rocks. *Canadian Mineralogist*, *37*, 513–524.
- Vernon, R. H. (2004). *A practical guide to rock microstructure*. Cambridge, UK: Cambridge University Press. 594 pp.
- Vielzeuf, D., Baronnet, A., Perchuk, A. L., Laporte, D., & Baker, M. B. (2007). Calcium diffusivity in aluminosilicate garnets: An experimental and ATEM study. *Contributions to Mineralogy and Petrology*, *154*, 153–170.
- Viete, D. R., Hermann, J., Lister, G. S., & Stenhouse, I. R. (2011). The nature and origin of the Barrovian metamorphism, Scotland: Diffusion length scales in garnet and inferred thermal time scales. *Journal of the Geological Society, London*, *168*, 115–132.
- Waters, D. J., & Lovegrove, D. P. (2002). Assessing the extent of disequilibrium and overstepping of prograde metamorphic reactions in metapelites from the Bushveld Complex aureole, South Africa. *Journal of Metamorphic Geology*, *20*, 135–149.
- Wessel, P., & Luis, J. F. (2017). The GMT/MATLAB Toolbox. *Geochemistry, Geophysics, Geosystems*, *18*, 811–823.
- Whitney, D. L. (1991). Calcium depletion haloes and Fe-Mn-Mg zoning around faceted plagioclase inclusions in garnet from a high-grade pelitic gneiss. *American Mineralogist*, *76*, 493–500.
- Whitney, D. L., Cooke, M. L., & Du Frane, A. (2000). Modeling of radial microcracks at corners of inclusions in garnet using fracture mechanics. *Journal of Geophysical Research*, *105*, 2843–2853.
- Whitney, D. L., & Evans, B. W. (2010). Abbreviations for names of rock-forming minerals. *American Mineralogist*, *95*, 185–187.
- Whitney, D. L., Mechum, T. A., Dilek, Y., & Kuehner, S. M. (1996). Modification of garnet by fluid infiltration during regional metamorphism in garnet through sillimanite-zone rocks, Dutchess County, New York. *American Mineralogist*, *81*, 696–705.
- Wilbur, D. E., & Ague, J. J. (2006). Chemical disequilibrium during garnet growth: Monte Carlo simulations of natural crystal morphologies. *Geology*, *34*, 689–692.
- Yang, P., & Rivers, T. (2001). Chromium and manganese zoning in pelitic garnet and kyanite: Spiral, overprint, and oscillatory (?) zoning patterns and the role of growth rate. *Journal of Metamorphic Geology*, *19*, 455–474.
- Yardley, B. W. D. (1977). An empirical study of diffusion in garnet. *American Mineralogist*, *62*, 793–800.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

Appendix S1. Table S1. EDS analyses of garnet traverses in Figure 1 (grt1) and those used to construct maps for Figures 5–8 (grt2, grt3, grt4 and grt5 respectively).

How to cite this article: Dempster TJ, Coleman S, Kennedy R, Chung P, Brown RW. Growth zoning of garnet porphyroblasts: Grain boundary and microtopographic controls. *J Metamorph Geol*. 2020;38:1011–1027. <https://doi.org/10.1111/jmg.12558>