SECTION B

A METHOD FOR CALCULATING EFFECTIVE BULK COMPOSITION MODIFICATION DUE TO CRYSTAL FRACTIONATION IN GARNET-BEARING SCHIST: IMPLICATIONS FOR ISOPLETH THERMOBAROMETRY

ABSTRACT

Quantitative P-T path determination in metamorphic rocks is commonly based on the variation in composition of growth-zoned garnet. However, some component of growth zoning in garnet is necessarily the result of an effective bulk composition change within the rock that has been generated by crystal fractionation of components into the core of garnet. Therefore, any quantitative calculation of the *P-T* regime of garnet growth should be completed using an accurate assessment of the composition of the chemical system from which garnet is growing. Consequently, a method for calculating the extent of crystal fractionation that provides a means of estimating the composition of the unfractionated rock at any stage during garnet growth is developed. The method presented here applies a Rayleigh fractionation model based on measured Mn content of garnet to generate composition versus modal proportion curves for garnet, and uses those curves to estimate the vectors of crystal fractionation. The technique is tested by calculating the precision of the equilibrium between garnet's three compositional variables within the chemical system determined to be appropriate for each of a series of microprobe analyses from garnet. Application of the fractionation calculations in conjunction with the *P-T* estimates based on intersecting compositional isopleths provides a means of calculating *P-T* conditions of garnet growth that is based on individual point-analyses on a garnet grain. Such spatially precise and easily obtainable *P-T* data allow for detailed parallel studies of the microstructural, the *P-T*, and the chemical evolution of metamorphosed pelites. This method provides a means of studying the dynamics of orogenic systems at a resolution that was previously unattainable.

1. INTRODUCTION

For many years metamorphic petrologists have used the composition of garnet in metamorphic rock as an indicator of the pressure and temperature through which the rock passed, and have used the nature of any compositional zoning within garnet to infer corresponding changes in the *P*-*T* regime imposed upon the rock (Florence et al., 1993). Because the composition of garnet is controlled by pressure (*P*), temperature (*T*) and the composition of the chemical system in which it is growing, changes to the rock composition during growth will influence isopleth thermobarometry if they are not recognised and accounted for. Because equilibrium is generally thought to be attained at the hand-sample scale provided that no clear evidence to the contrary is found (Chernoff & Carlson, 1997; Hirsch *et al.*, 2003), hand-sample scale specimens are crushed and analysed by XRF to provide an approximation of the sample's bulk composition. The term "effective bulk composition" is used to distinguish between the measured bulk composition of a sample, and the composition of the chemical system considered available for mineral reaction in that sample (Stüwe, 1997). There are two principle mechanisms by which the effective bulk composition of a rock can be altered during metamorphism:

1. The addition or removal of components from the rock by fluid passing through the rock or by deformation (i.e. open system behaviour), or;
2. The sequestration of components into the cores of growing porphyroblasts, where they are effectively isolated from the rest of the rock (i.e. crystal fractionation).

Whilst open system behaviour requires an external driving force to operate, crystal fractionation requires only the growth of species of porphyroblasts with low internal diffusivity that exhibit a significant degree of sluggishness in re-equilibrating both internally and with the matrix. Garnet is one such mineral species.

2. CRYSTAL FRACTIONATION VIA GARNET GROWTH

Crystal fractionation has been recognised as an important contributor to compositional zoning in garnet since Hollister (1966) first proposed a Rayleigh fractionation mechanism to explain Mn zoning in garnet. Many subsequent workers have recognised the problems that crystal fractionation presents to extracting *P-T* information from garnet composition (Atherton, 1968; Spear, 1988b; Spear et al., 1990; Frost & Tracy, 1991; Florence et al., 1993; Vance & Mahar, 1998; Marmo et al., 2002). However, until the advent of software capable of calculating pseudosections (Powell & Holland, 1988; Spear & Menard, 1989; Connelly & Petrini, 2002) it has been impractical to quantitatively investigate the effects of crystal fractionation on phase stability.

If any mineral grain exhibits a degree of compositional zoning then a chemical potential gradient will exist across that grain. By the Zeroth Law of thermodynamics, this means that not only is the grain internally in chemical disequilibrium, but also a large portion, if not all of the grain will be in disequilibrium with the surrounding matrix. For this to be the case, the parts of the grain that are in disequilibrium with the rest of the chemical system must be effectively isolated from the reacting system. Garnet subjected to temperatures less than of 700°C typically displays compositional zonation. Therefore, the majority of zoned garnet must be effectively removed from the effective bulk composition of the rock for the most of its history. This is quite plausible as all of the components within garnet have very low intragranular diffusivity below ~700°C (Tracy, 1982; Thompson & England, 1984; Spear, 1988b; Chakraborty &

Ganguly, 1992). With the core of a zoned porphyroblast chemically isolated from the rim, it is reasonable to argue that some component of the zoning profile (except in the rare case where the porphyroblast was growing in a ≤ 2-variance equilibrium, whereby the porphyroblast's composition is independent of the rock's bulk composition) is the result of changing effective bulk composition by crystal fractionation processes. Therefore, any attempt to calculate the P-T regime responsible for creating compositional zoning in garnet requires that changes in the rock's effective bulk composition caused by crystal fractionation be estimated and accounted for.

Previous studies that have sought to incorporate a consideration of the effects of garnet fractionation into P-T calculations have proceeded in two different ways. The approach of Spear *et al*. (1990) allows forward modelling of garnet composition profiles assuming crystal fractionation, but does not allow for empirically derived estimates of fractionation in real samples. Marmo *et al*. (2002) use quantitative compositional mapping of an entire thin-section to make estimates of fractionation volumes by geometric extrapolation from a two dimensional section to a three dimensional volume. The method presented here applies a Rayleigh fractionation model based on measured Mn content of garnet to generate composition-volume curves for garnet, and uses those curves to estimate the vectors of crystal fractionation. This method can be applied to a suite of garnet composition data from a single sample to provide an ongoing assessment of the composition of the chemical system in which the garnet was growing, and negates the potential errors that can be introduced by extrapolating from 2-dimensional maps into volumes.

3. METHODS

3.1. Using pseudosections to calculate mineral stability and composition in metapelites.

The theory and practice of using THERMOCALC to plot pseudosections was developed in Powell et al. (1998). Powell *et al.*'s (1998) methods are expanded here by using the mixing models of Vance and Holland (1993) to encompass the MnNCKFMASH system. P-T pseudosections are phase diagrams that map the stability fields of different mineral assemblages through P-T space for a specific bulk rock composition and, in addition, provide the composition and relative molar abundance of the participating minerals in each assemblage field. They are typically calculated for individual rock samples based on an XRF analysis of each sample. Values for the composition and molar abundance of minerals within each assemblage field are plotted as contours on the pseudosection, referred to as composition isopleths and modal isopleths respectively. Additionally, THERMOCALC calculates the 1σ-error for each of these isopleths based on errors propagated from the thermodynamic data. Intersections between isopleths plot as points in P-T space, and thus the intersections between different composition isopleths corresponding to measured mineral compositions can be used for thermobarometry. For example, the compositional variation in garnet is controlled by solid solution between four end members, and thus can be described in terms of three independent compositional variables. The variables chosen in this study are the molar concentration of iron, calcium and manganese. Significantly, each of the compositional isopleths generally has a slope in P-T space that is distinctly different from the other two and the factors controlling the absolute position of each isopleth in P-T space are independent from each other (Fig. 1). Isopleths for each of the compositional variables based on electron micro-probe analyses from garnet can be plotted in *P*-*T* space using THERMOCALC.

It is important that the composition upon which the pseudosection is based accurately represents the composition of the chemical system that was operating during metamorphism. In this study the accuracy of the pseudosection was assessed by plotting garnet compositional isopleths for the EPMA analysis with highest Mn. This analysis is considered to represent the earliest grown garnet (Carlson, 1989) and thus will be less likely to be influenced by effective bulk composition change due to crystal fractionation. If the three compositional isopleths all intersect within the overlap of their 1σ-error bars, then the modelling of the equilibrium between garnet and the bulk rock can be considered adequate within the constraints of the error on the thermodynamic data. There are three reasons why the isopleths might not intersect within error:

a) The analysis of the garnet used for the isopleths was not from the true centre of the garnet, but rather was from the middle of an off-centre slice through the garnet.
b) The bulk composition measured by XRF is different to that which was operating when the garnet used to plot the isopleths grew. This could be the result of geologically induced composition change after garnet growth or a poor sampling strategy in preparing the XRF analysis.
c) The primitive garnet did not grow in equilibrium with the bulk rock composition due to existing kinetic factors, such as fractionation of components into existing minerals.

In this study 62 EPMA analyses were taken from four garnets in Sample TE21 so that the full range of garnet composition was thoroughly documented, and so the chances of obtaining an analysis of the primitive core composition was maximised. In order to obtain a representative sample for XRF, approximately 1.5kg of sample was crushed for analysis. The choice of a relatively large sample was predicated by the fact that the multiple garnets analysed in thin section for each sample could have been sourced from anywhere within an approximately 1.5kg slab. Care was taken to ensure that where coarse compositional heterogeneities within the sample (e.g. relict sedimentary layering), individual layers were separated for the XRF sample and garnets were identified according to which layer they occurred in and correlated with the appropriate bulk composition measurment.

Practical approaches to rock thermobarometry using pseudosections and isopleths have been pursued by numerous workers (Vance & Holland, 1993; Ayres & Vance, 1997; Vance & Mahar, 1998; Marmo *et al.*, 2002). Thermobarometry based on intersecting isopleths is founded on the premise that garnet is growing in equilibrium with a particular bulk rock composition. If garnet exhibits growth zoning, and was growing in a >2-variance equilibrium, then changes in the bulk composition of the rock resulting from crystal fractionation *must* have contributed to its compositional zoning profile (Spear, 1988b). Therefore, at any time during the growth of garnet, the effective bulk composition of the rock will be evolving, and the outermost portion of each garnet will be trying to re-equilibrate with it. Garnet cores that have grown in equilibrium with the whole-rock bulk composition display isopleth intersections that are tightly clustered around the *P-T* point at which the core stabilised in composition (e.g. Vance & Holland, 1993; Vance & Mahar, 1998). Should the core of a garnet porphyroblast not show a tightly clustered set of isopleth intersections, it could not have grown in equilibrium with the measured bulk composition of the rock.

If the core of a growth-zoned garnet did grow in equilibrium with the whole-rock bulk composition, then garnet outboard of the core certainly did not. This can be demonstrated by plotting isopleths from point analyses on a core-rim traverse across a garnet (Fig. 2). The isopleth intersection sets from each analysis become increasingly poorly constrained from core to rim. Isopleth thermobarometry based on point analyses outboard of the core must take account of the evolving effective bulk composition. If the effective bulk composition can be predicted at any stage of garnet growth, then single point analyses from any point on a garnet can yield *P-T* values that reflect the conditions at which the analysed volume stabilised its composition.

3.2. A method for determining the quantity of Fe, Mg, Mn, Ca and Al fractionated into garnet

The objective of this method is to predict the proportion of components that have been effectively removed from the rock by crystal fractionation due to garnet growth. Garnet is treated as two concentrically arranged zones: a shell encompassing the periphery that interacts chemically with the rock matrix, and a core that is isolated from the rest of the rock. The shell is homogeneous, in equilibrium with the matrix, and free to change its composition with changing *P-T* conditions. The core is chemically isolated from the rest of the rock and is compositionally heterogeneous. The composition of any volume of garnet becomes fixed as soon as it becomes part of the core. Fractionation of components into garnet cannot begin until the radius of the garnet exceeds the thickness of the shell (Fig. 3). Consequently, the most primitive core composition (i.e. the most Mn rich) in the sample ideally represents the composition of garnet at the point at which the radius of the whole garnet first exceeded the thickness of the reactive shell, rather than being the composition at nucleation. This method deals neither with porphyroblast size distributions or estimations of the thickness of the reactive shell; it merely seeks to estimate the molecular proportion of components that make up garnet and the way in which they are grossly distributed between fractionated and unfractionated portions of garnet.

The method proposed for estimating the degree of fractionation of garnet components from the reactive system is founded on two central premises:

1. That the variation in Mn content within garnet is controlled by crystal fractionation, and is thus a function of the modal proportion of garnet within the sample (Hollister, 1966; Atherton, 1968); and,
2. That a simple, curvilinear relationship exists between the Mn content and the Fe, Mg and Ca contents of garnet within the sample.

The second premise must be tested by taking quantitative analyses from the core to the rim of several garnets from the sample. In this manner the complete range of garnet composition within the sample can be described, and the correlation between the relative concentrations of its constituent components can be assessed.

The method is based on two sets of calculations that relate to each of these premises:

1. A quantitative relationship between Mn content of garnet and the modal proportion of garnet present is defined, based on a Rayleigh fractionation mechanism; and
2. The relationships between the calculated modal proportion of garnet and the measured concentrations of Fe, Mg, Ca, Mn and Al in garnet is defined, and used to calculate the proportion of those elements contained within garnet relative to the bulk composition.

3.3. Relating the Mn content of garnet to the modal proportion of garnet

The effects of crystal fraction on effective bulk rock and porphyroblast compositions can be described by the Rayleigh fractionation equation (Atherton, 1968):

$$C_g = C_o K_d (1 - F)^{K_d - 1} \qquad 1.$$

where C_g is the concentration of the element in the garnet rim, C_o is the concentration of the element in the bulk rock, K_d is the bulk distribution coefficient for the element between garnet and matrix, and F is the molar proportion of garnet in the rock. In the context of this model, C_g is the mole fraction of the element in garnet calculated from microprobe analyses, K_d is calculated from the most primitive garnet core compositions, and C_o is the mole fraction of the element in the bulk rock, and is calculated from the bulk rock XRF analysis.

As C_o and K_d are constant for each sample, equation 1 can be rewritten so that F can be solved for given values of C_g:

$$F = 1 - \left(\frac{C_g}{C_o K_d} \right)^{\frac{1}{K_d - 1}} \qquad 1a.$$

The molar fraction of MnO in garnet, C_g is given by:

$$\frac{3}{8} * \text{ mol fraction of the spessartine content}$$

K_d is the bulk distribution coefficient of Mn between garnet and the rest of the rock expressed as the ratio:

$$C_{MnO,\ garnet} : C_{MnO,\ matrix}$$

where $C_{MnO,\ matrix}$ is the mole fraction of MnO in the matrix. The molar fraction of MnO in the matrix, C_m is given by:

$$C_m = \frac{C_0 - C_g}{1 - F}$$

Because the modal proportion of garnet is sub-parallel to its Mn content on a *P*-*T* pseudosection (Fig. 1), the value of F at the time the garnet core formed can be obtained from the THERMOCALC output for the Mn isopleth for the most Mn-rich analysis. The resulting K_d values should be between 30 and 90 (Atherton, 1968). The resulting value for K_d can then be put into equation 1a, allowing the calculation of the modal proportion of garnet that was fractionated based on the Mn content of each EPMA analysis. Additionally, the sub-parallelism of garnet Mn content and modal proportion implies that there is very little *T*-dependence on K_d in the model.

3.4. Estimation of the degree of fractionation of components into garnet

Each point analysis in garnet now has a value of modal garnet attributed to it that has been calculated from the Mn content at that location. This value represents the modal proportion of garnet that was fractionated out of the effective bulk composition at the moment when the volume analysed passed from the 'shell' to the 'core'. The molar concentration of Fe, Mg, Ca and Mn can then be plotted against the calculated value of modal garnet for each EPMA analysis. Plotting a trendline to these data provides an 'ideal' garnet profile for the sample that shows how garnet composition changes with respect to the proportion of garnet fractionated from the rock (Fig. 4(c)-(e)). To calculate the quantity of Fe, Mg, Ca, Mn and Al fractionated from the bulk composition for any garnet analysis, each of the trendline curves must be integrated between the limits of the modal garnet value for the most primitive core analysis, and the modal garnet value for the analysis in question. These values are subtracted from the bulk composition of the rock to give an estimate of the effective bulk composition at the time at which the portion of the garnet being analysed became part of the fractionated core. A choice of trendline for the component vs mode plots is arbitrary, however fourth order polynomial least squared regressions (calculated in Excel) have been used here, as they consistently had the highest R^2 values out of the selection of trendlines, and they are relatively easily integrated.

4. RESULTS

4.1. Using estimations of crystal fractionation to optimise thermobarometry

The methods for predicting the effects of crystal fractionation described here provide a means of estimating the chemical composition of the system in which garnet is growing, and thus allow calculations of the pressure and temperature of any stage of garnet growth to be made. An important requirement of this method is that the sample chosen displays a strong linear correlation between the concentration of Mn vs Fe, Mg and Ca. Fig. 5 shows that there is a linear correlation between Mn and the other components in TE21, confirming the suitability of the application of this method to this sample. Fig. 6 shows the isopleths for the same series of point-analyses as plotted in Fig. 2, however in this case the isopleths for each point analysis are calculated with respect to the effective bulk composition operating at each point as determined by the model. Note how the intersection of the isopleths from the core to the rim of the garnet show tighter intersections than in Fig. 2, and can indeed be calculated right out to the garnet rim, where no intersections could be found prior to the application of the fractionation model.

A *P-T* path has been generated from the isopleth data (Fig. 7). The error curve formed from the loci of the isopleth intersection triangles provides an assessment of the success of the fractionation model in predicting the composition of the equilibrating system. The curve formed by the loci of overlapping error-bars on the isopleths provides an assessment of the error propagated from the thermodynamic database on which the pseudosection calculations are founded. If the fractionation model error stays within the bounds of the thermodynamic error, any thermobarometry derived from the intersecting isopleths can be regarded as being as accurate as the thermodynamic dataset allows.

Another important feature of the phase diagrams in Fig. 6 is the change in the *P*-*T* position of the garnet-in line. The fractionation of garnet from the effective bulk composition causes the stability of the mineral to be pushed to increasingly higher temperatures. For example, the thermal maxima on the garnet-in line at point one is 535°*C* and steadily increases to 570°*C* at point five. In this case, the fractionation of garnet appears to have had negligible effect on the stability of the other phases modelled, implying that the pseudosection calculated for the unfractionated bulk composition is suitable for interpreting a *P*-*T* path from the progression of mineral assemblages.

5. DISCUSSION AND CONCLUSIONS

5.1. The fractionation model

An important feature of this model is that the composition of the garnet is not fixed from the moment that it grew, but is free to change until it has been armoured by sufficient rim growth, and is removed from the effective bulk composition. This implies that the chemistry of any volume of garnet is potentially the result of *P*-*T*-X conditions that occurred later in the rock's history than those that were operating at the time the particular volume of garnet grew. The temporal decoupling between the growth composition and the preserved composition of garnet will be controlled in part by the thickness of the reactive shell in each garnet. Whilst no attempt has been made in this study to measure the thickness of the reactive shell in any garnets, dimensionless estimates of the proportion of garnet occurring in the reactive shell relative to the other phases in the reactive rock were made with every isopleth calculation. The occurrence of well-constrained isopleth intersections on the margin of the garnet stability field (Fig. 6) implies that only a very small proportion of garnet was ever in chemical communication with the matrix, and hence the reactive shell was very thin. Consequently, the effects decoupling the growth and preserved composition is considered negligible in this instance. This result is consistent with results obtained by experimentation and modelling of the diffusivity of components within garnet at comparable temperatures and pressures (Tracy, 1982; Thompson & England, 1984; Spear, 1988b; Chakraborty & Ganguly, 1992).

One of the assumptions inherent in using a Rayleigh fractionation-based model to calculate garnet growth is that the manganese uptake into garnet from the bulk rock is not constrained by kinetic factors. At very low temperatures in relatively manganiferous rocks this assumption has been shown to be false (Hirsch *et al.*, 2003). Hirsch *et al.* (2003) documented spessartine garnet growing in part from the breakdown of Mn-rich ilmenite. The distribution of Mn concentration in garnet (measured by WDS mapping) can be used to test the validity of this assumption: where the Mn forms a bell-shaped distribution with concentration-contours paralleling crystal faces the assumption is good; where Mn distribution is patchy and appears to be controlled by pre-existing compositional heterogeneity the assumption is false. Fig. 4(a) shows that the sample used in this study has a smooth, bell-shaped Mn profile, and consequently the Mn concentration in garnet is not considered to be influenced by kinetics factors arising from local heterogeneity.

5.2. Isopleth thermobarometry

In addition to error stemming from uncertainties in the thermodynamic dataset and mineral a-X relationships, a major source of error in applying the intersecting isopleth method is the misrepresentation of the reactive bulk composition at the time the analysed volume of garnet stabilised in composition. The magnitude of this error can be readily recognised by the tightness of the intersection between the compositional isopleths. If well-constrained intersections between core isopleths, and poor to non-existent intersections between rim isopleths are found, then crystal fractionation can be assumed to be causing the apparent disequilibrium. Corrections to the calculations can then be applied using the fractionation model. Should garnet core compositions not provide a tight intersection of isopleths, one or all of three possible scenarios may have occurred. Firstly, the volume of garnet analysed may not be a true representation of the core composition, i.e. the garnet analysed was not sectioned through its core. Whilst it is very unlikely that any analyses taken from thin-sections made without the aid of either serial sectioning or X-ray CT will sample the true geometric centre of a garnet, the relatively flat compositional profile in the core of growth zoned garnets (e.g. Fig. 4(a)) will mitigate the effects of this for small variations around the true centre-cut. Secondly, the garnet being analysed may have nucleated after other garnets in the sample, meaning that crystal fractionation will have already begun to alter the bulk composition even at the core. The strong positive correlation between garnet size and the Mn content in the core (Carlson, 1989) implies that only the largest garnets should be analysed to ascertain the composition of the earliest grown garnet cores. Thirdly, the sample may have undergone bulk composition change since garnet growth. If this is the case then the quantitative use of pseudosections in *P-T* calculations must be ruled out; however, the manner in which the disequilibrium is expressed (i.e. in what direction the compositional isopleths are displaced from each other) can potentially be used to qualitatively identify the mechanism of bulk composition change.

5.3. Pseudosection topology

Fractionating garnet from the effective bulk composition created an unambiguous up-temperature shift of the garnet stability field. The magnitude of this shift was ~30°*C* in this sample. Significantly, the change in the effective bulk composition caused by fractionation only effects the *P*-*T* position of the first appearance of garnet; the stability of the other phases is largely unaffected. This means that in this instance the fractionation of garnet does not change the makeup of the chemical system sufficiently to influence the growth or breakdown of other minerals. Consequently, the pseudosection calculated from the unfractionated bulk rock composition was adequate for predicting the pressure and temperature of the first appearance of other mineral species such as staurolite and biotite.

A METHOD FOR CALCULATING EFFECTIVE BULK COMPOSITION MODIFICATION DUE TO CRYSTAL FRACTIONATION IN GARNET-BEARING SCHIST: IMPLICATIONS FOR ISOPLETH THERMOBAROMETRY

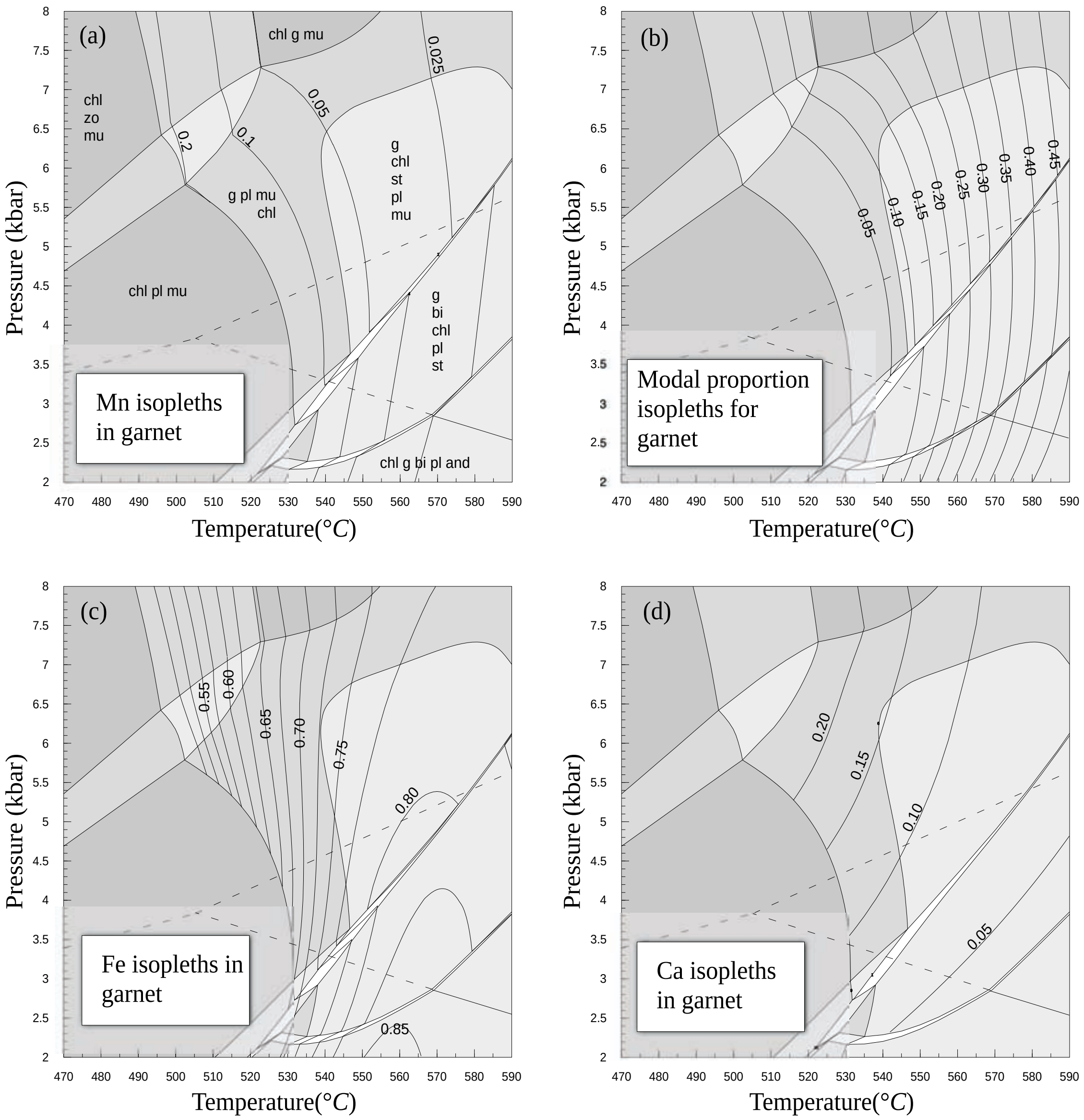


Figure 1. *P-T* pseudosection calculated for sample TE21. Isopleths shown are the: **(a)** spessartine content, **(b)** modal proportion, **(c)** almandine content, and **(d)** grossular content of garnet in the equilibrium assemblage for the sample.

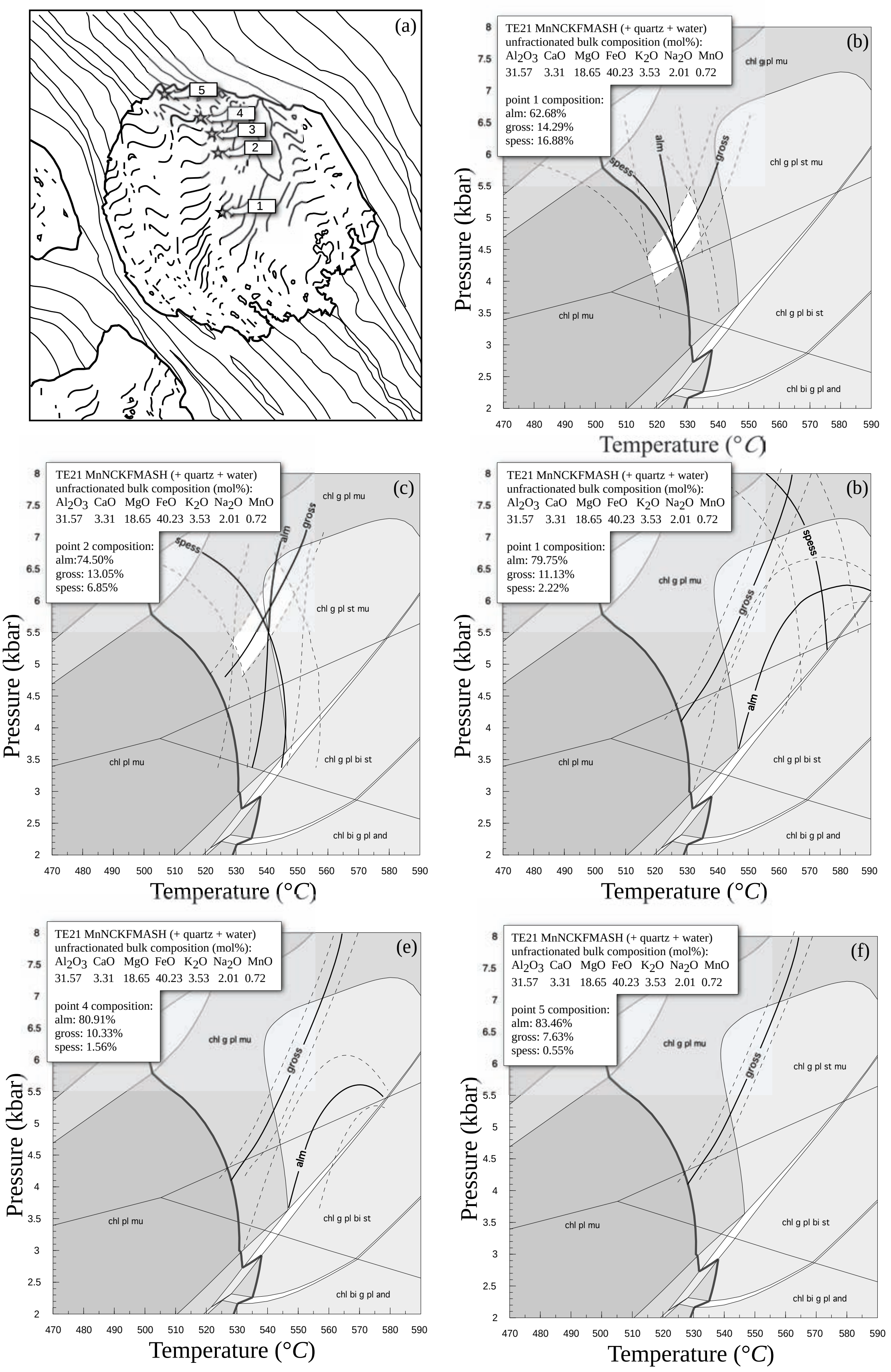


Figure 2. (a) Line diagram of garnet from TE21 showing the locations of the point analyses used to calculate the compositional isopleths displayed in **(b)-(f)**. The grey line shows the first appearance of garnet. Note the divergence of the isopleths from core to rim

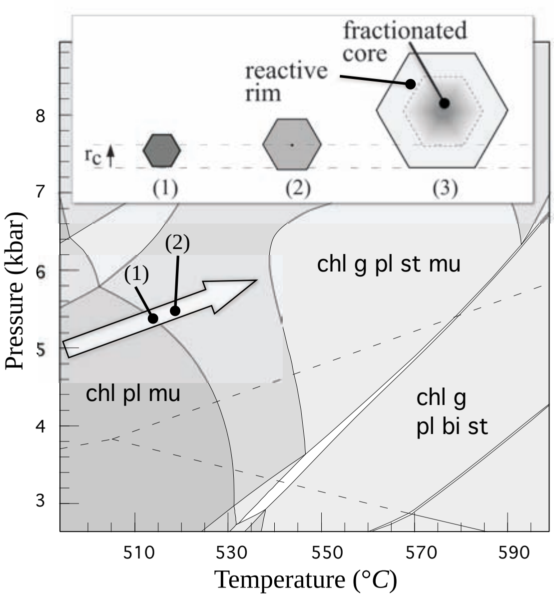


Figure 3. For the purposes of setting up fractionation calculations, garnet is divided into two parts, a rim of thickness r_C and a core. The rim is compositionally homogenous, and is free to chemically interact with the rock whilst the core is effectively isolated from the rest of the rock, its composition being heterogeneous and unchanging. The phase diagram shows a possible *P-T-t* path for sample TE21 over which garnet growth may have occurred. During garnet growth, the core can only begin to form once the garnet's radius exceeds r_C (e.g. **(2)**). Because the composition of garnet is only 'locked in' once it becomes part of the core, the oldest composition will reflect the point in *P-T* space at which rc was exceeded **(2)**, rather than the point at which garnet nucleated **(1)**. The final product is a porphyroblast with a core that is chemically isolated from the matrix, and a thin rim that is free to interact with the matrix. The actual thickness of r_C over the timescale of garnet growth is likely to be in the order of microns.

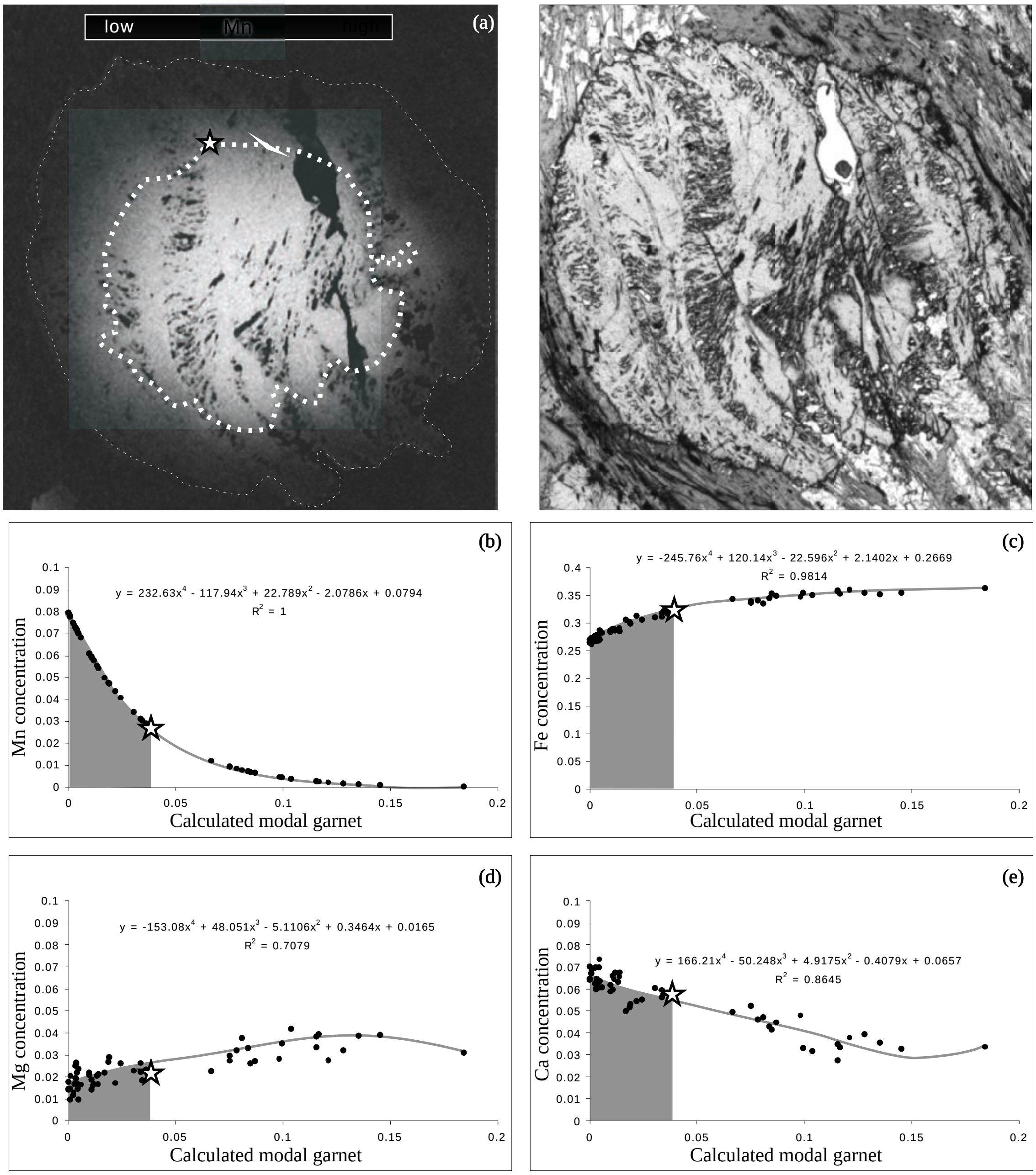


Figure 4. **(a)** X-ray element map of Mn in garnet in TE21. Star shows the location point analysis 3 (from Fig. 2(a) and (d)) and the heavy dashed line shows the compositional contour corresponding to that analysis. The fine dashed line traces the garnet rim. **(b)** Photomicrograph of the same garnet. **(c)-(f)** Plots of Mn, Fe, Mg and Ca vs. calculated modal garnet based on 63 point analyses from three garnets in TE21. The star on each plot marks the calculated modal garnet corresponding to point analysis 3. The shaded area under each curve represents the molar quantity of Mn, Fe, Mg and Ca that is contained within garnet at the time that point 3 first became part of the core. This value is calculated by integrating the trendline for each plot between the limits of the lowest modal value of garnet (highest Mn core analysis) and the modal value for the analysis in question.

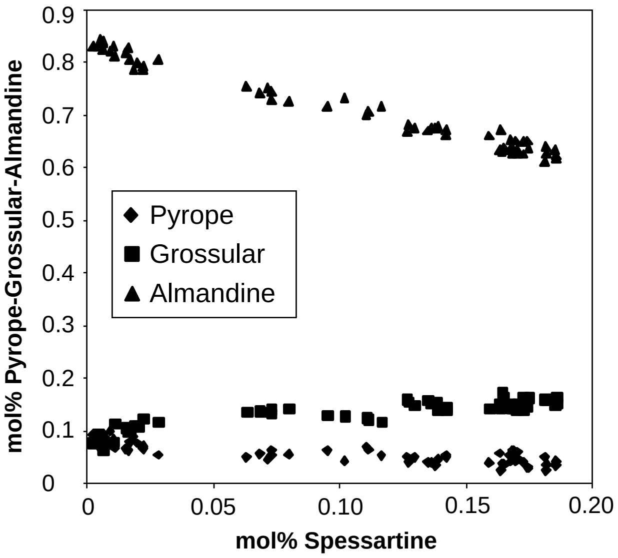
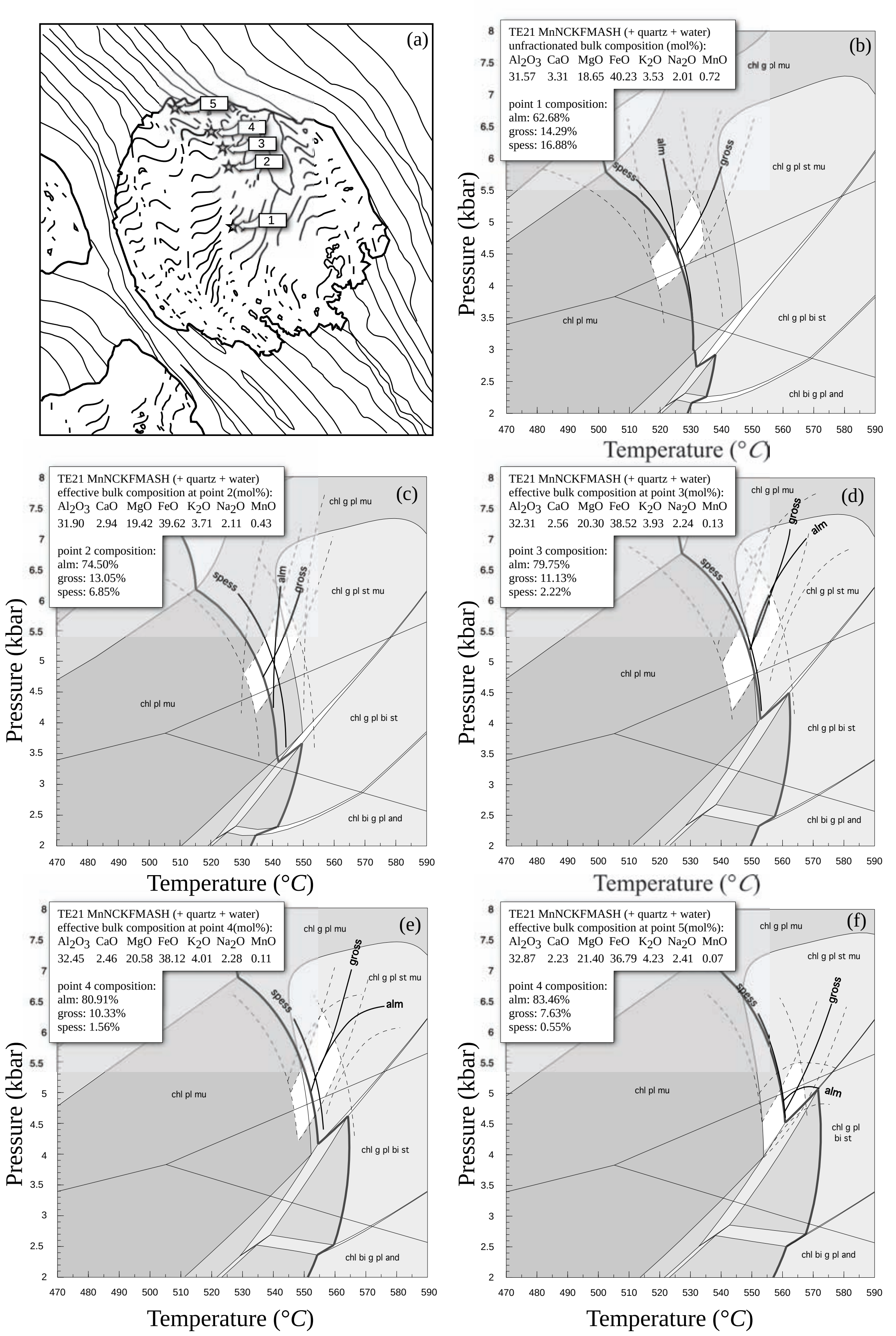


Figure 5. Plot showing the curvi-linear correlation between the compositional variables in garnet for sample TE21, confirming the sample's suitability to this method.



(b) TE21 MnNCKFMASH (+ quartz + water)
unfractionated bulk composition (mol%):

Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	MnO
31.57	3.31	18.65	40.23	3.53	2.01	0.72

point 1 composition:
alm: 62.68%
gross: 14.29%
spess: 16.88%

(c) TE21 MnNCKFMASH (+ quartz + water)
effective bulk composition at point 2(mol%):

Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	MnO
31.90	2.94	19.42	39.62	3.71	2.11	0.43

point 2 composition:
alm: 74.50%
gross: 13.05%
spess: 6.85%

(d) TE21 MnNCKFMASH (+ quartz + water)
effective bulk composition at point 3(mol%):

Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	MnO
32.31	2.56	20.30	38.52	3.93	2.24	0.13

point 3 composition:
alm: 79.75%
gross: 11.13%
spess: 2.22%

(e) TE21 MnNCKFMASH (+ quartz + water)
effective bulk composition at point 4(mol%):

Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	MnO
32.45	2.46	20.58	38.12	4.01	2.28	0.11

point 4 composition:
alm: 80.91%
gross: 10.33%
spess: 1.56%

(f) TE21 MnNCKFMASH (+ quartz + water)
effective bulk composition at point 5(mol%):

Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	MnO
32.87	2.23	21.40	36.79	4.23	2.41	0.07

point 4 composition:
alm: 83.46%
gross: 7.63%
spess: 0.55%

Figure 6. (a) The same sequence of point analyses as in Fig. 2 however, **(b)**-**(f)** show *P*-*T* pseudosections and isopleths that have been calculated with respect to the estimates of the effective bulk composition that was operating at each point. The garnet-in line is plotted as a heavy grey line, whilst the overlap the 1σ-error bars on the grossular, almandine and spessartine isopleths is plotted as the white-shaded area.

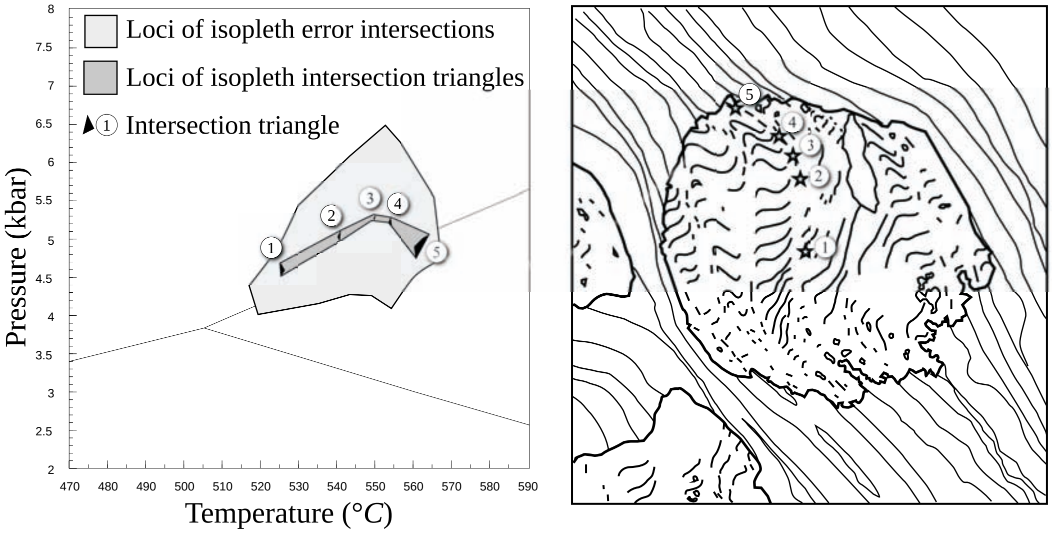


Figure 7. Shows the loci of all of the isopleth data from the fractionated pseudosections in Fig. 4. The *P-T* path is drawn from the loci of the isopleth intersection triangles. The width of this path defines the error introduced through the fractionation model. The light grey area around the path is the loci of the 1σ-error intersections (shaded white on Figs 2 and 6) and defines the error propagated from the thermodynamic dataset.