SECTION A

USING PSEUDOSECTIONS AND ISOPLETH THERMOBAROMETRY TO CONSTRAIN METAMORPHIC *P-T-t* PATHS: TECHNIQUES, CAVEATS, AND INSIGHTS INTO THE CHEMISTRY OF GARNET GROWTH

ABSTRACT

This section presents an analysis of the errors inherent to *P-T* pseudosection calculation in general, and to garnet compositional isopleth thermobarometry specifically. *P-T* pseudosections are mineral stability diagrams calculated for particular bulk compositions. They provide a means of predicting stable mineral assemblages throughout *P-T* space, and can be used to obtain estimates of the composition and relative abundance of the minerals in each assemblage field. Measured mineral compositions can be compared to the predicted ones to obtain estimates of the *P-T* conditions under which the assemblage formed. Garnet composition is frequently used in these calculations, as the mineral is common and preserves its original growth composition over a wide range of *P*-T space. A review of this technique is presented herein. Additionally, an analysis of the contributions of thermodynamic error, analytical error and geological error is undertaken. The thermodynamic error is systematic, whilst the analytical and geological error contributions are random. Systematic error contributes to the overall accuracy of the pseudosection calculations, whilst random error contributes to their precision. This means that the two error types contribute differently to the relative and absolute uncertainty in the results, and consequently need to be addressed separately. Methods are developed herein that provide means of assessing the contribution of analytical and thermodynamic error, and recognising and minimising the effects of geological error.

WDS compositional mapping was undertaken to assess the influence of geological error on isopleth calculations. This technique highlighted two important sources of geological error. The first is a variation in the relative proportions of Mn, Fe, Mg and Ca between the bulk of the garnet, and parts that are adjacent to crenulation hinge zones. This is thought to be caused by the partial re-equilibration of garnet with

the matrix adjacent to crenulation hinges due to fluid infiltration near the metamorphic peak. The second is a thin shell of elevated Mn at the rim of garnet. Here it is argued that is the result of the influx an externally derived Mn-rich fluid very late in the retrograde metamorphic history of the rock, and not as has been previously postulated, the result of garnet resorption.

1. INTRODUCTION

P-T pseudosections have proved to be a popular and powerful means of predicting and explaining mineral paragenesis of metamorphic and igneous rocks (Vance & Holland, 1993; Vance & Mahar, 1998; Marmo et al., 2002). They provide a far more complete description of the chemistry of metamorphism than traditional thermobarometers, and are considerably more effective and appropriate than petrogenetic grids for interpreting petrographically observed mineral reactions. Additionally, the software used to calculate them, such as THERMOCALC (Powell & Holland, 1988), can propagate errors through from the thermodynamic dataset upon which the calculations are based. Pseudosections are built from calculations of the relative stability, composition and modal proportion of minerals within a specific bulk composition for a given *P-T* window; they are essentially an application of Duhem's Theorem (Spear, 1988a; Powell et al., 1998) to metamorphic systems. Isopleth thermobarometry (Vance & Mahar, 1998) is the application of pseudosection-type calculations to particular mineral and bulk rock compositions. This technique involves calculating the *P-T* of equilibration between one or more minerals and the bulk composition in which the minerals have grown.

Clearly, the use of *P-T* pseudosections to describe the metamorphic history of specific samples relies on the assumption that all of the minerals within the sample have grown in equilibrium, both with each other, and with the bulk composition of the sample. However, given that:

1. A metamorphic cycle will invariably occur over a range of *P*-*T* conditions, and the minerals making up the rock will reflect part of that range.
2. Minerals formed by solid solution between end-members are rarely compositionally homogenous, and therefore cannot represent part of an equilibrium assemblage within the rock as a whole.
3. The components making up the chemical system all have different diffusivities, and, will equilibrate over varying length-scales in the rock.

The assumption that pseudosection usage is founded on seems shaky at best. However, careful application of pseudosection calculations to specific equilibria within each sample can provide useful thermobarometric information that does not contravene the principal assumption of the method. This paper describes techniques for building *P*-*T* pseudosections, for performing isopleth thermobarometry, for collecting and qualifying data to use in those techniques in terms or error analysis and propagation, and to interpret the results generated, and to that end lays some foundations for the work described in the following sections. Additionally, two commonly observed, but rarely documented features of garnet compositional distribution – variation adjacent to overgrown crenulation hinges, and Mn highs on the rim are described and new models for their development are proposed.

2. CALCULATING PSEUDOSECTIONS AND ISOPLETHS

2.1. How THERMOCALC solves mineral equilibria problems

The equilibrium relation for a balanced chemical reaction is:

$$0 = \Delta G^0 + RT \ln K \qquad [1]$$

Where ΔG^0 is the change in Gibbs free energy of the reaction, R is the Boltzmann constant and K is the reaction coefficient.

In equation [1] the ΔG^0 term is a function of P and T:

$$\Delta G^0 = \Delta H_{f(1,298)} - T\Delta S_{(1,298)} + P\Delta V_{(1,298)} \qquad [2]$$

Where $\Delta H_{f(1,298)}$ is the standard state change in enthalpy, $\Delta S_{(1,298)}$ is the standard state change in entropy, and $\Delta V_{(1,298)}$ is the standard state change in volume.

The values of $\Delta H_{f(1,298)}$, $\Delta S_{(1,298)}$ and $\Delta V_{(1,298)}$ are calculated directly by THERMOCALC from values supplied in the dataset (Holland & Powell, 1985; Holland & Powell, 1990; Holland & Powell, 1998). The K term in [1] can be described mathematically by the relationship:

$$K = \frac{\prod_{i=1}^{n}\left(a_{\mathrm{products}_n}\right)^{p_{\mathrm{product}_n}}}{\prod_{i=1}^{n}\left(a_{\mathrm{reactants}_n}\right)^{p_{\mathrm{reactant}_n}}}$$

Where $p_{product/reaction}$ is the stoichiometric reaction-coefficient for the particular end-member in the reaction and a is the activity of that end-member. K describes the progress of a reaction in terms of a ratio of the activities of products to reactants; if a reaction has yet to begin, $K = 0$; if it is going to completion, $K \rightarrow \infty$. Activity (a) is the thermodynamically effective concentration, and broadly relates to the molar abundance of a phase. The activity of end-members in compositionally variable minerals relates to the composition of the mineral via the activity-composition (a-X) relationship:

$$a_k^e = (X_k^e \gamma_e)^\alpha \qquad [4]$$

Where a_k^e is the activity of end-member e in phase k, X_k^e is the molar proportion of e in k, γ_e is the activity coefficient for end-member e, and α is the site multiplicity (the number of atoms that can mix on the site). In phases where mixing between end-members is ideal, $\gamma = 1$; where mixing is non-ideal, γ is a function of P and T. The method used by THERMOCALC for formulating γ is described by Powell & Holland (1993).

For a complex equilibrium involving phases undergoing solid solution, the equilibrium relationship can be described in terms of an independent set of reactions of the form of [1] written between the participating end-member phases. At this stage, the dimension of the solution-space to a set of equations will be equal to the number of unknowns (activities of end-members, P and T) minus the number of equations. Consequently, the equilibrium can only be solved to unique values of P and T for 1- and 0-variant equilibria. Pseudosection calculations are founded on Duhem's Theorem. They add a set of mass-balance equations to the matrix of equilibrium relations described above that relate the molar proportion of each component in the bulk composition to the molar abundance of each end-member in each phase and to the modal proportion of each phase. The result is that the set of equations describing the equilibrium and mass-balance relationships always have a 2-dimensional solution space. Consequently, a linear solution in P-T space requires that one variable, such as the modal proportion of a phase or the value of one compositional variable of a phase (e.g. the Fe content of garnet) be specified, whilst a point solution requires that two variables be specified. Detailed descriptions of the implementation of Duhems Theorem can be found in Powell et al. (1998) and Spear (1988a).

2.2. Constructing pseudosections

The lines that make up P-T pseudosections are phase stability boundaries. These are either univariant reaction lines, or zero-mode isopleths (lines calculated by setting the modal proportion of one phase in a given assemblage to zero). Pseudosections are built up by initially calculating the stability of the lowest variance assemblage (i.e.

assemblage with the highest number of phases), and gradually working up through to the highest variance assemblages that stem from them. In the MnNCKFMASH (a system built from the components MnO, Na_2O, CaO, K_2O, FeO, MgO, Al_2O_3, SiO_2 and H_2O) system, on which this study is based, a univariant line must, by Gibbs' Phase Rule, be an equilibrium between nine phases (in addition to quartz and water). In all of the pseudosections calculated herein, the lowest variance equilibria found to be stable was a divariant (eight phases plus quartz and water) field consisting of biotite, chlorite, garnet, plagioclase, staurolite, muscovite and either andalusite or sillimanite. This field was generally the starting point for all of the calculations used in building each pseudosection, with increasingly higher variance fields stemming from it. Consequently, all of the lines defining phase boundaries calculated herein are zero-mode isopleths.

The mineral composition isopleth is another line that can be calculated with THERMOCALC. In contrast to zero-mode isopleths, the mineral composition isopleth is calculated by fixing the value of one compositional variable in one mineral, reducing the degrees of freedom of the solution space to one, thus producing a solution that forms a line through *P*-*T* space. The value set for the compositional variable will be derived from an Electron Probe Micro-Analyser (EPMA) analysis of that particular mineral in the sample in question.

2.3. Isopleth thermobarometry

A *P*-*T* pseudosection displays the equilibrium mineral assemblage for a particular bulk composition within a specified *P*-*T* window. As such, it can only accurately describe samples that have equilibrated at a point in *P*-*T*-*X* space. Given that metamorphism invariably occurs along a path in *P*-*T* space, and that the mineralogy of the sample will reflect at least part of that path, *P-T* pseudosections will never completely describe the mineralogy of the samples they are based on. The occurrence of chemically zoned minerals in a sample also indicates the operation of crystal fractionation. This means that the chemical reservoir from which minerals are growing (that is normally represented by the whole-rock bulk composition) will be changing whilst the zoned mineral is growing. Consequently, the rim of any chemically zoned porphyroblast will not have grown in equilibrium with the measured bulk composition. Employing isopleth thermobarometry can circumvent these problems. This technique applies the pseudosection method to specific equilibria by calculating the *P-T* stability of particular *mineral* compositions with respect to the *bulk rock* composition. Compositional isopleths are calculated by setting a compositional variable of a mineral to a particular value, usually one that reflects the measured composition of that mineral. The compositional variables for a mineral are a set of independent variables that algebraically describe the total range of that mineral in composition-space. For example, garnet composition in regionally metamorphosed metapelites typically varies by solid solution between four end-members: grossular ($Ca_3Al_2Si_3O_{12}$), almandine ($Fe_3Al_2Si_3O_{12}$), spessartine ($Mn_3Al_2Si_3O_{12}$) and pyrope ($Mg_3Al_2Si_3O_{12}$), to have a general composition $(Ca,Fe,Mn,Mg)_3Al_2Si_3O_{12}$. Therefore, garnet compositional variations can be uniquely described by specifying the relative concentrations of any three of those end-members in garnet; the concentration of the fourth end-member will be one minus the sum of the other three.

The most reliable equilibrium relationship to use for isopleth thermobarometry in amphibolite facies pelitic rocks is between the core of garnet porphyroblasts (the composition of which is measured by EPMA) and the bulk rock composition (measured by X-Ray Fluorescence, XRF). There are two reasons why this relationship is consistently the most reliable:

1. Values for a mineral's individual compositional variables (e.g. the Fe content of garnet) plot as contours on *P*-*T* pseudosections. To establish the *P*-*T* point at which the mineral grew, an intersection between two compositional contours needs to be found. To assess the accuracy of the *P*-*T* estimate, a third contour that relates to the same equilibrium needs to be plotted. If all three intersections lie within error, then the composition of the phase(s) analysed can be considered to have been in equilibrium with the bulk composition at the *P*-*T* point of the intersection. Here it is important that all three compositional variables plotted represent the same equilibrium. If the compositional variables all come from a single point analysis of a compositionally complex phase, they are much more likely to represent a single equilibrium than if they come from analyses of several different phases. Garnet is one of the few common minerals in metapelites that has more than two independent compositional variables that are measurable by EPMA analysis, making it ideal for isopleth thermobarometry.
2. Garnet is also one of a small number of minerals in metapelites that will preserve its growth composition, due to its very low intragranular diffusivity below 700°C. This has a twofold effect on the usage of pseudosections in describing rock-mineral equilibria. Firstly, it means that the *P*-*T* history of garnet growth can be preserved in the range of garnet composition, provided that the rock was not heated over ~700°C (Tracy, 1982; Spear, 1988b; Chakraborty & Ganguly, 1992). Secondly, the low intragranular diffusivity of garnet causes the mineral to be effectively removed from the bulk rock; the Fe, Mg, Ca, Mn, Al and Si that are present in garnet are not available for growing other minerals

(or indeed more garnet). Therefore, the bulk composition of the rock will not be an accurate description of the chemical system that was operating at any time after garnet started growing. This means that only the very earliest grown garnet can be used for isopleth thermobarometry, unless calculations are made to estimate the effects of crystal fractionation resulting from garnet growth.

In this study, the composition of garnet is described by the relative proportions of the garnet compositional end-members, almandine, grossular and spessartine. These variables were chosen because the precision of Mg analyses from the Jeol 840A microprobe used throughout this study is much lower than it is for the other components. This is a consequence of the low peak to background ratio, and peak overlaps that occur in the EDS spectrum around the Mg-Kα peak.

Ideally, if the composition of the portion of garnet analysed grew in equilibrium with the bulk composition used for the calculation, then the three isopleths will intersect at the point in *P*-*T* space that the garnet grew. In this manner, the composition of garnet can be used in conjunction with the bulk composition of the rock in which it was growing to generate information on the metamorphic *P*-*T* history of the rock. However, a poorly constrained equilibrium between garnet and bulk rock can also be an important and useful result. This would imply that the measured bulk composition does not represent the effective bulk composition that was in operation when garnet grew. Estimates of the vectors of the change in effective bulk chemistry of the rock can be made, and can potentially be linked to geological causes other than the *P*-*T* history, such as metasomatism, crystal fractionation and equilibrium domain constraints.

3. DATA AQUISITION

The goal of applying pseudosection calculations to real rocks is generally to estimate the *P-T* conditions at which particular minerals grew within a rock. To this end, two sets of chemical data need to be obtained:

1. The composition of the minerals of interest in a particular sample.
2. The composition of the chemical system in which those minerals are thought to have grown.

The former is obtained through electron microprobe point-analyses of thin-sections taken from the sample in question. The latter is made from XRF analyses of what is thought to be a representative sample of the rock. Determining what constitutes a representative sample can be problematic, as assumptions are made about the relationship between the scales of equilibrium of components in the rock and the degree of compositional heterogeneity within the rock. The nature of these assumptions must be recognised and justified to maintain the integrity of the modelling.

3.1. Obtaining bulk composition data

All of the pseudosections herein were calculated from bulk compositions derived from XRF analyses of particular samples. Typically, around 500-1000g of sample was washed, trimmed, crushed and then milled. The mass of rock analysed was chosen, such that it represented the rock within which the garnets that were analysed grew. Technicians at the JCU Advanced Analytical Centre prepared fused pellets and conducted major element analysis using the Siemens SRS3000 X-ray Fluorescence Spectrometer at the facility.

Pseudosections were constructed with respect to the relative proportions of MnO, Na_2O, CaO, K_2O, FeO, MgO, Al_2O_3, SiO and H_2O (MnNCKFMASH). Despite the apparent complexity of this system, it is still a simplification of the actual system operating in pelitic schists. Major element analyses invariably report small, but significant proportions of TiO_2 and P_2O_5. Petrographic analysis of each sample is essential to determine which minerals these components are present in. Typically, TiO_2 will be present in either ilmenite or rutile, and P_2O_5 will be present in apatite or monazite. Because both ilmenite and apatite contain a proportion of FeO and CaO respectively, the presence of these phases will affect the overall proportion of FeO and CaO that is available within the MnNCKFMASH system. Consequently, if apatite or ilmenite are observed in the sample, Fe and Ca must be removed from the bulk composition used in THERMOCALC on the basis of the amount of Ti and P in the XRF analysis. Fe and Ca occur in ilmentite and apatite in 1:1 and 1:3 molar ratios with Ti and P respectively, and are subtracted from the bulk composition in accordance with these ratios. Technically, this is equivalent to the pseudosection being calculated in the MnNCKFMASHTiP system with ilmentite and apatite assumed to be in excess. However, whilst this technicality has been implemented, it will not be mentioned elsewhere due to the complexity that it adds to the notation.

3.2. Obtaining garnet composition data

A well-developed strategy for the collection of garnet composition data is clearly an important part of isopleth thermobarometry. A method for calculating the effects of crystal fractionation on garnet growth is presented in the second section of this thesis. Consequently, the strategy for collecting compositional data that is outlined below focuses on collecting a suite of data that describes garnet's complete compositional range. Additionally, strategies will be developed that identifying portions of garnet that have been affected by post growth changes to composition, and differentiating them from portions that have not.

Element concentration mapping of garnet via EPMA is the simplest and most cost effective method of assessing the spatial variation of composition within garnet. Figure 1 shows WDS relative concentration maps of Fe, Mg, Ca and Mn from three garnets in the same sample. Texturally, compositional zonation broadly mimics the crystal shape of the garnet. However, where garnet has overgrown quartz-rich crenulation hinges, the zonation deviates from a crystallographic control. Because the primary growth composition of garnet is required for isopleth thermobarometry, it is important to establish whether these deviations formed during garnet growth, or as the result of post-growth diffusional modification of a growth-related composition. Figure 2 shows that the relative concentrations of Ca, Mg and Mn in garnet that has overgrown the quartz seams are quite different to those in portions of the garnet with no quartz inclusions. It is important to note that the relative concentrations of Ca, Mg and Mn stay fairly constant in the inclusion-poor areas, but vary significantly in the inclusion-rich areas, particularly towards the rim of each porphyroblast. If this texture represents a primary growth feature, it implies that the composition of garnet must be controlled very locally by microstructural domains within the rock. The contours plotted for each of the porphyroblasts in figure 2 represent approximately the same concentrations of each element in each porphyroblast. In the inclusion-free regions, the contours correlate reasonably accurately within and between porphyroblasts. Therefore, whilst the contours correlate variably within the zones of deviation it seems unlikely that kinetic controls during growth are responsible for the deviations. Moreover, the fact that the deviations are far more pronounced at the rim than they are at the core of the garnet suggests that they were caused by garnet locally re-equilibrating following growth along grain boundaries in crenulation hinges. This means that analyses should only be obtained from quartz-poor regions of garnet, where compositional contours can be seen to be parallel to the crystal faces of the porphyroblast.

Another feature made evident from WDS mapping is the Mn high on the rim of each garnet. This zoning pattern is fairly common in metamorphic garnets, and a number of workers have suggested mechanisms for its formation (Kretz, 1973; Banno, 1978). Figure 1 shows that the Mn high is not uniform around the garnets, but is larger in wavelength and amplitude where the garnet rim is adjacent to a more quartz rich region of matrix. In addition, the Mn high is present at the rim of the garnet where the garnet appears to have been pseudomorphed by chlorite, but is smaller than in adjacent rim that abuts quartz. This constrains the timing of the formation of the Mn high on the garnet rim to after the pseudomorphic growth of chlorite, and implies that it is structurally controlled by quartz domains. This suggests that very late-stage, retrograde fluid-flow through quartz seams was responsible for this zonation pattern, and that the source of the Mn is external to the rock, and not derived locally from either garnet or chlorite breakdown. Whilst the actual amount of Mn added to the system is negligible, and probably beyond the resolution of XRF major element analysis, the very rim of the garnet clearly does not have its original growth composition, and consequently should not be included in the quantitative dataset of growth composition.

A suite of quantitative compositional data was collected from the three porphyroblasts via EDS point-analysis in accordance with the strategies developed above. Figure 3 shows how well correlated the relative proportions of each compositional variable are throughout the entire range of garnet composition.

4. UNCERTAINTY PROPOGATION IN ISOPLETH CALCULATION

It is important to recognise each source of error involved in isopleth thermobarometry, and understand how they impinge on the accuracy and precision of the results. Complete discussions of error analysis in THERMOCALC, and the errors associated with input parameters have been discussed in detail by the program's authors (Powell & Holland, 1988; Powell & Holland, 1994; Worley & Powell, 2000). The types of error involved in isopleth thermobarometry can be broadly grouped as either systematic, referring to the uncertainty of a value that is constant throughout all of the calculations, or random, the uncertainty relating to values that are specific to individual analyses.

4.1. Sources of systematic error

Systematic error generates uncertainty in the overall accuracy of the thermobarometric results, that is, the absolute *P*-*T* position of the results. However, because it describes an error in values that are constant throughout all of the calculations, it does not contribute to the relative uncertainty between different results.

4.1.1. Thermodynamic data

The internally consistent thermodynamic dataset of Holland and Powell (1985, 1990, 1998) contains calculated uncertainties in the enthalpies of formation ($\Delta_f H,$) of all of the mineral end-members. These uncertainties can be propagated through all calculations in THERMOCALC to give the uncertainties in calculated *P*-*T* values and mineral compositions. $\Delta_f H$ is a constant value for each end-member phase, however, its actual value is generally quite poorly constrained experimentally. The "least squares approach" of Holland and Powell (1985) minimises the uncertainties on these values, but, uncertainties associated with $\Delta_f H$ still contribute significantly to the overall uncertainty of the results.

4.1.2. Activity-composition models

Activity-composition (*a-X*) models are a set of parameters that describe the effects that mixing between end-members in complex phases has on the thermodynamic properties of the mixture. Inaccurately formulated *a-X* models are widely considered to be the largest contributor to error in thermobarometry (Hodges & Mckenna, 1987; Kohn & Spear, 1991). As with $\Delta_f H$, the mixing relationships in complex phases such as garnet and staurolite are poorly constrained. Worley and Powell (2000) postulated that because error introduced here was constant between different calculations of the same type (e.g. the calculation of the *P-T* of equilibration of garnet in the presence of chlorite, muscovite, plagioclase, quartz and water), *a-X* error is systematic. Consequently, if the bulk composition and mineral composition do not vary significantly between samples, this error type would contribute little to the relative uncertainty between different *P-T* points.

4.2. Random error

The term "random error" is used to differentiate sources of uncertainty that have errors that vary between calculations. Whilst the magnitude of the uncertainty may be known, the magnitude of the error is not, and will not necessarily be the same between analyses. The two main sources of random error are analytical and geological error. These serve to limit the precision with which the composition of rocks and minerals can be measured, and with which the composition of minerals can be modelled and predicted. Consequently, analysis of random error provides important controls on the validity of compositional modelling used in the calculation of *P-T* paths from garnet zoning (Evans, 2004).

4.2.1. Analytical error

Analytical error refers to the precision of measurement of the mineral and rock compositions used in thermobarometry. Typically, this is determined directly from the raw data collected from the measuring apparatus, for example, the analytical precision of EPMA analyses are derived from the *estimated standard deviation*, the square root of the number of raw counts for each element. This type of error is grouped as random, and is differentiated from systematic error because it describes the uncertainty on a value that changes from calculation to calculation (e.g., the composition of garnet), rather than a value that remains constant (e.g., the thermodynamic properties of the end members of garnet). For parameters affected by systematic error, the residual (the magnitude of the difference between the value that is used in the calculations and the actual value) will always be unknown, but constant between calculations, affecting all calculations equally. The residual for parameters affected by random error will be unknown and will vary between calculations, adding uncertainty to the relative precision of different results.

4.2.2. Geological error

Geological error refers to errors introduced into the calculations by chemical processes that act to contravene one or more of the assumptions underlying isopleth thermobarometry. The most common sources of geological error are: disequilibrium between minerals, between compositional variables within a mineral, or between minerals and the bulk rock composition. This type of error is certainly not systematic, however it can be minimised through the methods of optimal sampling and processing outlined in sections 3.1 and 3.2.

There are two important sources of geological error that require discussion here:

1. Variation in the scale of chemical equilibrium during mineral growth; and,
2. Changes to the effective bulk composition caused by crystal fractionation.

Variation in the length scale of equilibrium between different components can potentially introduce serious and insurmountable error into isopleth thermobarometry. Chernoff & Carlson (1997) and Hirsch et al. (2003) describe instances where Ca and Mn are equilibrating over a length-scale smaller than the mean distance between garnet porphyroblasts. They demonstrate that the Ca and Mn content of garnet can be controlled by local heterogeneity in the rock’s composition. This means that two different volumes of garnet that have grown simultaneously can potentially have different compositions, and consequently would not be in equilibrium with each other. This contravenes an important assumption of isopleth thermobarometry: that all garnet that has grown at the same time will have the same composition. Clearly, the influence of this type of geological error needs to be assessed before isopleth thermobarometry is performed.

Crystal fractionation as a source of geological error is discussed in detail by Marmo et al. (2002) and Evans (2004). Whilst geological error stemming from crystal fractionation is in principle the same as that stemming from variations in the scale of equilibrium, the two are separated because the effects of crystal fractionation are predictable, and can be compensated for (e.g Marmo et al., 2002; Evans 2004). However, situations of the kind described by Chernoff & Carlson (1997) and Hirsch et al. (2003) cannot be corrected for.

4.2.3. Analysing and processing random error

Mapping the composition of porphyroblasts prior to acquiring point-analysis data helps to minimise the input of geological error into the compositional dataset. However, once the point analysis data has been acquired, it is still necessary to assess the magnitude of the geological error within the dataset before commencing isopleth thermobarometry. It is important to ascertain whether the analytical error is greater in magnitude than the geological error for each set of compositional data.

If the Mn content of garnet at growth is controlled by crystal fractionation, and post-growth diffusion has not modified the composition significantly, then it will continually decrease throughout garnet growth, allowing it to be used as a proxy for the relative time of growth (e.g., Chernoff & Carlson, 1997). Consequently, plotting Fe, Mg and Ca against Mn will provide an indication of how the Fe, Mg and Ca contents of garnet change with time. Trendlines fitted to scatter-plots of Fe, Ca, and Mg versus Mn provide an ideal model composition for garnet, where the residuals between the data and the trendline (the model error) can be regarded as a combination of the effects of analytical error and geological error (Figure 3). The magnitude of the analytical error is calculated from EPMA counting statistics; the errors on the measured weight percent values for each element are simply propagated through the mineral recalculation spreadsheets. This approach gives a reasonable approximation of the uncertainty on each analysis in terms of mol percent. Alternative approaches, such as Monte Carlo simulation are impractical, given the constraints on data input in THERMOCALC. The magnitude of the model error can be found by calculating the residuals between the model line and the data. Calculating the ratio of the sum of the residuals to the sum of the analytical errors provides an indication of the relative magnitudes of the contributing errors. A ratio that is less than one indicates that the geological error associated with the garnet composition data is, on average less than the analytical error associated with the EPMA, and is therefore small enough to be beyond the resolution of the analytical precision of the EPMA. In this case, the analytical error from the microprobe can be propagated through the isopleth calculations to provide an estimate of the non-systematic error associated with the thermobarometric results. If the ratio is greater than one, geological error contributes significantly to the composition of garnet. In this situation, the assumptions that pseudosection-based methods are founded on are contravened. This situation can potentially be remedied by investigation of the outlying data, removing that which has been collected from regions within garnet that have suffered post-growth alteration.

5. INTERPRETING PSEUDOSECTIONS AND ISOPLETH RESULTS

One of the most powerful elements of isopleth thermobarometry is that it provides assessment of the equilibrium between mineral compositions and the bulk composition used in the calculations. If at least three isopleths intersect within error, then the *P-T* of the intersection is regarded as being the *P-T* of equilibration. However, if they do not intersect, the apparent lack of equilibrium between the mineral and the bulk rock could be an indication of the actions of one or more of several chemical processes. Accordingly, the significance of results that indicate that both equilibrium and disequilibrium behaviour needs to be assessed, the former to provide information on the *P-T* conditions of metamorphism, the latter to provide information on chemical processes that may have operated during metamorphism.

5.1. Equilibrium

Where three or more compositional isopleths intersect within error of each other, the *P-T* point of the intersection forms the basic result for isopleth thermobarometry. How the uncertainties are plotted will depend on what thermobarometric data are presented, and that in turn will depend on the aims of presenting it. If the intersection of three isopleths from a single *P-T* point is plotted, with the aim being to define the *P-T* point at which that volume of mineral grew, then the uncertainties stemming from analytical error and thermodynamic error need to be summed to accurately represent the total uncertainty of that *P-T* point. This typically generates huge uncertainties around individual *P-T* points, severely limiting their usefulness in geological interpretation. If multiple sets of isopleth intersections are investigated, with the aim being to assess the relative change in *P* and *T* between each set, then a more subtle approach to plotting uncertainties can be used, and acceptably precise *P-T* paths can be defined. If for example, a metamorphic field gradient is being calculated based on the composition of garnet cores from a suite of garnet-biotite-muscovite schists taken from a transect across a field area, the equilibrium being calculated will involve the same minerals, that have all grown within very similar bulk compositions. Consequently, the systematic error can be ignored between the different samples. Only random error will be generating uncertainty in the difference between *P-T* conditions for garnet core growth across the area. Whilst the absolute *P-T* position of the field gradient will be relatively poorly constrained, the magnitude of the gradient will be known with a high degree of precision, which is arguably more useful for understanding the tectonic processes leading to metamorphism. Figure 4 shows garnet core isopleth intersections from two garnet-staurolite-biotite schists from the Salmon Hole Brook Syncline, NH, to illustrate how the different types of error constrain field gradient calculations. Typically, error estimates from isopleth thermobarometry have been plotted as polygons formed by the overlap of the error curves (e.g. Vance & Mahar, 1998). Here, ellipses lying within the overlapping sections of the error curves are plotted as P-T estimates in a crude approximation of the methods used in Powell & Holland (1994). A means of mathematically determining the dimensions of the error ellipses is desirable, and is coded into the avPT mode in THERMOCALC, but integrating this with isopleth thermobarometry is beyond the scope of this study. Employing this crude approximation of the ΔPT approach of Worley & Powell (2000), random error is considered to affect the precision of P-T calculations, whilst systematic error affects their accuracy.

5.2. Disequilibrium

The isopleth intersection method deals with the equilibration between one or more minerals and the chemical reservoir from which the minerals are growing. The term 'disequilibrium' is used with some reservation to describe the situation where the prescribed composition of the reservoir is not that operating at the time when the garnet used for the isopleth calculations grew. It does not imply that garnet was out of equilibrium with its surroundings when it grew, merely that it was never growing in equilibrium with what was measured as the bulk rock composition. There are two chemical mechanisms for generating apparent disequilibrium between garnet and bulk rock. These are kinetics and mass-transfer.

5.2.1 Disequilibrium driven by kinetics

Kinetically controlled disequilibrium occurs where the access of material to the growing face of the garnet is restricted by diffusive controls, making the proportion of components available to the garnet (the effective bulk composition) different from the measured bulk composition. Accordingly, disequilibrium will only be seen where the availability of different components is altered differently. Kinetically driven disequilibrium is present in all chemically zoned minerals; indeed chemical zonation is one of the more obvious indicators of the influence that kinetics has on mineral composition. If a mineral grain is chemically zoned, then a chemical potential gradient (the prerequisite for chemical reaction) exists across that grain. This means that the reaction (which will move components so as to flatten the chemical potential gradient) has been so profoundly hindered by the slow diffusion of components within garnet that the zoning can remain over a geological timescale.

There are two main instances where kinetics will affect the growth composition of garnet:

1. Where crystal fractionation resulting from garnet growth is changing the effective bulk composition; and,
2. Where the length-scale of Ca, Fe, Mg or Mn diffusion is shorter than the length-scale of compositional heterogeneity within the rock, within the time-scale of garnet growth.

The first case will not be dealt with in detail here, as it is described exhaustively in section B of this thesis. However, it is worth noting that it is common to calculate a well-constrained equilibrium between the core of a zoned garnet and the bulk composition, and a very poorly constrained equilibrium between the rim and the bulk composition (Vance & Mahar, 1998). The general effect of fractionation is to push the almandine and grossular isopleths to higher temperature and lower pressure, and push the spessartine isopleth to both higher temperature and pressure (Figure 5).

The second case refers purely to the movement of components through the rock matrix to the growing garnet. The occurrence of this can be identified from either WDS maps or plots of the relative concentrations of Fe, Mg, Ca and Mn in garnet before isopleth thermometry is performed. If a WDS map shows any zoning pattern that follows pre-existing structure from the matrix (e.g., Hirsch et al., 2002), then local heterogeneity in the overgrown matrix has influenced garnet composition. If there are differences in the relative concentrations of components between different porphyroblasts that texturally appear to be primary growth features (e.g., Chernoff & Carlson, 1997), then localised changes in the effective bulk composition may have occurred. The occurrence of either of these scenarios will render isopleth thermobarometry untenable, as unlike crystal fractionation, their effects will be difficult, if not impossible to quantify.

5.2.2 Disequilibrium driven by mass-transfer

Mass-transfer processes can generate an apparent disequilibrium between the measured bulk composition and the composition of garnet, if they occurred after garnet grew. If the bulk composition is altered by the addition or removal of components from the rock after garnet growth, what is measured as the bulk composition by XRF analysis of a crushed sample will clearly not be representative of the system in which garnet was growing. Some potential causes of bulk composition change are: addition or removal of melt species from the rock, metasomatic addition or removal of components, deformation controlled dissolution of minerals, and weathering.

If the compositional isopleths from the core of a garnet fail to intersect within error, then, assuming all activity formulations are adequate, bulk-composition change post garnet growth is likely. Identifying the mechanism by which the bulk composition has changed can be challenging. This is because it is only possible to determine in which direction in *P*-*T* space each has moved relative to the other, and not how far or in which direction individual isopleths have moved. However, an inductive approach to this problem can potentially yield results. If we begin with a garnet-bulk rock system that is in equilibrium, the results of various bulk composition changes on isopleths can be modelled. For example, the removal of the anorthitic plagioclase from the rock after garnet growth will cause the grossular isopleth to be pushed to higher pressures.

6. CONCLUSIONS

Whilst pseudosections are inadequate for the complete, quantitative description of mineral occurrence and composition in metamorphic rocks, they can be used to quantitatively predict the composition of minerals in particular equilibria. The composition of the garnet cores equilibrating with the bulk rock is a good example of this. Analysis and propagation of error types other than thermodynamic error has largely been neglected by workers performing isopleth thermobarometry. It is argued here that analytical error is the most important error contribution to metamorphic field gradients, *P*-*T* paths or any other *P*-*T* calculations that derive significance from the difference between two or more results.

A poorly constrained intersection between isopleths indicates that the mineral compositions plotted did not form in equilibrium either with each other, or with the bulk composition used. This suggests the occurrence of either crystal fractionation, bulk composition change after mineral growth, or kinetically stimulated disequilibrium between the plotted mineral compositions. If the first and last reasons can be eliminated, then the magnitude of the bulk composition change can potentially be predicted by iteratively changing the bulk composition used in the pseudosection until a well-constrained intersection is found. In this manner, both the cause and the magnitude of the metasomatism can be predicted.

Two common, post-growth changes to garnet composition have been described and interpreted. The first involves the peak metamorphic re-equilibration of garnet with the matrix along crenulation hinges. This manifests itself as an increase in Mg concentration relative to Mn and Fe where garnet has overgrown crenulation hinges. The structural control of this chemical process suggests that either enhanced fluid-flow along crenulation hinges compared to crenulation limbs occurs, or that the larger surface area to volume ratio of garnet that has overgrown these quartz-rich structures contributes to the reaction rate of the equilibration process. The second process concerns the Mn high very commonly observed on the rim of metamorphic garnet. This has been temporally constrained to occur after the cessation of the garnet to chlorite retrograde reaction (possibly the temperature at which it occurs is too low for the breakdown of garnet to chlorite to be progressing at a significant rate). The source of the Mn must be external to the rock, and the proportion that is introduced appears to be insignificant with respect to the bulk rock composition, as it does not effect core isopleth intersections.

USING PSEUDOSECTIONS AND ISOPLETH THERMOBAROMETRY TO CONSTRAIN METAMORPHIC *P-T-t* PATHS: TECHNIQUES, CAVEATS, AND INSIGHTS INTO THE CHEMISTRY OF GARNET GROWTH

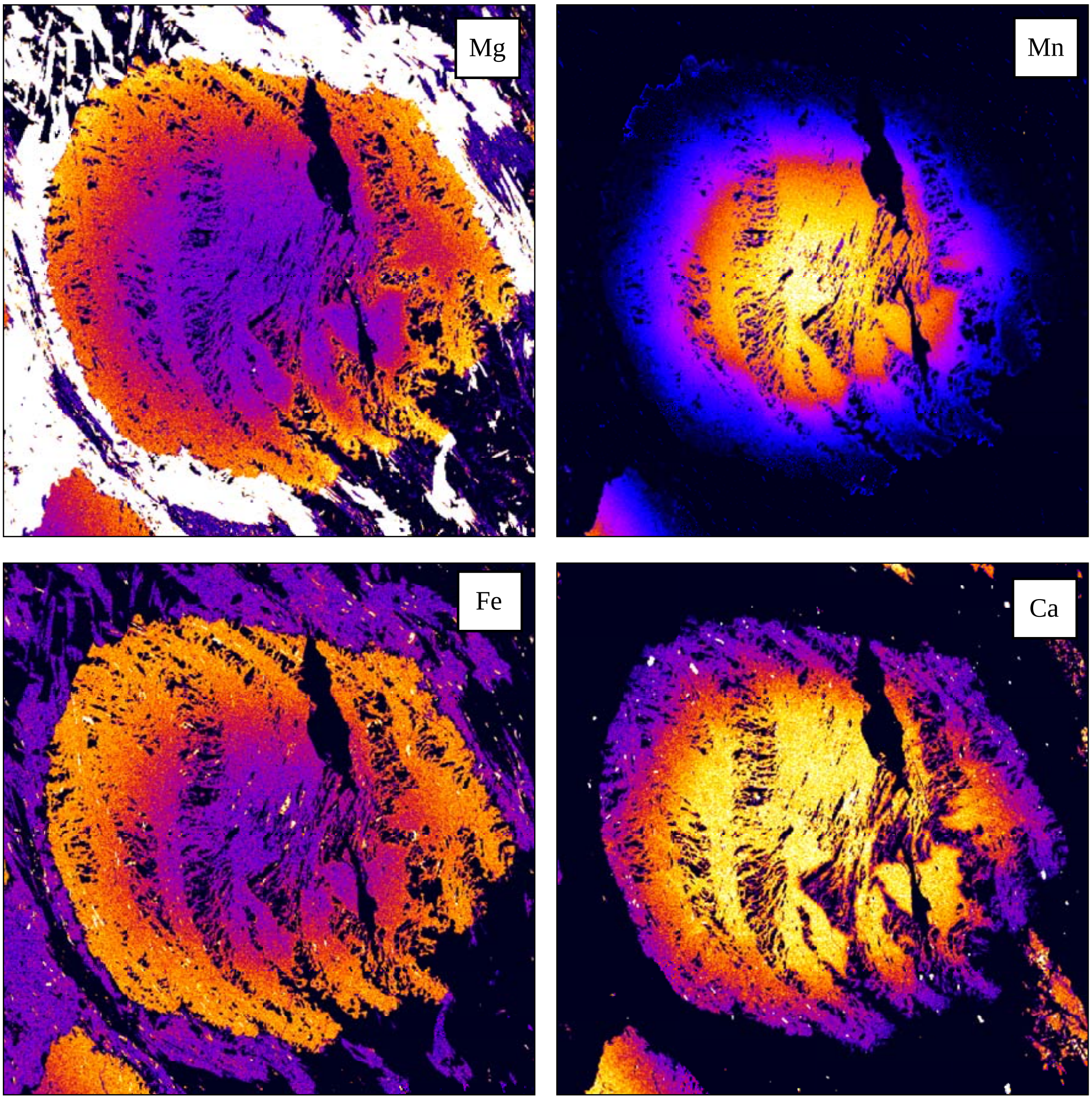

Figure 1(a). WDS X-ray intensity maps of a garnet in sample TE21

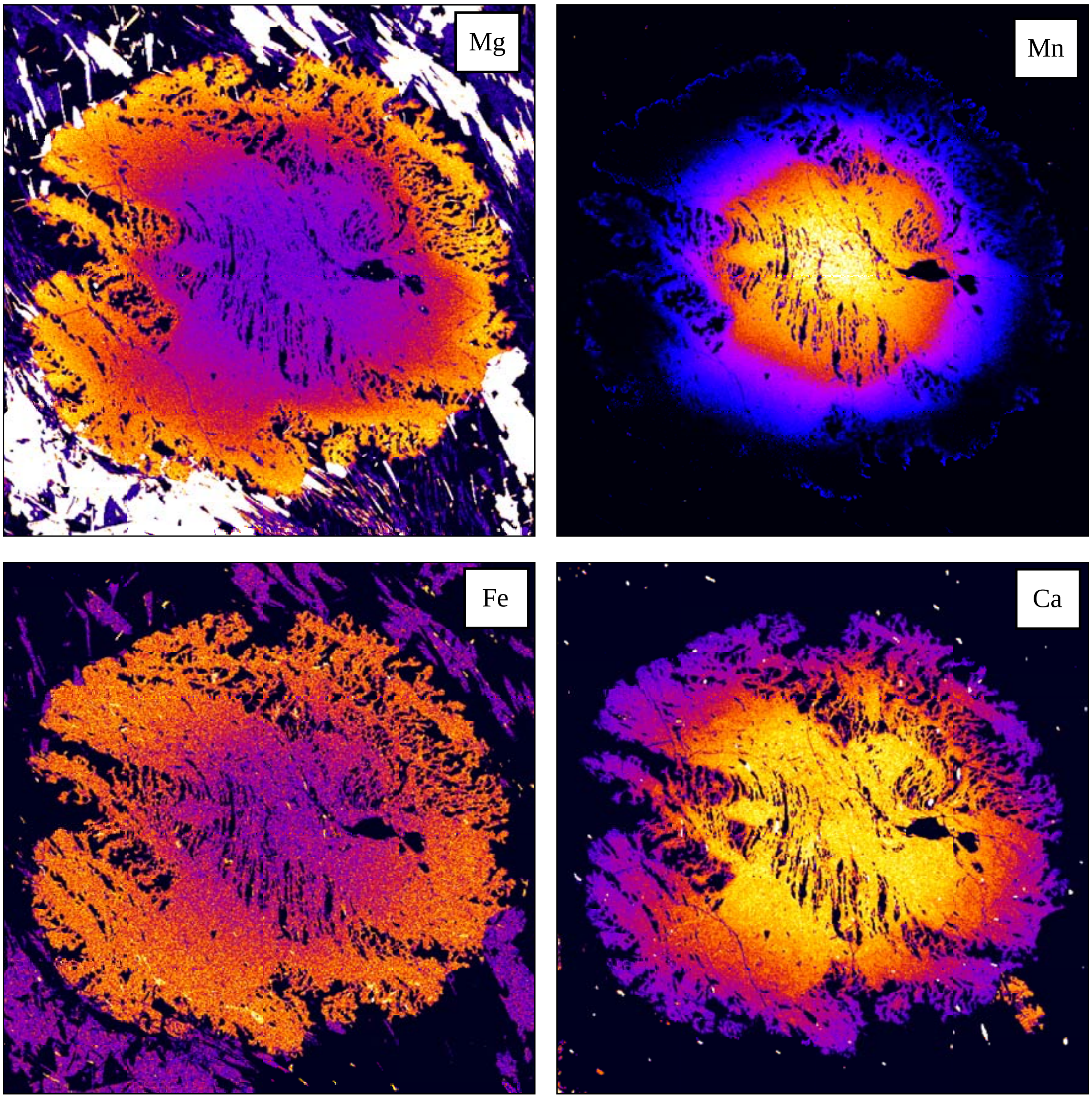

Figure 1(b). WDS X-ray intensity maps of a garnet in sample TE21

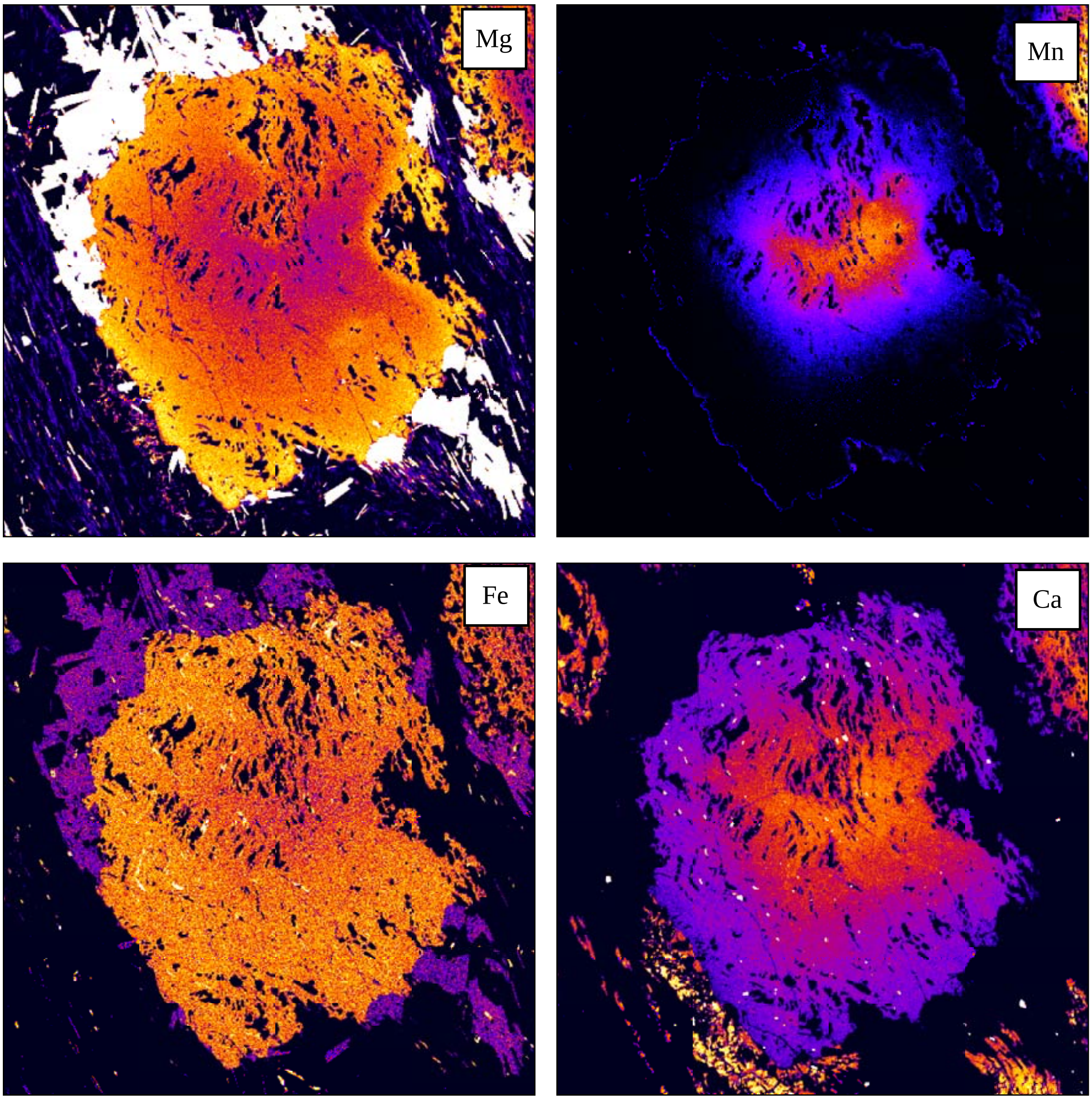

Figure 1(c). WDS X-ray intensity maps of a garnet in sample TE21

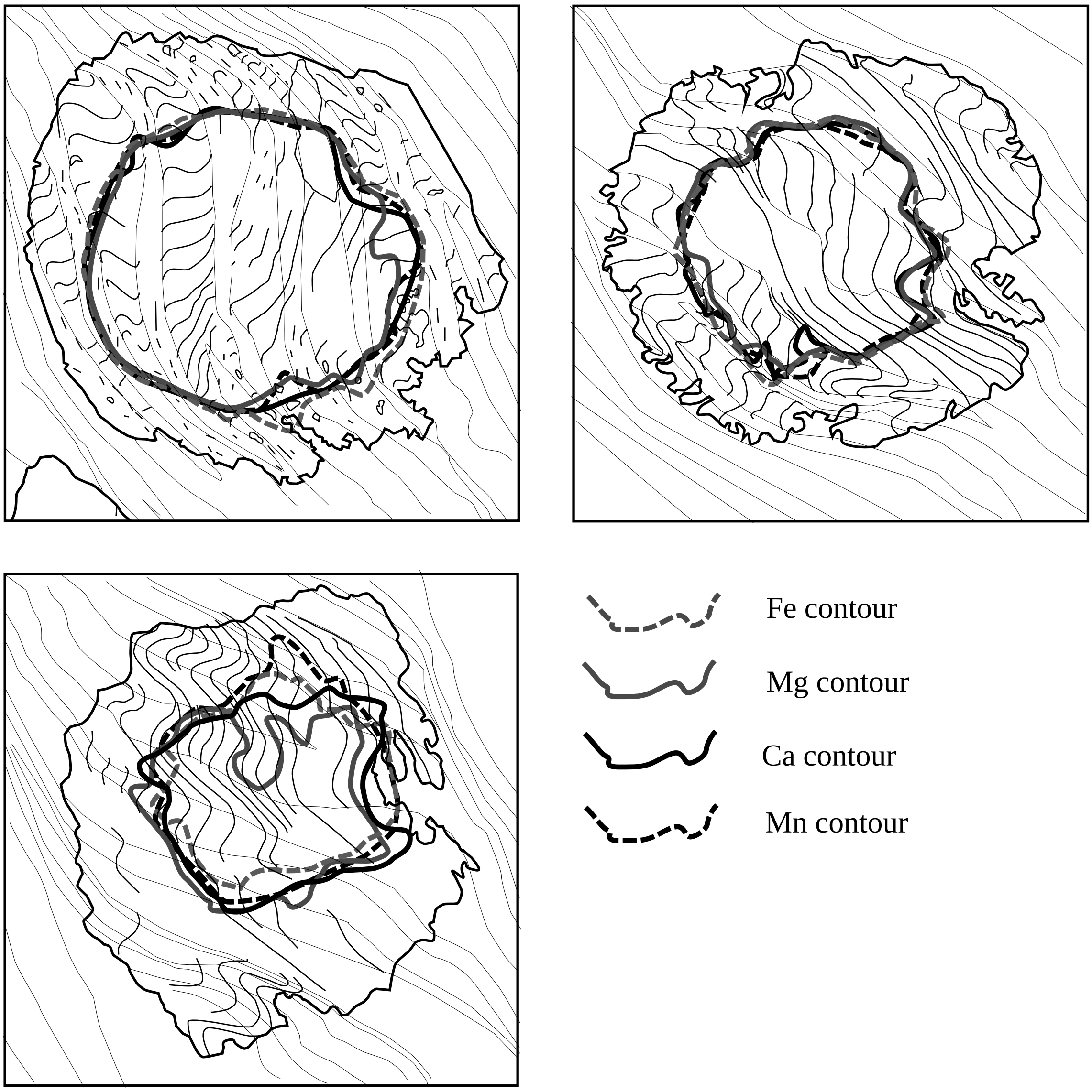

Figure 2. Line drawing of the garnet shown in figure 1(a)-(c) showing the geometry of the internal microstructure and the correlation between lines of equal concentration of Fe, Mg, Ca and Mn. Note the varying degrees of divergence between the lines in the overgrown crenulation hinges

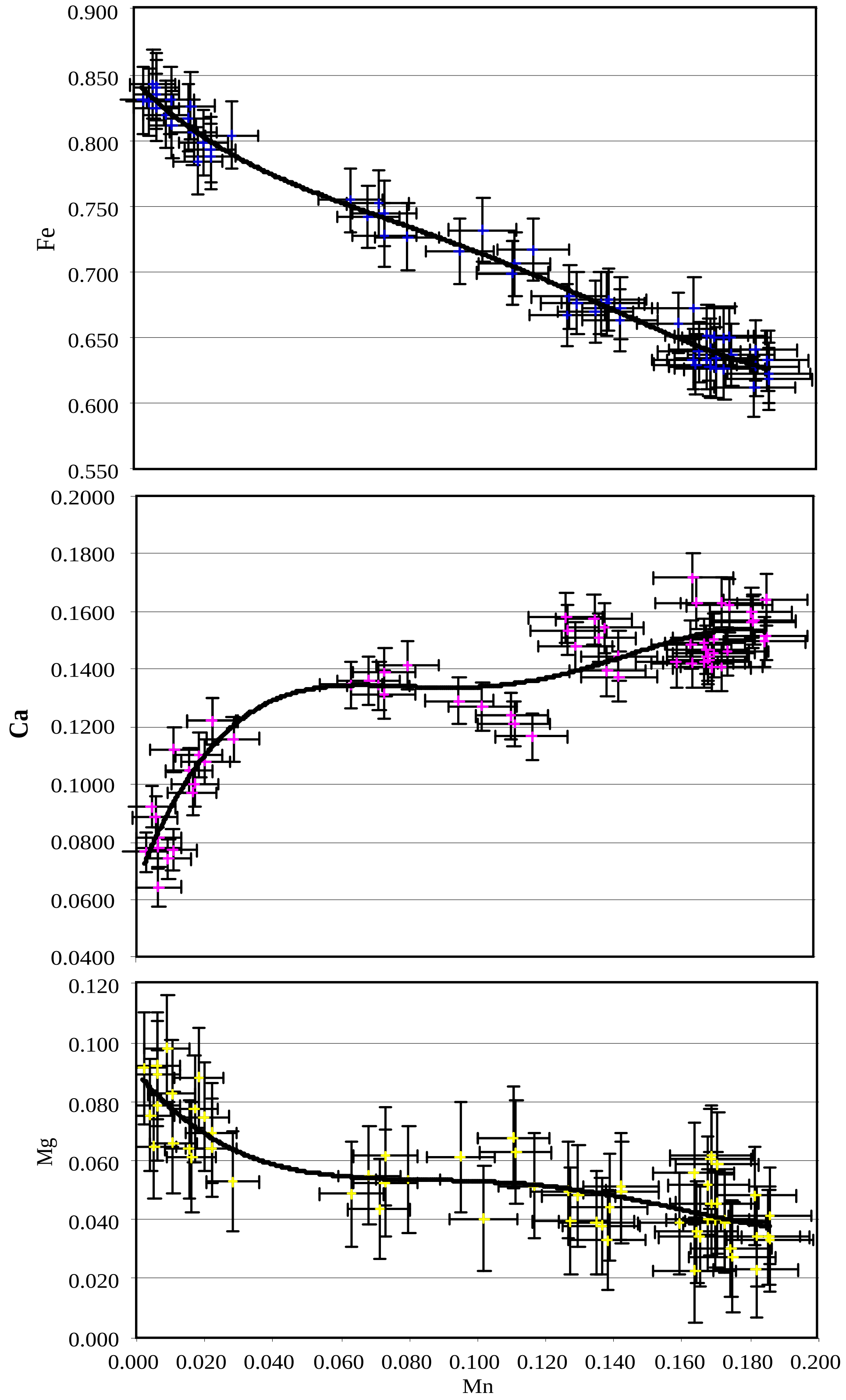

Figure 3. Plots of Fe, Ca and Mg versus Mn concentration for a series of microprobe analyses of garnet. Error bars indicate the magnitude of the estimated analytical error for each analysis. The trendline is a 4th-order polynomial best fit line, calculated in Excel™

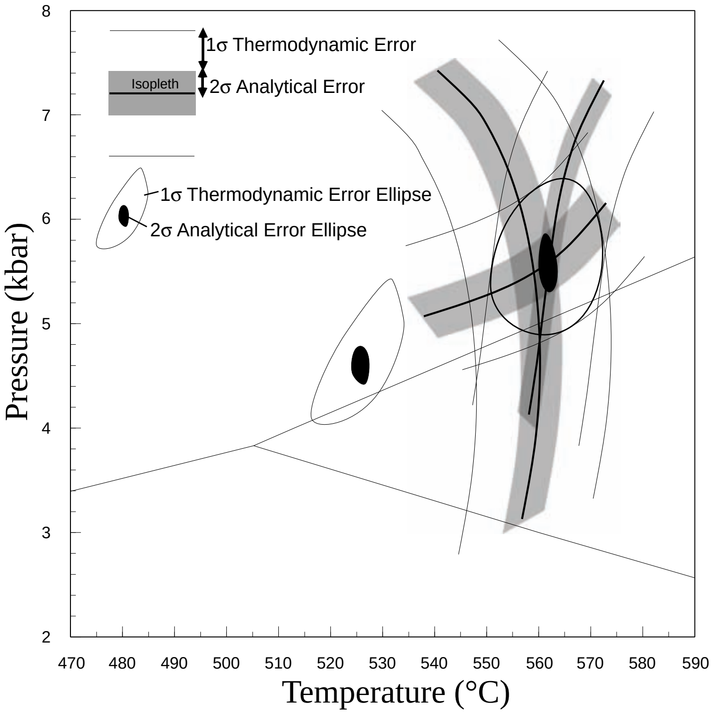

Figure 4. Calculated compositional isopleths for two garnet core from different samples showing the calculable systematic and random error contributions, and the ellipses used that represent the overlap of the different errors. The relative uncertainty in *P-T* position between the growth of these cores is represented by the black ellipses. The absolute accuracy of the calculations is represented by the unfilled ellipses. i.e., a *P-T* vector between the two black ellipses can only be absolutely constrained to within the confines of the unfilled ellipses at a 1σ confidence interval.

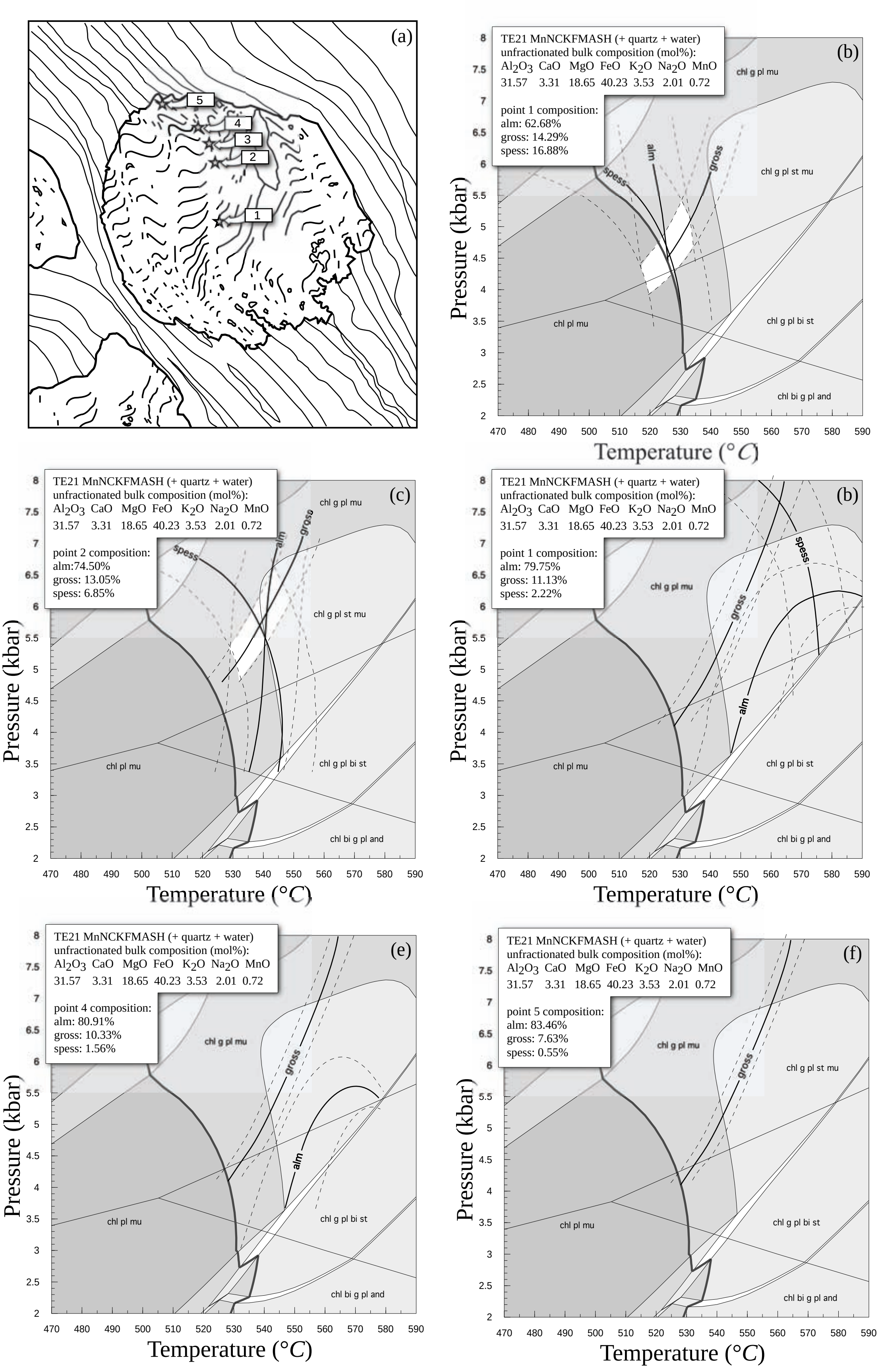

Figure 5. (a) shows the locations of the point analyses used to plot the sets of isopleths displayed in **(b)-(f)**. The pseudosection is calculated from an XRF emasurement made from the sample (TE21). Note the increasing divergence of the isopleths from the core to rim analyses. Error bars show systematic error only in these diagrams.