# Pressure-Temperature Paths and the Relationship Between Garnet Producing Reactions, Microstructural Truncations, and Mineral Zoning

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**ABSTRACT.** P-T pseudosections and X-ray compositional maps of garnet porphyroblasts were used to establish reaction histories for low-Al pelites and calc-pelites where multiple deformation and metamorphic histories have been revealed by inclusion trail geometry. These garnet porphyroblasts from the Chester and Athens Dome region in southeastern Vermont commonly preserve truncated foliations within garnet grains as well as foliations in the garnet rims that are truncated by matrix fabrics. P-T pseudosections were modelled in the system MnNCKFMASH so that the full reaction history involving the grossular component of garnet and plagioclase could be examined and contrasted with progressive development of inclusion trails. Detailed thermobarometry calculated in conjunction with these pseudosections was used to model the P-T paths.

The P-T paths determined from garnet core-rim thermobarometric estimates indicate that garnet growth occurred along an up-pressure path while the rocks were being heated, reaching a peak pressure of 13-14 kbars followed by a peak temperature of approximately 650°C at slightly lower pressures (11-12 kbars). The P-T pseudosections for calc-pelites show a simple reaction history given such a path. Garnet growth resulted from the breakdown of chlorite in the presence of biotite, muscovite and plagioclase until chlorite was consumed. The P-T pseudosections for low-Al pelites show that biotite was not stable and plagioclase was removed from the assemblage early in the reaction history given the same path.

The P-T pseudosections for each of the samples described herein are in excellent agreement with the mineral assemblages and textural relationships present in those samples. Calculated P-T paths superimposed on pseudosections predict a simple continuous reaction history for these samples. However, the presence of truncated inclusion trails in the porphyroblasts indicate that garnet growth must have been episodic as successive foliations developed around progressively developed grain margins and are subsequently overgrown. Compositional maps of garnet porphyroblasts show intricate zoning patterns that can be correlated with the microstructural truncations. These data show that deformation must play an integral role in mineral reactions. When P-T pseudosections are combined with the microstructural studies, the evolution of each mineral assemblage can be modelled such that the deformation history can be integrated directly with metamorphic processes. This combined approach reveals that metamorphic reactions are commonly overstepped and proceed only where deformation is partitioned through rocks at the scale of the porphyroblasts.

# INTRODUCTION

Inclusion trails in porphyroblasts have long been recognised as having importance for the understanding of the relationship between the timing of deformation and metamorphism. Curved inclusion trails in porphyroblasts have been recognised in nearly every major orogenic belt. The interpretation of the origin of these curved inclusion trails is significant for the structural and tectonic modals that result from them (Bell and Johnson, 1989; Bell and others, 1992; Williams and Jiang, 1999). The textural relationships of inclusion trails in porphyroblasts also have significance for understanding the nature of mineral growth in deformed rocks (Williams, 1994). Curved inclusion trails are commonly used as an indication of syn-deformational mineral growth although this criterion alone may be ambiguous (Johnson, 1999). Although there is considerable debate as to the nature of curved inclusion trails in porphyroblasts there remains a clear link between the processes involved in deformation and mineral growth.

The geology around the Chester and Athens Domes in southeastern Vermont has some spectacular examples of curved inclusion trails in garnet porphyroblasts (Rosenfeld, 1968). Many samples contain garnet porphyroblasts with simple trails, which have less than 90° of apparent rotation and are continuous with matrix foliations, although complex inclusion trails are a common feature as well. For samples with simple trails a simple growth model may be appropriate, but for samples with complex trails such as greater than 90 of apparent rotation or strong truncations, a more complex mechanism for garnet growth is required.

To fully understand the processes that occur during deformation and mineral growth resulting in porphyroblasts with complex inclusion trails, the mineral reaction(s) must be known, the pressure and temperature history (P-T path) must be established, and the spatial relationship between mineral zoning and microstructure must be examined. This study attempts to further elucidate the relationship between deformation and metamorphism through a detailed petrologic examination of garnet growth for samples with complex inclusion trails. P-T pseudosections, garnet compositional maps and detailed thermobarometry were utilised to try to better understand the relationship between mineral growth and the deformation. A model of mineral growth that is consistent with thermodynamic modelling (P-T pseudosections), quantitative microstructural analysis, mineral zoning and thermobarometry is provided.

## GEOLOGIC SETTING

The Appalachian Orogen in southeastern Vermont contains an array of lithotectonic blocks, which preserve a prolonged history spanning nearly 700 million years, involving 6 major parautochthonous to allochthonous lithotectonic units that are subdivided based on distinctive sequences that have been recognised within them (Stanley and Ratcliffe, 1985; Ratcliffe and other, 1992). Middle Proterozoic Basement Gneisses of the Green Mountain Massif are unconformably overlain Cambrian rift and passive margin metasedimentary rocks of the bounding the eastern edge of the Laurentian margin. East of the Green Mountain Massif are the Middle Proterozoic allochthonous basement gneisses of the Chester and Athens Domes which are overlain by Late Proterozoic to Early Cambrian Hoosac Formation. The contact between the Hoosac Formation and the underlying basement gneisses is problematic and likely represents a zone of syn-metamorphic detachment (Ratcliffe and others, 1997). These two blocks of Proterozoic gneiss are separated by the highly tectonized Cambro-Ordovician Rowe-Hawley Belt, which is comprised of calcareous, pelitic and semi-pelitic metasedimentary and, mainly mafic, metavolcanic and intrusive rocks of the Rowe-Moretown lithotectonic unit. The youngest of the lithotectonic belts in southeastern Vermont is the thick Siluro-Devonian sequence of the Connecticut Valley Trough. These rocks are separated from the Rowe-Hawley belt by an angular unconformity (Ratcliffe, 1997).

Across this portion of the Appalachians the stratigraphic succession and the dominant phase of metamorphism generally gets younger from west to east. The Laurentian basement to the west was metamorphosed during the Precambrian Grenville Orogeny. The Siluro-Devonian Connecticut Valley Trough to the east reached peak metamorphic condition during the Devonian Acadian Orogeny. The Cambro-Ordovician Rowe Halley Belt lying between these two belts is thought to have been metamorphosed during the Taconic Orogeny and then subsequently overprinted during the Acadian (Stanley and Ratcliffe, 1985; Armstrong and others, 1992). The Taconic Orogeny resulted in the collapse of the Laurentian passive margin with large-scale west-directed thrusting that was terminated with docking of an Ordovician Island Arc (Bronson Hill Anticlinorium). The Acadian Orogeny continued with the closure of the Iapetus Ocean resulting in greatly thickened crust. Metamorphism to the west of the Green Mountain Massif is generally attributed to the Taconian Orogeny (Laird and others, 1984; Sutter and others, 1985) whereas the complex folding and high-grade metamorphism about the Chester and Athens Domes is considered to be Acadian in age (Bradley, 1983; Hepburn and others, 1984; Armstrong and others, 1992). The peak of the Acadian in southeastern Vermont is thought to have occurred at 380 Ma (Vance and Holland, 1993; Armstrong and Tracy, 2000). Monazite ages obtained in conjunction with study from Cambrian and Ordovician age rocks show a spread of ages ranging from 430 Ma to as young 320 Ma show that metamorphism and deformation was far more protracted.

## SAMPLES and PETROGRAPHY

A large number of spatially oriented samples (more than 400) of metasedimentary, garnet bearing, pelitic to semi-pelitic phyllites and schists were collected by Tim Bell and Ken Hickey from a range of Cambrian (Proterozoic?) to Siluro-Devonian stratigraphic units for the microstructural work. Sampling focussed on lithologies containing garnet porphyroblasts primarily from: the Hoosac, Rowe, Moretown, Cram Hill, Northfield and Waits River Formations. Garnet bearing samples from these lithologies vary widely in bulk composition from highly aluminous schists to feldspathic schists and amphibolites. Mineral compositional data, bulk rock compositional data, and compositional maps of garnet porphyroblasts have been collected for a number of lithologies around the Spring Hill Synform (Fig. 1) for samples ranging in age from the Cambrian through to the Silurian. Virtually all of the samples collected in southeastern Vermont have inclusion trails in garnet porphyroblasts suitable for quantitative microstructural work. The relationships between the microstructural development further complexities in matrix structures are described in detail by Bell and Hickey (1997), Bell and others (1998) and Hickey and Bell (2001). It should just be noted that the dominant matrix fabric is a subvertical crenulation cleavage striking roughly NNE-SSW and that the dominant axis of curvature found for inclusion trails in garnet porphyroblasts trends between NNW and NNE. All of the textures and fabrics described herein come from vertical thin-sections cut so that they are roughly orthogonal to inclusion trails and matrix fabrics.

This study examines the relationship between inclusion trail microstructure, compositional zoning and mineral reactions in simple and calcareous pelites for the area around the Spring Hill Synform. In an effort to establish these relationships, two samples of low-Al pelite from the Cram Hill Formation and two samples of calc-pelite from the Moretown and Rowe Formations are discussed in detail. The definitions for low-Al and calc-pelite used here are somewhat arbitrary but are based on mineral assemblages present in the rocks, which are of course related to their bulk compositions. The bulk compositions do cluster together on an AFM projection as will be discussed later in this chapter. Low-Al or simple pelites are considered here to be garnet, biotite, quartz schists and phyllites that may contain chlorite and/or staurolite depending on metamorphic grade with only minor plagioclase and lacking epidote. The term calc-pelite used here follows the nomenclature of Menard and Spear (1993) for schists and phyllites that contain garnet, biotite, quartz with abundant epidote and plagioclase as well as chlorite and/or staurolite depending on grade.

The two samples of low-Al pelites, V436A and V436B are from the Ordovician Cram Hill Formation and one calc-pelite, V261, from the Cambrian Rowe formation and the other calc-pelite, V257, is from the Moretown Formation. The two low-Al pelites have been previously described as they contain garnet porphyroblasts with monazite inclusions that were used for geochronologic studies, (see chapters 1 and 2 of this dissertation).

Sample V436B is a garnet-muscovite schist with numerous garnet porphyroblasts in a matrix dominated by muscovite and to a lesser extent biotite, quartz and ilmenite (Fig. 2). Garnet porphyroblasts tend to be equant and contain well-developed inclusion trails. Most garnet porphyroblasts contain several euhedral bands of graphite accumulations that are parallel to crystal faces (Fig. 2). Inclusion trails in the cores are dominated by quartz whereas the inclusion trails in the rims are dominated by graphite. The trails are generally sigmoidal in the cores and become more tightly curved at the core/rim interface. Inclusion trails in the rim are roughly orthogonal to those in the garnet cores and are also truncated by the strongly developed cleavage in the matrix comprised predominantly of muscovite. Plagioclase and epidote were not found either as an included phase or in the matrix.

Sample 436A is a garnet-muscovite-quartz schist containing garnet with distinctly equant cores and elongate rims, in a matrix of muscovite, quartz and lesser biotite and ilmenite (Fig. 3). The matrix contains roughly equal modal proportions of quartz and muscovite with minor biotite and rare plagioclase porphyroblasts. Both garnet cores and rims contain well-developed inclusion trails (Fig. 3) with inclusions in the cores dominated by quartz and inclusions in garnet rims dominated by ilmenite. Inclusion trails in the cores are sigmoidal and tend to be orthogonal to inclusion trail in the rims at the core/rim interface (Fig. 3). Elongate garnet grains or garnet rims follow muscovite seams in the matrix and as such the inclusion trails are continuous with the matrix fabric.

Sample 261A is a garnet-muscovite-biotite- plagioclase schist from the Cambrian Rowe formation with few garnet porphyroblasts in a quartz-rich matrix with relatively abundant plagioclase. The matrix contains a widely spaced crenulation cleavage defined by both muscovite and quartz (Fig. 4). Garnet porphyroblasts have spectacular inclusion trails that curve through 180° or more. Garnet cores contain quartz-feldspar rich zones but inclusion trails are dominated by elongate grains of ilmenite and smaller grains of quartz and plagioclase (Fig. 4). Epidote inclusions in garnet were found but were not abundant and no epidote was found in the matrix.

Sample V257 is a garnet-muscovite-biotite-quartz schist from the Ordovician Moretown formation with abundant garnet porphyroblasts in a muscovite-biotite-plagioclase rich matrix. The matrix contains well-developed spaced cleavage defined by both muscovite and biotite. Garnet porphyroblasts have sigmoidal inclusion trails that contain abundant plagioclase and epidote and quartz but epidote is not present in the matrix (Fig. 5).

## METHODS AND RESULTS

### *Mineral Compositions and Compositional Maps*

Electron microprobe point analyses and X-ray compositional maps were collected using the JEOL 840 microprobe at James Cook University.  X-ray compositional maps were collected for garnet porphyroblasts before point analyses so that zoning patters and compositional domains could be identified. Compositional maps were collected for garnet and point analyses were collected for garnet, muscovite, biotite as well as plagioclase and epidote where present. Mineral compositions were determined by quantitative energy dispersive analysis using an accelerating potential of 15 kV and a probe current of 10 nA. Standard ZAF corrections were used to determine oxide percentages. Analyses were done in triplicate for each area of interest and then mean values were used for all calculations. Plagioclase and epidote inclusions were analysed along with surrounding host (garnet) from cores through to rims for the calc-pelites. Mineral pairs were analysed for all microstructural positions and compositional domains that could be identified in garnet porphyroblasts. Matrix minerals were analysed in several locations and mean values were used. Representative probe data for the 4 samples are given in Tables 1-4 and a full set of microprobe data used for this study can be found in the appendix.

Compositional zoning preserved in garnet porphyroblasts provides one of the most fundamental pieces of information related to the history of mineral growth in metamorphic rocks. Garnets from southeastern Vermont commonly preserve complex zoning. Combined WDS/EDS compositional maps were collected on the JEOL 840 microprobe at James Cook University. Ca, Mg, and Mn maps were collected on the WDS spectrometers and Si, Al Ti, Fe, P, Na, K and Ti on the EDS detector. Porphyroblasts were mapped as 512x512 pixel images with step sizes or pixel size determined by the size of the area being mapped. Ca, Mg, and Mn compositional maps of representative garnet porphyroblasts from low-Al pelites and calc-pelites are shown in figures 6 through 9.

The two low-Al pelites preserve similar zoning patterns. Both samples have garnets with Mn-rich cores with Mn content decreasing sharply from garnet core to rim. Garnet rims have only trace amounts of Mn in a broad band around garnet rims. Mn zoning patterns generally mimic grain shapes but are somewhat rounded (Fig. 6 and 7). Compositional maps of Mg show the reverse of Mn with Mg content lowest in the cores and increasing towards the rims. Maps of V436B show a continuous increase from core to rim with highest Mg content at the rim (Fig. 6). Maps of V436A show a similar pattern for the equant portions of garnet porphyroblasts but elongate overgrowths have lower Mg content (Fig. 7). Point analyses from the overgrowths are extremely almandine rich with very low concentrations of grossular, spessartine and pyrope (see Table. 2). Again, Mg zoning patterns generally mimic the grain shapes but are somewhat rounded. Ca zoning patterns for both samples are far more striking. Compositional maps show that garnet cores have high Ca zones that are strongly euhedral. In sample V436B, thin-sections containing cuts through the absolute cores of garnet porphyroblasts are marked by a small zone of lower Ca. Apart from the absolute cores, the Ca content decreases from the core towards the rim. Ca content reaches a minimum just inside the garnet rims before increasing sharply at the garnet edge. Compositional maps for V436A show very similar patterns for Ca, with it being highest in the cores and decreasing sharply and then increasing sharply at the rims of the equant part of the grains. In this case the Ca increase forms a very thin film (< 10 μm) around the edge of the equant part of grain (see Fig. 7). Zoning patterns for all elements are also roughly continuous around the grains and do not show any truncations that might indicate later alteration.

Compositional maps for the two calc-pelites also exhibit similar zoning patterns. Mn content is highest in the garnet cores and decreases towards the rims (Figs. 8 and 9) whereas Mg is lowest in the garnet cores and highest at the garnet rims. The example provided from sample V257 has zoning patterns for Mn and Mg that generally mimic the grain shape. The same is true for sample V261 but garnet porphyroblasts have complicated shapes due to the complex inclusion trails included within the grain (Fig. 8). Ca zoning patterns in the calc-pelites also tend to be more complex than for other elements. The general zoning pattern exhibited in the compositional maps is with Ca content highest in the garnet cores and decreasing towards the rims. However, within this general pattern, Ca content is patchy at a similar scale to the size of the inclusions, 0.1-0.2 mm (Figs. 8 and 9).

### ***Bulk Compositions and Chemical Systems***

Estimates of the bulk composition of a rock used to construct P-T pseudosections can be obtained by integrating point-counting statistics along with microprobe data for each of the minerals present in a thin section. At best, this method would provide an estimate of the bulk composition as these samples contain complex inclusion suites and with many phases exhibiting chemical zoning. It is also difficult to determine the identity of opaque phases in transmitted light. There can be a high degree of dependence of predicted mineral reactions on bulk composition (Tinkham and others, 2001). For these reasons, major element bulk-rock analyses were obtained by XRF analysis from the crushed fraction for samples discussed herein. Hand specimen size pieces that appeared to be homogeneous at the scale of the hand sample and which characterized the mineral assemblages present in thin-section were crushed and prepared for XRF analysis. The samples showed no indication of alteration such as quartz veining or iron oxide staining. Table 5 contains the major element data for samples collected for the study area along with data for Shaw's average pelite (Shaw 1956) for comparison. The bulk compositions were plotted on an AFM projection using compositions corrected for $Al_2O_3$ by subtracting $Al_2O_3$ in proportion to $Na_2Al_2O_4$ and $CaAl_2O_4$ molecules (Fig. 10). There is no absolute correct way to reduce the larger chemical system down to its KFMASH equivalent for the purposes of projecting. In this case, the AFM projections are only used as a guide because the pseudosections are calculated in the expanded system. The low-Al pelites all plot between the g-chl and FeO-MgO tie-lines on the AFM projection and the calc pelites all project below the FeO-MgO line. Although they are not discussed in detail in this chapter, a series of high-Al pelite are included in figure 10 and plot above the g-chl tie-line.

P-T pseudosections used for this study were modelled in the system MnO-$Na_2O$-CaO-$K_2O$-FeO-MgO-$Al_2O_3$-$SiO_2$-$H_2O$ (MnNCKFMASH). Although the simplified system, $K_2O$-FeO-MgO-$Al_2O_3$-$SiO_2$-$H_2O$ (KFMASH), has been shown to be very useful for establishing the phase relation of the pelitic rocks, it cannot be used to model the relationship between the grossular component of garnet and plagioclase. This relationship becomes increasingly important in calcareous pelites where garnet and plagioclase can be the dominant phases throughout much reaction history for those rocks. In addition, the compositions of garnet and plagioclase are highly dependent on pressure, which makes this pair ideally suited to thermobarometric calculations.

### *Pseudosections*

P-T pseudosections for the two low-Al pelites (V436B and V436A) and the two calc-pelites (V261 and V257) and are shown in figures 11 and 12. As described above the pseudosections were modelled in the MnNCKFMASH system so that the phase relations of a full set of minerals commonly found in pelitic rocks including Ca bearing phases could be modelled. P-T pseudosections were constructed according to the methods described by Powell and others (1998) using the program THERMOCALC version 3.21 and the Holland and Powell (1998) dataset with the most recent upgrades. A copy of the data used to calculate pseudosection is given in the appendix. Pseudosections were constructed to clarify the progression of mineral reactions available to low-Al pelites in contrast to calc-pelites. The system MnNCKFMASH was used because Mn has been recognised as having significant effect on garnet-chlorite stability as well as controlling the position of the garnet producing reactions (Symmes and Ferry, 1992; Mahar and others 1997). Additionally, Tinkham and others (2001) clearly establish the effect of $Al_20_3$ and Mg/Mg+Fe on mineral stability. The absolute content of $Al_2O_3$ does clearly have an effect on the stability of chloritoid or the relative stability of biotite and staurolite. However, the amount of $Al_2O_3$ available for garnet and staurolite producing reactions can be highly dependent on CaO in the bulk composition as both anorthite and zoisite are extremely aluminous phases.

An important difference in the construction of pseudosections in the expanded system is that there is no petrogenetic grid to use as a base. Most of the univariant reactions in KFMASH can be modelled with quartz, muscovite and $H_2O$ in excess such that 4 additional phases are required to define a univariant line in P-T space. A univariant reaction in the expanded system MnNCKFMASH would require that 7 phases are involved in the reaction in addition to quartz, muscovite and $H_20$. As such, there are no true invariant points or univariant reactions on any of these pseudosections. The pseudosections are calculated to include quartz, muscovite, plagioclase, zoisite, chlorite, biotite, garnet, staurolite, chloritoid, alumino-silicate, and H2O. This selection of phases is thought to represent as closely as possible the phases that were likely to have been present during some stage of the rocks evolution through P-T space. Chloritoid was not found to be stable for any bulk composition as was expected because the compositions used are all below the garnet-chlorite tie-line on an AFM projection (see Fig. 10). The stability of cordierite is limited to low pressure. Even though the area being studied is thought to have evolved at moderate to high pressure, stability fields containing cordierite were checked. No cordierite bearing fields were found in any of the examined bulk compositions. The choice of an epidote group mineral is problematic because ferric iron is not included in the chemical system being used. Epidote is not found as a matrix mineral in any of the samples that have been examined but occurs as an included phase in garnet in the calc-pelite samples whereas clinozoisite/zoisite have not been recognised at all. Although clinozoisite and epidote may be more comparable, clinozoisite has a smaller stability field on the pseudosection and as a result zoisite was used to try to model the maximum stability of an epidote group mineral.

### ***Thermobarometry***

Thermobarometric calculations were done using THERMOCALC V3.21 and the Holland and Powell 1998 dataset with subsequent upgrades. Pressure and temperature conditions for equilibrium assemblages were estimated using average P-T mode for sets of independent reactions following the methods of Powell and Holland (1994). Estimates of the peak P-T conditions were made using the composition of garnet rims along with compositions of matrix minerals using the mineral data given if Tables 1-4. Several samples were chosen with inclusion suites so that a series of P-T points relating to garnet growth could be calculated in addition to the peak P-T conditions. The calc-pelites that were used contain plagioclase and epidote inclusions whereas the low-Al pelites do not. Compositions from garnet and plagioclase pairs were used with average compositions for muscovite and biotite. Table 6 summarises the results of P-T calculations used for this study along with results from Chapter 3 of this dissertation. The calc-pelites are well suited to thermobarometric calculations because they contain garnet, plagioclase and biotite and samples that contained plagioclase as inclusions were targeted for this study. In contrast, the low-Al pelites lack plagioclase and as such, temperature and pressure estimates were done independently as average-pressure (ave-P) and average-temperature (ave-T). The P-T conditions for these samples are not as well constrained but show general agreement with calc pelites as well as the high-Al pelites.

The thermobarometric estimates described above are essentially independent of the pseudosections because they use mineral data collected by microprobe analysis that do not rely on bulk composition data and have no relationship to mineral modes. However, the calculation of modal isopleths (modal contours) and compositional isopleths (compositional contours) is inherent in the construction of P-T pseudosections. This provides another independent means for determining P-T points for minerals of known composition. The intersections of compositional isopleths for the measured values of garnet cores were also calculated to estimate the P-T conditions for the onset of garnet growth. All of the compositional isopleths should intersect at a point in P-T space if the bulk composition used reflects the composition of the rock at the time garnet growth began (Foster and others 2002). The intersections of the isopleths should diverge as garnet growth continues and the effective bulk composition evolves away from the growing phase, in this case garnet. The THERMOCALC datafile is constructed such that isopleths of Fe-garnet (F(g)), Mn-garnet (M(g)) and Ca-garnet (C(g)) can be calculated. In turn, if the mineral assemblage present at the onset of garnet growth is known then the intersections of the isopleths can be calculated. The P-T positions of the intersections of these three compositional isopleths were calculated for the low-Al pelites and the calc-pelites and the results are summarised in Table 6.

The peak temperature condition recorded in this region is □ 650°C at 11.5 kbars, which was calculated using the composition of the garnet rim along with the average composition of matrix mineral for sample V261A (calc-pelite). This is thought to represent the peak temperature for the rocks flanking the Chester and Athens Domes. These results are consistent with calculations from the other calc-pelite, V257. The highest pressure recorded for calc-pelites was 12.6 kbars, which was calculated using a plagioclase inclusion trapped near the edge of a garnet in V261. These P-T conditions were well within the diagnostics guidelines outlines by Powell and Holland (1994) and are thought to represent a reasonable estimate for peak conditions. A pressure of 13.6 kbars was calculated for the garnet median in a high-Al pelite from the Cram Hill formation that may represent the highest pressure experienced by these samples, which is at a slightly lower temperature than the peak recorded in the calc-pelites. Temperature estimates for the low-Al pelites are much less well constrained, which may in part due to the small number of end members available for use in calculations. However, pressure estimates are in good agreement with the calc-pelites with ave-P conditions calculated at  12 kbars.

As described above, estimates for the P-T conditions for the garnet cores were calculated in two ways: (1) using average P-T mode in THERMOCALC and (2) by calculating intersecting isopleths for composition of garnet cores. Average P-T calculations for garnet cores were not possible for the low-Al pelites. However, the calc-pelites yielded consistent results showing that garnet cores equilibrated at lower temperature and pressure than garnet rims. The average P-T conditions recorded for garnet cores was  570°C and 8-9 kbars. These results are also consistent with results from high-Al pelites (V240 and V634) which recorded P-T conditions for garnet cores at  550°C and 9.5 kbars using a different set of equilibria (see Table 6). The intersections of the isopleths were calculated for the assemblage chl-bi-g-pl-mu (5 in Fig. 12) for the calc-pelites and for the assemblage chl-g-pl-mu (5 in Fig. 11) for the low-Al pelites. The composition for the garnet cores or the most primitive garnet was chosen as the point with the highest spessartine content rather than estimating the geometric center. Results from the intersecting isopleths for the calc-pelites are all tightly clustered at 525°C and 7.0 kbars for V261A and 535°C and 7.0 kbars for V257. The 2 low-Al pelites do not show the same consistency. Sample V436A has intersections that are tightly clustered at 525°C and 4.5 kbars whereas V436A results range fro 513-528°C and 3.4-7.0 kbars.

## INTERPRETATIONS

### *General Phase Relationships and Pseudosections*

Although there are no true invariant points or univariant reactions in the MnNCKFMASH system, all of the calculated pseudosections contain three trivariant fields, labelled 11, 12 and 13 (Figs. 11 through 12), that can be thought of effectively as MnNCKFMASH univariant reactions. These three trivariant fields intersect at a small divariant field (labelled A), which in turn acts as the chloritoid-cordierite invariant point. In contrast to a true invariant point, the position of the divariant field shifts with varying bulk composition (see Figs. 11 and 12). The three trivariant fields (labelled 11, 12, and 13 on figures 11 and 12) can be thought of as the reactions:

11) chlorite + garnet + muscovite → biotite + staurolite + $H_2O$
12) biotite + staurolite → garnet + alumino-silicate + $H_2O$
13) chlorite + muscovite → alumino-silicate + biotite + $H_2O$.

As the trivariant fields are effectively pseudo-univariant reactions, they occupy very little space on the diagram. These fields mark the limited coexistence of reacting phases, e.g. staurolite and chlorite in field 11. These fields or reactions are most significant for tectonic environments that evolve at low to moderate pressures. At higher pressure, it is the 4-variant and 5-variant fields that dominate the topology of the calc-pelite pseudosections (Fig. 12) as well as the 6-variant and 7-variant fields in low-Al pelites pseudosections (Fig. 11).

Fields 11, 12 and 13 were found to be stable for all bulk compositions and related work on high-Al pelites (Fig. 10) show that that these fields are stable for those compositions as well. There are, however, important shifts in the stability of mineral assemblages with varying bulk composition that are illustrated on the pseudosections shown in figures 11 and 12. The most significant of these shifts seen for the bulk compositions examined here is the relative stability of biotite and plagioclase. As would be expected, the stability range for plagioclase is highly dependent on bulk composition, specifically CaO and $Na_2O$ and corresponding $Al_2O_3$. Plagioclase is stable across the entire P-T range for the calc-pelites whereas plagioclase becomes unstable in the low-Al pelite pseudosection at high pressure (Figs. 11 and 12). The limit of plagioclase stability (labelled as *pl-out* on Fig. 11) shifts to higher pressure with increasing temperature. Similarly, biotite has a much smaller stability field for the low-Al pelites than for the calc-pelites. Biotite is stable across most of the calc-pelite pseudosections except for the region at high-pressure and low temperature (above the line labelled *bi-in* on Fig. 12). For low Al-pelites, biotite stability is limited to low pressure and high temperature (below the *bi-in* line in Fig. 11).

### Garnet Producing Reactions

The relative stability of biotite, zoisite and plagioclase has significance for garnet producing reactions. Garnet growth occurs as the result of chlorite breakdown regardless of the bulk composition but the exact equilibria involved in that reaction is dependent on the pressure at which garnet growth commences.

For the low-Al pelites, garnet growth is predicted to occur in the absence of biotite except at very low pressures where there is limited stability of biotite before garnet (below field 1 on Fig. 11). At low pressure (□ 1-5 kbars) the onset of garnet growth occurs in the absence of any calcic phase or biotite. However, above □ 5 kbars garnet growth is predicted to occur in the presence of zoisite and plagioclase or just zoisite. There is a small field where plagioclase and zoisite coexist (labelled 2 on Fig. 11) above which plagioclase becomes unstable. The position of that transition is significant because garnet growth in most Barrovian metamorphic sequences should occur around that transition.

For the calc-pelites, plagioclase was calculated to be stable across the entire P-T range except for a small area at very high pressure and low temperature (Fig. 12) such that the addition of garnet to the mineral assemblage must occur in the presence of plagioclase. In this case the compositions of plagioclase and coexisting garnet should be controlled by pressure and temperature. Garnet growth below the *bi-in* line should take place in equilibrium with biotite and plagioclase below 6 kbars (field 5 in Fig. 12) or in equilibrium with biotite, zoisite and plagioclase above 6 kbars (field 2 in Fig. 12). Above the *bi-in* line, garnet growth occurs in the absence of biotite and solely with the calcic phases zoisite and plagioclase.

### P-T Evolution

One of the limitations of P-T pseudosections is that they are calculated for a fixed bulk composition such that every point on the pseudosection represents the equilibrium assemblage with a fixed mineral composition for that point. This assumption may not be valid for all of metamorphic P-T space, especially for rocks that contain high modal abundance of garnet at lower amphibolite facies where a large degree of fractionation can be a factor. If the bulk composition used to model a sample adequately represents the sample then the pseudosection should correctly model the initial portion of garnet bearing fields in terms of garnet composition and mode (Vance and Mahar, 1998). For the three samples that have tightly clustered compositional isopleths, the position of the intersection should represent the P-T conditions for the earliest phase of garnet growth. For the two calc-pelites, the position of for the garnet cores (□ 525°C and 7 kbars) is 25-50°C higher than the garn-in line. Vance and Mahar (1998) report similar results, they describe and infer a maximum position P-T position for the onset of garnet growth. Garnet core compositions obtained by microprobe analysis typically intersect at garnet modal isopleths of □ 1%. This may in part be the result of garnet compositions being partly modified by a small degree of post-growth diffusion. Given that the modal percent is calculated in the absence of quartz, the true modal abundance will be less than 1% and in practice the 1 modal % line may be a better indication of the true garnet-in line.

Average P-T conditions calculated for garnet cores are found at to be 50°C and 2 kbars higher than the position for intersection of compositional isopleths. These calculations were done using matrix muscovite and biotite and may be artificially shifted towards higher temperatures. The isopleths are interpreted to represent the minimum conditions for the onset of garnet growth and the average P-T for the core are thought to represent the maximum for the start of garnet growth. Regardless of the exact starting point, garnet growth is inferred to have occurred along an up-pressure path starting at or above 525°C and 7 kbars reaching a maximum of 12.5 kbars and 650°C. An interpreted P-T path for these samples showing the P-T points and associated errors for sample V261 is given in figure 13.

### *P-T Path in Relation to the Pseudosections*

The P-T path given in figure 13a was drawn using the P-T estimates from the calc-pelites as a guide. The earliest preserved P-T conditions for the calc-pelites are taken as the positions of the intersections of isopleths for garnet cores. This indicates that garnet growth began in the chl-bi-g-pl-mu field (5 in Fig. 12**)** and requires that the garnet in reaction be over-stepped by 50°C. Given that both of the calc pelites have garnet porphyroblasts with epidote inclusions, the pre-garnet assemblage would likely have evolved above 5kbars. Once garnet growth began, epidote must have been removed from the assemblage as it only occurs as an included phase. The interpreted P-T path in figure 13a shows that garnet growth would have continued along an up-pressure path across the chl-bi-g-pl-mu field (5 in Fig. 12) reaching peak pressure just past the *chl-out* (Fig. 13a) reaction in the bi-g-pl-mu field (6 in Figs. 12). The pseudosections predict that chlorite remains stable well past the zo-out reactions such that garnet and biotite growth occurs at the expense of chlorite to the *chl-out* as suggested by Menard and Spear (1993). Garnet growth should cease at peak temperature and pressure as modal biotite is predicted to increase along a decompression path in the bi-g-pl-mu field (6 in Fig. 12). This path suggests a very simple reaction history with garnet and biotite growth at the expense of chlorite spanning 100°C and 5 kbars.

If the same path is applied to the low-Al pelites, garnet growth is predicted to occur outside the biotite stable region and straddling the *plag-out* reaction (Fig. 13b). This path predicts that zoisite should have been stable before garnet growth for these samples as well, but no there is no evidence that zoisite grew in these samples. A P-T path was plotted for sample V436B that begins at the position of the intersecting isopleths for V436B and follows a similar as in figure 13a. Garnet core isopleths for sample V436A intersect at lower pressure than the calc-pelites (□ 4 kbars) that supports the lack of epidote in this sample. Regardless of the initial pressure, garnet growth would have occurred in chl-g- mu field probably initially in the presence of plagioclase and then without (Fig. 13b). If garnet growth occurred along this up-pressure path, garnet the composition should become more calcic, which would effectively remove Ca from the effective bulk composition and further depress the *plag-out* line to lower pressure (Fig. 13b). Peak pressure calculated for this sample is plotted on figure 13b and matches the peak pressure for the modelled P-T path at □ 625°C. In this scenario, garnet growth would have continued from a single reaction across □100°C and as much as 8 kbars. This places the peak conditions for this sample in the g-mu field (7 in Fig. 11), which is effectively the assemblage for this sample. Biotite is present in the sample as a late phase overgrowing matrix (Fig. 2), which is further supported by the pseudosection, as the decompression path would predict late biotite growth in the mu-bi-g-pl field (9 in Fig. 11).

### *Mineral Zoning and Truncations*

The predicted P-T paths for these samples (Figs. 13a and 13b) as plotted on the pseudosections suggest that garnet growth resulted from the breakdown of chlorite over a large range of P-T space. The P-T positions for garnet cores and rims for both the calc-pelites and the low-Al pelites suggest that garnet growth began near the garnet-in reaction and proceeded to the chlorite out line at high pressure (Fig. 13). General zoning patterns for the elements Mg and Mn in garnet porphyroblasts for the samples described above are consistent with garnet growth through prograde reactions (Tracy, 1982). The general pattern of Ca zoning for the calc-pelites is also consistent with prograde growth whereas the Ca zoning in low-Al pelites is not. One striking feature present in the Ca maps for the low-Al pelites is the sharpness of the zoning patterns, which is not present in the compositional maps for the calc-pelites (e.g., Fig. 6 vs. Fig 8). Both the calc-pelites and low-Al pelites preserve complex inclusions in garnet and in the case of the low-Al pelites there is a direct correlation between the shifts in Ca content and microstructural relationships. Chernoff and Carlson (1997) reported similar zoning patterns to those reported here for the low-Al pelites, which they described as disequilibrium textures. Several grains were mapped from each sample and all the maps show a direct correlation to microstructures. Compositional contours were plotted on the pseudosections for V261A (Fig. 14) and V436B (Fig. 15) so that this relationship between Ca zoning and microstructure could be further explored.

The predicted path for V261 roughly follows the compositional contours for grossular and lies between the 16% and 20% grossular lines (Fig. 14b). With increasing temperature garnet compositions should shift slightly towards lower grossular content and with increasing pressure, the grossular content should remain constant. The predicted path and the zoning patterns are in excellent agreement with the pseudosection. The inclusion trails in the sample shown in figure 14c indicate that the garnet core overgrew an early crenulation hinge shown as $S_a$ and $S_b$ and was then strongly truncated by a later fabric $S_c$. This fabric should indicate a hiatus in mineral growth and yet there is no significant shift in composition across the boundary. These growth events are interpreted to represent distinct periods of garnet growth but in this case we should not expect to see any significant composition shifts because the mineral assemblage and grossular content are effectively buffered by the presence of plagioclase. Even if there is a significant shift in the P-T conditions for garnet growth, there are no major compositional shifts that should occur as the majority of the P-T path remains within a single field. Garnets in this sample also grew in the presence of biotite, which produced a similar effect for Mg zoning (Fig. 8).

In contrast, the path shown for the low-Al pelites crosses the pl-out reaction (Fig. 15a) and as such it would be expected there should be some evidence preserved in the zoning for these samples. The shape of the grossular contours is not significantly different from those in figure 14a, but the zoning patterns that result are strikingly different. Again, in the example given in figure 15c, garnet cores have overgrown an early vertical fabric $S_a$ that is strongly truncated by a later horizontal fabric $S_b$ (Fig. 15c). In this case there is a sharp compositional shift that correlates directly with that truncation. Garnet cores (grossular content labelled 9 on figure 15b) for this sample are interpreted to have grown at the P-T conditions shown for the intersecting isopleths. The bulk of the garnet core shown in figure 15b grew at some later stage in coincident with the development of the curvature of $S_a$ or the truncating fabric. Zoning patters remain sharp, which suggests that growth occurred rapidly and, for this case is thought to coincide with the *pl-out* reaction. This sample also contains a relatively high modal proportion of garnet, which would have the effect of strongly partitioning Ca from the bulk composition, especially if garnet growth occurred coincident with the loss of plagioclase. This would also have the effect of further lowering the pl-out line and shifting the grossular contours to lower temperature above that line (Fig. 15a). The bulk of garnet growth occurred well above the garnet-in reaction and in direct response to deformation.

## DISCUSSION

### *Equilibrium and Reaction Overstepping*

The P-T pseudosections for each of the samples described herein, combined with the microstructure, allow the evolution of each mineral assemblage to be modelled and reveal the power of this approach for examining mineral reaction history and P-T paths. A qualitative assessment of mineral stability can be easily inferred from each pseudosection but they can also be used to compare real mineral compositional data and mineral modes with calculated mineral stability. This approach provides significant insight into the nature of equilibrium during metamorphism.

The intersection of the garnet isopleths at a point in P-T space for the three independent compositional variables is a clear indication that the bulk composition used to construct the pseudosections represents that for the sample at the time garnet growth began. In these cases the garnet composition used represents the first garnet to grow in that rock, and, most significantly, the compositional contours quickly diverge for garnet compositions away from the core as the effective bulk composition evolved by fractionating out garnet (Vance and Mahar 1998). If it can be argued that the bulk composition used to construct the pseudosection represents the composition of the garnet-forming rock then the lack of an intersection could be the result of a garnet composition that is not the most primitive, or the result of garnet growth well beyond the garnet-in reaction. However, this is not a simple question to resolve as evidence to suggest a lack of shifting bulk composition will be hard to find. The samples discussed herein all retain strong zoning profiles, which is important for establishing the position of garnet cores. For the one example where the isopleths in the garnet core did not intersect, V436A, every effort was made to find the true garnet core. Given that none of the other samples show any strong evidence for volume loss it seems unlikely that this one underwent any (see Table 6). Consequently, the lack of an intersection most likely resulted from overstepping of the garnet-in reaction.

### *Equilibrium and Deformation*

P-T pseudosections are constructed assuming an equilibrium mineral assemblage across all of P-T space such that if the bulk composition is known, lines of zero modal proportion can be calculated (Powell and others 1998). The relationships involved in the calculations cannot take into account other variables such as deformation and kinetic factors in real rocks (e.g., Bell & Hayward, 1991; Chernoff and Carlson, 1997; Spear and Daniel, 2001). If initial garnet growth occurs rapidly by overstepping reactions, then the initial garnet modes may be higher than those predicted by THERMOCALC, and as such the initial garnet compositions may not match those predicted by THERMOCALC, but the bulk composition could still have been that at the time that garnet growth began. Where the compositions were measured using a microprobe, and the isopleths do intersect at a point, then the bulk composition used for the pseudosection must be the bulk composition of the that rock at the time garnet growth began. If garnet grows across a single field via a single reaction then the composition and zoning should reflect the temperature and pressure at which that mineral grew. However, if garnet growth occurs across a mineral stability field boundary, then there should be some reflection of the change in the mineral reaction present in garnet zoning but there need not be anything in the matrix to suggest that a phase was lost or gained. Where a well-constrained P-T path placed on a pseudosection crosses such a boundary, there should be some evidence such as that shown in figure 15. The position of the plagioclase-out reaction and the zoning patterns present in garnet porphyroblasts from V436A and V436B (Figs. 6 and 7) provide strong evidence for garnet growth at or above the plagioclase-out reaction. If the bulk of garnet growth occurs at or above that reaction, this would suggest a certain degree of disequilibrium, as the garnet-in reaction would have to be significantly overstepped. The zoning patterns are consistent across all porphyroblasts in thin-section, which suggests that this is a rock-wide feature and that the intergranular diffusion must have been rapid. This evidence combined with the clear link between zoning and truncated inclusion trails suggests that deformation must also play a key role in influencing metamorphic reactions.

### *Metamorphic and Microstructural Significance*

The thermobarometric estimates and modelled P-T paths presented herein are consistent with those given for high-Al pelites discussed in chapter 3 of this thesis. These P-T paths suggest that the bulk of garnet growth occurred along an up-pressure path with heating to peak pressures of 13-14 kbars, and with peak temperatures reached along a decompression path. However, there is little evidence for significant heating along this decompression path because peak temperatures recorded here developed immediately after peak pressure and above 10 kbars (see Table 6). The predicted P-T paths given for both samples suggests that garnet growth should have occurred over a temperature range of high 100°C and pressures ranging as much 8 kbars. A continuous mineral reaction progressing uninterrupted over this range seems unlikely. The complex inclusion trails preserved in these samples provide further evidence that garnet growth did not occur as continuous reaction in time and P-T space, but rather as discreet episodic growth events. Figure 16 highlights the relationship between mineral zoning and microstructural truncations in three garnet porphyroblast. All three of these examples contain inclusion trails with near orthogonal geometries that are interpreted to represent discrete foliations that formed along early porphyroblast rims before being overgrown in a subsequent garnet growth event (see also Bell and Johnson, 1989). In some cases the microstructural truncation can be linked to a probable reaction (loss of plagioclase) as in sample V436B (Fig. 16a) and in some cases not, as in sample V261A (Fig. 16c). However, the presence of truncations suggests that garnet growth must have ceased during the development of younger foliations and recommenced at some later time.

Bell and others (1998) identified 4 distinct periods of garnet growth (referred to as FIAs 1-4) with only the last event relating to matrix, in rocks from this region. Garnet porphyroblasts with inclusion trails truncated by matrix fabrics are a common feature of the study area (e.g., Figs. 16a and 16c), which further suggests that deformation continued after porphyroblast growth had stopped for much of the area. It would be expected that if the bulk of garnet growth occurred along an up pressure path with little heating during decompression then the bulk of porphyroblasts should be truncated by later foliations. Some growth must have occurred during decompression as some samples contain garnet porphyroblasts with rims that are continuous with matrix microstructures (e.g., Fig. 16b). Compositional zoning patterns present in porphyroblasts from this sample are consistent with this relatively late garnet growth. Garnet rims show a reversal in Mg content that is not seen in other samples and the thin Ca spike at the core/rim interface is interpreted to correlate with garnet rim for V436B (Fig. 16).

### *Regional and Tectonic Significance*

Acadian metamorphism in southeast Vermont was previously thought to have peaked at about 680°C and 10.5kb at 395-385 Ma and has been generally considered to be a consequence of crustal thickening alone with little or no magmatic heating (Armstrong and others, 1992; Ratcliffe and others, 1992; Ratcliffe and Armstrong, 1995). Thermobarometric work done as part of this study suggests that temperatures reaching 650°C are only preserved locally. The peak temperatures were most likely reached close to the start of decompression from peak pressures that had reached 13-14 kbars. Temperatures recorded using garnet core compositions are consistent in the samples used herein and show that garnet growth began around 525°C. The pressure estimates that coincide with these temperatures vary by from 4 to 7 kbars. If these estimates are correct, this suggests that the region would have undergone rapid burial at the onset of metamorphism. This initial loading may have been the result of burial. However, the complex inclusion trail geometries and high peak pressure are more consistent crustal thickening due to orogenic shortening with a component of subduction. The resulting over-thickened crust would have quickly become unstable resulting in rapid exhumation with little or no heating. Monazite ages presented in the first chapter suggest that metamorphic mineral growth began in the early Silurian (430 Ma) and the thermobarometric data presented herein indicate that garnet growth began at moderate to high pressures and continued along an up-pressure path. Current stratigraphic and tectonic models (e.g., Bell and others 1998; Ratcliffe and others, 1997) assign a Siluro-Devonian age to the cover sequence, which is thought to have undergone the same peak metamorphism as the underlying Cambro-Ordovician rocks. The geochronologic and thermobarometric results suggest that the thick package of rocks must have been assembled by the Silurian, which brings into question the stratigraphic age assignments for the cover rocks or the timing of juxtaposition. Further geochronologic studies are needed to better constrain the timing for the onset of metamorphism in both basement and cover rocks along the axis of the New England Appalachians before tectonic models can be fully resolved.

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