Quantifying the Pressure, Temperature, and Timing of Metamorphism in the Montresor Belt, Nunavut, Canada

by

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Abstract

P-T-t conditions are determined for the Montresor belt (Rae Province, Nunavut) using modern thermodynamic modeling and in-situ U-Th-Pb monazite geochronology. Phase equilibrium modeling yields peak P-T estimates of 355 - 455°C and <4200 bar for the upper Montresor belt and 500 - 580°C and <4000 bar for the lower Montresor belt, with a high geothermal gradient of ca. 57°C/km during metamorphism. Forward modeling of garnet crystallization suggests growth along a clockwise, nearly isobaric P-T path from ca. 539 – 544°C and 3090 – 3140 bar. Chemical age dating of metamorphic monazite indicates peak P-T conditions occurred at ca. 1837 ± 8.6 Ma. Altered monazite domains suggest a fluid-mediated alteration event during cooling at ca. 1792 ± 10.1 Ma, associated with the emplacement of dykes into the lower Montresor group. These fluids increased the bulk rock K and caused modification to garnet growth zoning and mechanical fracturing of garnet.

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Table of Contents

Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Tables	vii
List of Figures	vii
List of Appendices	x
Chapter 1: Introduction	1
Chapter 2: Regional Geology	4
2.1 The Canadian Shield	4
2.2 The Montresor Belt	6
2.3 The Trans-Hudson Orogeny	11
2.4 Previous Work on the Montresor Belt	12
Chapter 3: Methods	14
3.1 Whole-Rock Chemistry	14
3.2 Electron Probe Micro-Analysis	14
3.3 X-Ray Micro Computed Tomography	15
3.4 Statistical Analysis of Garnet Distribution	16
3.5 Phase Equilibrium Modeling	20
3.6 Garnet Crystallization Modeling	23
3.7 Geochronology	26

Chapter 4: Results	29
4.1 Whole-Rock Chemistry	29
4.2 Petrography	32
4.3 Mineral Composition	40
4.4 X-Ray Micro Computed Tomography	43
4.5 Statistical Analysis of Garnet Distribution	50
4.6 Garnet Composition	53
4.7 Phase Equilibrium Modeling	73
4.8 Garnet Crystallization Modeling	84
4.8.1 Scenario 1: No Changes	86
4.8.2 Scenario 2: No Staurolite	93
4.8.3 Scenario 3: K-Metasomatism	102
4.9 Heating After Garnet Crystallization	111
4.10 Summary of Modeling Results	126
4.11 Geochronology	127
Chapter 5: Discussion	134
5.1 Clustering of Garnet Porphyroblasts	134
5.2 Variation in Garnet Composition	136
5.3 The Effect of Fluids on Mineral Composition and Texture	139
5.4 Interface vs. Diffusion Controlled Garnet Growth	143
5.5 Geochronology	147
5.6 Pressure-Temperature Estimates	150
5.7 Pressure-Temperature-Time Path	156

5.8 Low-Pressure High-Temperature Metamorphism	162
5.9 Potential for Polyphase Metamorphism	166
5.10 Limitations in Thermodynamic Modeling	169
Chapter 6: Conclusions	175
References	178
Appendices	188
A.1 Mineral Abbreviations	188
A.2 Trace Element Geochemistry and EPMA Mineral Chemistry	189
A.3 Monazite Trace Element Data	191
A.4 EPMA Garnet Compositional Maps for Additional Elements	193
A.5 THERIAK_DOMINO and THERIA_G Input Files	198

List of Tables

2.4.1	Sample Locations	13
4.1.1	Bulk Rock Chemistry	30
4.3.1	Amphibole Composition 14PBA-94A	42
4.6.1	Garnet Composition 14PBA-94A	54
4.6.2	Garnet Porphyroblast Core Composition	55
4.8.1	P-T-t Path for Scenario 1	87
4.8.2	P-T-t Path for Scenario 2	96
4.8.3	P-T-t Path for Scenario 3	105
4.9.1	P-T-t Path for Scenario 1 with a Late Thermal Pulse	115
4.9.2	P-T-t Path for Scenario 2 with a Late Thermal Pulse	115
4.11.1	Monazite Age Data 12PBA-27A – 1	132
4.11.2	Monazite Age Data 12PBA-27A – 2	133
A.2.1	Bulk-Rock Trace Element Geochemistry for Selected Samples	189
A.2.2	Example Calculation of Garnet Chemical Formula	189
A.2.3	Representative Mineral Chemistry for 12PBA-27A	190
A.3.1	Monazite Trace Element Data – 1	191
A.3.2	Monazite Trace Element Data – 2	192

List of Figures

2.1.1	Geological Map of the Western Churchill Province	5
2.2.1	Geological Map of the Montresor Belt	8
2.2.2	Schematic Cross Section of the Montresor Belt	10

3.3.1	Example of Rock Cores for XR- μ CT	17
3.3.2	Example of a Reconstructed XR- μ CT Slice	17
3.4.1	Schematic of Scale-Dependent Statistics	20
3.5.1	Gibbs Free Energy Minimization in Phase Equilibrium Modeling	22
4.1.1	AFM and ACF Bulk-Rock Geochemical Plots	31
4.2.1	Representative Thin Section Photos - 1	36
4.2.2	Representative Thin Section Photos - 2	39
4.3.1	BSE images of Amphibole Grains in 14PBA-94A	41
4.4.1	Representative XR- μ CT Cross Sections of Garnet-Bearing Samples	44
4.4.2	Visualization of the Garnet Distribution in 12PBA-27A & 14PBA-99A	45
4.4.3	Stereographic Projection of the Long/Short Axes of Garnet in 12PBA-27A	47
4.4.4	Example of Garnet Clustering in 14PBA-99A	48
4.4.5	Garnet Crystal Size Distributions for 12PBA-27A & 14PBA-99A	49
4.5.1	Reduce3D Results for Garnet in 12PBA-27A	52
4.6.1	Comparison of Ideal XR- μ CT and Thin Section Garnet Central Cut	54
4.6.2	EMPA Garnet Compositional Profiles 12PBA-27A - 1	57
4.6.3	EPMA Garnet Compositional Maps 12PBA-27A Size Class 1	58
4.6.4	EPMA Garnet Compositional Maps 12PBA-27A Size Class 2	60
4.6.5	EPMA Garnet Compositional Maps 12PBA-27A Size Class 7	62
4.6.6	EMPA Garnet Compositional Profiles 12PBA-27A - 2	64
4.6.7	EPMA Garnet Compositional Maps 12PBA-27A Size Class 13	66
4.6.8	EPMA Garnet Compositional Maps 14PBA-94A	68
4.6.9	EPMA Garnet Compositional Profiles 14PBA-99A	70

4.6.10	BSE Images with Location of EMPA traverses on Garnet	72
4.7.1	Phase Equilibrium Diagram for 14PBA-43B.	74
4.7.2	Phase Equilibrium Diagram and Garnet Isopleths for 12PBA-27A	75
4.7.3	Phase Equilibrium Diagrams for 14PBA-67A, -85A, -97A, and -100	77
4.7.4	Phase Equilibrium Diagram and Garnet Isopleths for 14PBA-94A	78
4.7.5	Phase Equilibrium Diagram and Garnet Isopleths for 14PBA-99A-A	81
4.7.6	Garnet Isopleth Intersections for 14PBA-99A-A	82
4.7.7	Phase Equilibrium Diagram and Garnet Isopleths for 14PBA-99A-B	83
4.8.1	Modification of Garnet Growth Zoning along Fractures and Inclusions	85
4.8.2	Phase Relations Before/After Garnet Growth and P-T-t Path Scenario 1	87
4.8.3	Garnet Crystallization Modeling Results Scenario 1 – 1	89
4.8.4	Garnet Crystallization Modeling Results Scenario 1 – 2	92
4.8.5	Phase Equilibrium Diagram and Garnet Isopleths Scenario 2	94
4.8.6	Phase Relations Before/After Garnet Growth and P-T-t Path Scenario 2	96
4.8.7	Garnet Crystallization Modeling Results Scenario 2 – 1	98
4.8.8	Garnet Crystallization Modeling Results Scenario 2 – 2	101
4.8.9	Phase Equilibrium Diagram and Garnet Isopleths Scenario 3	104
4.8.10	Phase Relations Before/After Garnet Growth and P-T-t Path Scenario 3	105
4.8.11	Garnet Crystallization Modeling Results Scenario 3 – 1	107
4.8.12	Garnet Crystallization Modeling Results Scenario 3 – 2	110
4.9.1	Phase Relations After Garnet Growth and Late Thermal Pulse P-T Paths	115
4.9.2	Garnet Crystallization Modeling Results Scenario 1 Thermal Pulse – 1	117
4.9.3	Garnet Crystallization Modeling Results Scenario 1 Thermal Pulse – 2	120

4.9.4	Garnet Crystallization Modeling Results Scenario 2 Thermal Pulse – 1	122
4.9.5	Garnet Crystallization Modeling Results Scenario 2 Thermal Pulse – 2	125
4.11.1	Representative Elemental Distribution Maps for Matrix Monazite	128
4.11.2	Monazite Age Histograms 12PBA-27A	129
4.11.3	Lotion of Monazite Inclusions in Garnet	133
5.4.1	Schematic for Diffusion vs. Interface Control Crystal Growth	144
5.4.2	Compilation of Garnet Compositional Profiles for 12PBA-27A	146
5.6.1	Comparison of P-T Estimates for Lower Montresor Group Samples	155
5.7.1	Comparison of Best Fit P-T-t Paths for 12PBA-27A	161
A.4.1	12PBA-27A Compositional Maps for Additional Elements – Size Class 1	193
A.4.2	12PBA-27A Compositional Maps for Additional Elements – Size Class 2	194
A.4.3	12PBA-27A Compositional Maps for Additional Elements – Size Class 7	195
A.4.1	12PBA-27A Compositional Maps for Additional Elements – Size Class 13	196
A.4.1	14PBA-94A Compositional Maps for Additional Elements	197

List of Appendices

A.1	Mineral Abbreviations	188
A.2	Trace Element Geochemistry and EPMA Mineral Chemistry	189
A.3	Monazite Rare-Earth Element Data	191
A.4	EPMA Garnet Compositional Maps for Additional Elements	193
A.5	THERIAK_DOMINO and THERIA-G Input Files	198

Chapter 1: Introduction

The Trans-Hudson orogeny was a continental-scale orogenic event spanning the Canadian Shield that was responsible for widespread metamorphism, deformation, and plutonism (Corrigan *et al.*, 2009). Determining the pressure, temperature, and timing (P-T-t) of metamorphic events is of paramount importance when reconstructing the tectonic evolution of the Earth. This study aims to better understand the tectono-metamorphic history of the Trans-Hudson orogeny in the central Rae Province, using modern techniques such as x-ray micro-computed tomography, phase equilibria and garnet crystallization modeling, and in-situ monazite geochronology.

The mineralogical, textural, and micro-structural information contained within rocks may be used to infer the processes and rates of ancient geological events. By understanding the changes that occur within rocks during a metamorphic event, it is possible to determine the P-T conditions experienced (Brown, 2014). Small-scale textural or chemical changes in rocks are driven by regional or global tectonic activity and thus can be used to aid in the understanding of these processes. The mineralogical, chemical, and textural changes a rock will experience during metamorphism have been well documented. Thus, these can be used to infer the P-T conditions of their formation (e.g. Borghi *et al.*, 2002; Brown, 2014; Tirone and Ganguly 2010; Tinkham and Ghent, 2005). Rock specific phase-equilibrium modeling using software such as THERIAK-DOMINO (de Capitani and Petrakakis, 2010) or Perplex (Connolly, 1990) may be utilized to obtain P-T conditions from mineralogical information (Best, 2012). In this case, phase equilibrium modeling utilizes bulk composition and thermodynamic data to calculate

stable mineral assemblages and reactions in P-T space based on Gibbs energy minimization (de Capitani and Petrakakis, 2010). The comparison of the predicted phase equilibria with the observed petrological record preserved in the rocks enables the quantification of metamorphic P-T conditions.

Garnet is one of the most commonly utilized minerals for the study of metamorphic P-T conditions. Prograde chemical zoning of garnet has been extensively shown to be sensitive to the P-T of metamorphic events (e.g., Borghi *et al.*, 2002; Evans, 2004; Gaidies *et al.*, 2006; Gaidies *et al.*, 2008A; Tirone and Ganguly, 2010). The usefulness of garnet is due in part to its stability over a wide range of P-T conditions (Brown, 2014) and well-described thermodynamic properties (e.g. Berman, 1988; Holland and Powell, 1998). Prograde chemical zoning in garnet is often retained during metamorphism due to slow intracrystalline diffusion (Gaidies *et al.*, 2008A). Given the T and time dependence of diffusion, any modification to prograde growth zoning in garnet due to intracrystalline diffusion may be used to estimate the rate of metamorphism, or the heating and cooling rate. This allows for the determination of a relative metamorphic P-T-t path (e.g. Gaidies *et al.*, 2006; Massone, 2014; McCarron and Gaidies, 2014; Stern and Berman, 2000). The amount of diffusion that a garnet crystal will experience is strongly dependent on its size, peak T, and metamorphic heating/cooling rate (Caddick, 2010; Florence and Spear, 1991; Gaidies *et al.*, 2008A). THERIA_G software (Gaidies *et al.*, 2008A) models both the prograde growth zoning and diffusional modification of garnet zoning along a pre-specified P-T-t path considering the influence of crystal size, peak T, and t (e.g. Gaidies *et al.*, 2008B; McCarron 2013, Moynihan and Pattison, 2013). As the smaller grains of a garnet population in a rock are most sensitive to diffusional

modification, these may be used to determine the rate of metamorphism, whereas larger grains may be more reflective of the P-T path (McCarron, 2013).

Determining the absolute timing of metamorphic events is critical when reconstructing tectonic processes (Brown, 2014; Foster *et al.*, 2002). Zircon has widely been the preferred mineral for the determination of magmatic crystallization ages, monazite is most often used for dating metamorphic events, as it is a common accessory mineral in metapelitic rocks (Parrish, 1990). Monazite (CePO_4) is a light rare earth element phosphate that is ideal for U-Th-Pb geochronology, as U and Th are readily incorporated into the crystal structure during growth. Monazite also has a high closure T of ca. 675 - 730°C for these components (Gasser *et al.*, 2012; Parrish, 1990; Stern and Sanborn, 1998). In general, monazite is thought to appear during prograde metamorphism via allanite breakdown reactions at mid-amphibolite facies (ca. 500 - 600°C) (Catlos *et al.*, 2002; Gasser *et al.*, 2012; Spear, 2010). In-situ analysis of monazite grains allows textural relationships to be preserved (i.e. Foster *et al.*, 2002; Stern and Sanborn, 1998; Williams and Jercinovic, 2002, Williams *et al.*, 2007). Combination of P-T-t information allows for the determination of the duration and style of metamorphic events, increasing the understanding of the tectonic and geological evolution of an area (Brown, 2014; Tirone and Ganguly, 2010). In this study, metamorphic monazite ages are combined with metamorphic P-T estimates obtained from phase equilibria and garnet crystallization and diffusion modeling to determine the absolute P-T-t path experienced by rocks from the Montresor belt.

Chapter 2: Regional Geology

2.1 The Canadian Shield

The Canadian Shield forms the nucleus of North America, spanning from Baffin Island to Hudson Bay and into the northern continental United States (Fig 2.1.1, inset). It is comprised of several Archean cratons that are separated by Proterozoic orogenic belts (Hoffman, 1988). The oldest of these cratons is the Slave, which contains the oldest rocks found on Earth, the Acasta Gneiss, dated at ca. 4.03 Ga (Stern and Bleeker, 1998). Other cratons include the Rae, Hearne, Wyoming, Superior, and other smaller continental blocks. Each craton consists of Archean metamorphic and plutonic rocks that may be overlain by Paleoproterozoic sedimentary and/or volcanic cover sequences (Hoffman, 1988). Proterozoic amalgamation of these cratons into the Canadian Shield caused regional deformation, metamorphism, magmatism, and sedimentation (Percival *et al.*, 2015B). This resulted in a complex metamorphic history and some of the most extensively reworked continental crust on Earth (Berman *et al.*, 2010), with some parts of the shield having experienced more than eight tectonic events between ca. 2.8 and 1.7 Ga. As a result, evidence for older tectonic events is often obscured by the overprinting of younger tectonic events (Berman, 2010).

The Rae and Hearne cratons, along with the Meta-Incognita microcontinent and Chesterfield block were originally referred to collectively as the Western Churchill Province (Figure 2.1.1). The Rae and Chesterfield block were amalgamated prior to 2.61 – 2.58 Ga (Davis *et al.*, 2006). Later the Hearne was added at ca. 1.9 Ga and the Meta-

Figure 2.1.1: Simplified geological map of the Western Churchill Province. Groups belonging to the Rae Cover Sequence (i.e. Montesor Group, Amer Group, Ketyet River Group) are shown in yellow. The Montesor Belt and approximate location of Figure 2.2.1 is shown by the black dashed box. Mo = Montesor Belt. CB = Chesterfield Block. STZ = Snowbird Tectonic Zone. CFZ = Chesterfield Fault Zone. CMZ = Chantrey Mylonite Zone (Modified after Rainbird *et al.*, 2010).

Incognita microcontinent at 1.88 - 1.85 Ga (Berman, 2010). Together, they form approximately one third of the area of the Canadian Shield (Pehrsson *et al.*, 2013). The Western Churchill Province is dominantly composed of Archean (2.9 – 2.56 Ga) amphibolite to granulite grade gneisses and greenstone belts, which are overlain by ca. 2.45 - 1.75 Ga sedimentary and volcanic rocks (Berman *et al.*, 2007; Berman *et al.*, 2010). Nd isotope signatures suggest that the oldest crustal rocks in the Western Churchill Province are ca. 3.3 Ga, with Nd isotopic evidence for rocks as old as 3.5 – 3.6 Ga (Peterson *et al.*, 2010).

The Rae cover sequence is a widespread but discontinuously preserved package of metasedimentary rocks (Rainbird *et al.*, 2010), interpreted to unconformably overlie Archean basement rocks (ca. 2.6 Ga) of the Rae Craton (Davis *et al.*, 2014; Percival *et al.*, 2015 A, B, C). Preserved parts of the Rae cover sequence include the Amer, Ketyet River, Montresor, Chantrey, and Penrhyn groups (Berman *et al.*, 2015; Davis *et al.*, 2014; Pattison, 1986; Rainbird *et al.*, 2010). The Rae cover sequence formed during the breakup of the supercontinent Kenorland and the subsequent formation of the supercontinent Nuna (Rainbird *et al.*, 2010). Detrital zircon geochronology constrains deposition of the Rae cover sequence to 2.19 – 1.92 Ga (Percival *et al.*, 2015A).

2.2 The Montresor Belt

The Montresor belt is located in central Nunavut, approximately 250 km north of the community of Baker Lake (figure 2.1.1). It is one of the smaller northern outliers of preserved Rae cover sequence rocks (Rainbird *et al.*, 2010). The Montresor Belt was first discovered in 1961 during Operation Northern Keewatin, a reconnaissance program of

the area run by the Geological Survey of Canada (Heywood, 1961) and was first studied in detail by Frisch and Patterson (1983).

The belt is 73 km long and 8 km wide, extending from the Montresor River in the northeast to the Back River in the southwest (Frisch, 2000). It structurally forms an open synclinal fold with the southeast limb dipping at 30° and the northwest limb dipping 40 - 70°, with localized dip up to 80° (Percival *et al.*, 2015A). The base of the syncline is prominently visible as a magnetic low in modern aeromagnetic maps (Tshirhart *et al.*, 2015). The Montresor belt is dominantly composed of meta-arenite and carbonate, with minor pelitic schist (Frisch and Patterson, 1983; Percival *et al.*, 2015C). At its deepest part, the Montresor Belt is estimated to be ca. 1800 m thick (Frisch, 2000). It has been suggested the Montresor belt formed in a shallow water or continental depositional environment (Rainbird *et al.*, 2010). Archean basement rocks to the Montresor Belt are dominantly of a tonalite-granodiorite-granite composition (Frisch, 2000; Percival *et al.*, 2015A).

The Montresor belt is primarily comprised of low-grade, weakly metamorphosed siltstone and dolostone of the upper Montresor group (Figure 2.2.1). These overlie higher-grade amphibolite facies meta-arenites, calc-silicates, and metapelites of the lower Montresor group that are discontinuously exposed on the edges of the syncline. Amphibolite facies metamorphism resulted in tremolite-forsterite-diopside assemblages in calc-silicate rocks and muscovite-garnet-biotite-andalusite-cordierite-sillimanite assemblages in pelitic schists. The lower Montresor group is commonly cut by granodiorite, granite, and pegmatitic dykes (Percival *et al.*, 2015A, C). Previous studies suggested that these higher-grade amphibolite facies rocks belong to the basement

Figure 2.2.1: Geological Map of the Montesor belt. (A) and (B) show the locations of samples used in this study (Modified after Percival *et al.*, 2015A).

(Frisch, 2000; Frisch and Patterson, 1983), but recent work has demonstrated that these units are part of the Montresor belt (Percival *et al.*, 2015C). The low-grade rocks are collectively referred to as the ‘upper Montresor group’, and the higher-grade rocks form the ‘lower Montresor group’. These rock sequences can be regionally correlated with rocks seen in other Rae cover sequence groups, such as the Amer belt located 50 km to the south (Percival *et al.*, 2015A).

A mylonitic ductile fault zone separates the lower Montresor belt from the Archean basement. Observed imbrication of the Archean basement and lower Montresor group suggest the presence of thrust faults at the base of the syncline (figure 2.2.2) (Percival *et al.*, 2015A). It has been suggested that this faulting may relate to folding and thrusting described in the Amer belt (Figure 2.1.1) (Pattison, 1986; Percival *et al.*, 2015A, Rainbird *et al.*, 2010). The upper and lower Montresor Belt are separated by a low angle detachment fault. A difference in metamorphic grade between the greenschist facies upper Montresor group and amphibolite facies lower Montresor group suggests the detachment fault is late to post-metamorphic with a vertical offset of several km (Percival *et al.*, 2015A). Later folding created the synclinal structure observed today (Percival *et al.*, 2015A).

Two major orogenic events occurred within the northwestern Rae Province after the deposition of the Rae cover sequence, these are referred to as the Thelon-Taltson orogeny (ca. 2.0 - 1.92 Ga) and the Trans-Hudson orogeny (ca. 1.91 - 1.75 Ga). However, a lack of ca. 2.0 Ga accessory mineral growth suggests that the extent of the Thelon-Taltson orogeny did not reach the Montresor belt (Berman, 2010). This, along with a prominence of ca. 1.85 Ga metamorphic monazite ages (Davis *et al.*, 2014), suggests that

the Montresor belt was regionally metamorphosed solely during the Trans-Hudson orogeny (Percival *et al.*, 2015C). It has also been suggested that metamorphism may have been associated with localized pegmatitic intrusions (Frisch, 2000).

Figure 2.2.2: Schematic cross section of the Montresor Belt showing thrust faulting and imbrication of the Archean rocks and lower Montresor group and the detachment fault between the upper and lower Montresor groups (Percival *et al.*, 2015A).

2.3 The Trans-Hudson Orogeny

The Trans-Hudson orogenic belt is the largest Proterozoic orogenic belt preserved in the Canadian Shield (Corrigan *et al.*, 2009). This orogeny was caused by the collision between the Rae/Hearne and Wyoming cratons to the Superior Province starting at ca. 1.91 Ga (Hoffman, 1988), during the closure of the Manikewan Ocean and subsequent formation of the supercontinent Nuna at ca. 2.0 - 1.8 Ga (Corrigan *et al.*, 2009; Pehrsson *et al.*, 2013). In total, the Trans Hudson Orogeny took place over ca. 120 Ma (ca. 1.92 – 1.80 Ga) (Corrigan *et al.*, 2009). The Trans-Hudson Orogeny occurred in two distinct phases, referred to as the Snowbird phase (ca. 1.91 Ga) and the Main phase (ca. 1.86 Ga) (Berman *et al.*, 2007; Berman, 2010).

During the Snowbird phase at ca. 1.91 - 1.87 Ga, the Rae collided with the Hearne and the Meta-incognita microcontinent. The Rae and Hearne collision occurred at ca. 1.91 Ga and the Meta-Incognita microcontinent collision at ca. 1.87 Ga (Berman, 2010; Berman *et al.*, 2007; St-Onge *et al.*, 2006). The main phase of the Trans-Hudson orogeny occurred between ca. 1.86 and 1.75 Ga (Berman 2010), with the terminal collision of the Superior craton to the southeast of Rae-Hearne block occurring at ca. 1.82 Ga (Berman, 2010; Corrigan *et al.*, 2009). The Trans-Hudson orogeny is spatially and temporally associated with two distinct periods of syn- to post-tectonic magmatism, the ca. 1845 – 1795 Ma Hudson suite and the ca. 1765 - 1750 Ma Nuelin suite (Davis *et al.*, 2014; Peterson *et al.*, 2002; Van Breemen *et al.*, 2005).

The resulting orogenic zone extended from South Dakota to Hudson Bay and Baffin Island, and is approximately 500 km wide (Berman, 2010; Corrigan *et al.*, 2009; Hoffman, 1988). The orogenic event resulted in sub-greenschist to eclogite facies

metamorphism (Corrigan *et al.*, 2009). While the Trans-Hudson orogeny was wide, it is inferred to have produced only moderate crustal thickness with a peak thickness of ca. 52 - 58 km. This is significantly less than that of other major orogens such as the Grenville, where crustal thickness is estimated to have been 70 – 80 km (Corrigan *et al.*, 2009). In the northwestern Rae Province, the Trans-Hudson orogeny caused low-P metamorphism at amphibolite to granulite facies, with an estimated peak P of 5 kbar (Berman, 2010).

2.4 Previous Work on the Montresor Belt

A previous study on a sample from the lower Montresor Belt (12PBA-27A) has yielded some P-T-t information. This sample experienced amphibolite facies conditions of 3.3 kbar and 575°C (Berman *et al.*, 2014), and two in-situ U-Th-Pb monazite analyses yielded metamorphic ages of 1861 ± 7 and 1844 ± 6 Ma (Berman *et al.*, 2015; Davis *et al.*, 2014). The timing and low-P style of metamorphism has been interpreted to be a result of crustal thickening due to the Trans-Hudson orogeny. Furthermore, metamorphism in the Montresor belt has been interpreted as being due to the Snowbird phase of the Trans-Hudson Orogeny at ca. 1.91 - 1.87 Ga (Berman *et al.*, 2015). This estimate gives a 10 - 30 Ma time lag to allow for crustal thickening and thermal incubation of the rocks (Berman, 2010). Greenschist facies metamorphism in the upper Montresor group has been dated at 1847 ± 15 Ma by U-Th-Pb monazite geochronology (Percival *et al.*, 2015A).

Fieldwork in the summer of 2014 was completed as part of the Geological Survey of Canada's Geo-Mapping for Energy and Minerals Program (GEM). For a complete summary of field activities in the Montresor belt see Percival *et al.* (2015C).

Representative samples of both low and high-grade rocks were collected from two areas of the Montresor Belt, the locations of which are highlighted in figure 2.2.2. Detailed sample locations are given in table 2.4.1. These samples have been used in this study to constrain P-T-t estimates for metamorphism and deformation, with the aim to further understand the influences of the varied tectonic and metamorphic effects of the Trans-Hudson orogeny on the Montresor belt and across the Rae craton. Sample 12PBA-27A was chosen for the most detailed thermodynamic modeling in this study, as it contains the most well preserved garnet porphyroblasts.

Table 2.4.1: Sample locations.

Sample	Easting	Northing
12PBA-27A	578147	7325917
14PBA-43B	613317	7356790
14PBA-67A	578149	7325933
14PBA-85A	577392	7325307
14PBA-94A	578989	7326569
14PBA-97A	578370	7325495
14PBA-99A	578200	7325859
14PBA100	578828	7325118

NAD 1983 UTM Zone 14N

Chapter 3: Methods

3.1 Whole-Rock Chemistry

Whole rock composition was analyzed at Actlabs in Ancaster, ON. Samples for major element chemistry were prepared from sections of rock that were macroscopically viewed to be chemically homogeneous and representative of the rock. Samples were crushed, ground, and fused into a glass; thus ensuring chemical homogeneity in the analyses. Major and trace element composition was analysed using inductively coupled plasma mass spectrometry (ICP-MS) on a Perkin Sciex ELAN 6000, 6100, or 9000 ICP/MS, with a detection limit of 0.01 wt% for all major elements. FeO was also measured by titration in order to determine the ratio of FeO to Fe₂O₃ in the total iron value provided by ICP-MS analysis. There is a detection limit of 0.1 wt% on the FeO titration. Carbon and Sulfur were analysed using an Eltra CS-800 or CS-2000 infrared detector, with a detection limit of 0.01 wt%. Major Element Chemistry is provided in table 4.1.1. Trace element chemistry for selected samples is provided in Appendix A.2.

3.2 Electron Probe Micro-Analysis

Quantitative electron probe micro-analyses (EPMA) were completed using a Cameca Camebax MBX electron microprobe at Carleton University. Operating conditions of the microprobe were an accelerated voltage of 20 kV and a beam current of 20 nA. All measurements were done using a wavelength dispersive x-ray (WDS) detector. This method gives an accuracy of $\pm 1 - 2\%$ on major elements (>10 wt%), and $\pm 3 - 10\%$ for minor elements ($<10\%$) with a detection limit of approximately 0.1 wt%.

Peak counting times ranging from 15 – 45 s on each analysis were chosen to obtain around 40,000 counts on each element. Background measurements on each side of the analysed peak were done at 50% of the total peak counting time. A Cameca PAP matrix correction procedure was used to convert counts into elemental weight% (see Pouchou and Pichoir, 1985). Several well-defined natural and synthetic standards were used for internal calibration of the microprobe. Garnet traverses were completed on samples 12PBA-27A and 14PBA-99A, for Fe, Mg, Mn, Ca, and Y with a spacing of 10 μm between analyses. Analyses that coincided with inclusions were removed from the dataset. Garnet core compositions for each of these analyses can be found in table 4.6.2. A complete mineral dataset for 12PBA-27A can be found in appendix A.2.

Qualitative elemental distribution maps of garnet in samples 12PBA-27A and 14PBA-94A were done at the University of Ottawa using a JEOL 8230 microprobe. The operating conditions used an accelerated voltage of 20 kV and a beam current of $1.00\text{E-}7$ A. A WDS detector was used to analyse major element chemistry (Fe, Mg, Ca, Mn, and Y) with a dwell time of 200 ms on each analysis. An energy-dispersive (EDS) detector was used to analyse other elements (Ti, Si, Al, K, Na, O, C, P, S, Zn, and Zr). These maps can be found in appendix A.4. For 12PBA-27A a pixel size of 7 μm^2 was used for garnets 1 and 2, 5 μm^2 for garnet 4, and 3 μm^2 for garnet 7. The single garnet map from sample 14PBA-94A uses a pixel size of 5 μm^2 .

3.3 X-Ray Micro Computed Tomography (XR- μ CT)

XR- μ CT was done using a Bruker Skyscan 1173 tomography scanner at Carleton University. Samples were scanned in order to both locate garnet and determine the size,

shape, and abundance of crystals. From each sample, a 2.5 cm diameter by 3 – 5 cm long cylindrical core was drilled for scanning (figure 3.3.1). These samples were scanned over a period of 2 hours, as they were rotated 180° within the x-ray field with a rotation step of 0.4°. At each rotation step an image was taken with an exposure time of 1.35 s, resulting in an image pixel size of 14.9 µm. The scans used operation setting of 130 kV and 61 µA for the x-ray source. X-rays were filtered through a 0.25 mm brass filter before hitting the sample to pre-harden the beam and to reduce beam-hardening effects. Flat field corrections were performed every 60 min throughout each scan. Raw image data was converted into cross-sections using Skyscan NRecon software (i.e. figure 3.3.2). Quantification of the distribution and size of garnet in the sample was done with BLOB 3D software (Ketcham, 2005). 3D imaging and visualization was achieved using commercially available Avizo software. Stereonet visualization of garnet orientation was done with OSX Stereonet (Cardozo and Allmendinger, 2013).

3.4 Statistical Analysis of Crystal Distribution

A statistical analysis of the 3D distribution of garnet in sample 12PBA-27A was done using Reduce 3D Software (Hirsch, 2011). A brief introduction to Reduce 3D and the statistical methods is presented below. For a complete description of the Reduce 3D software, parameters, and statistical methods, see Hirsch (2011), Hirsch *et al.* (2000), and Petley-Ragan *et al.* (2016).

Reduce 3D software uses scale dependent statistical methods to quantify the spatial distribution of porphyroblasts within 3D space. This requires information about the location of each crystal center (x-y-z coordinates) and its radius. This information is

Figure 3.3.1: Example of rock cores scanned for XR- μ CT. Cores measure approximately 2.5 cm in diameter and 3 - 5 cm tall.

Figure 3.3.2: Example of a reconstructed XR- μ CT slice through a scanned rock core. Garnet crystals and iron oxides have high x-ray attenuation and are shown as bright grey values. Mid-level gray scale values represent biotite grains. Dark grey scale levels correspond to muscovite, quartz, and feldspar.

obtained from XR- μ CT. The program compares the observed crystal distribution with a random distribution (null hypothesis) of crystals of the same number and size created by simulating interface controlled mineral growth. By comparing the observed crystal distribution with the simulated distribution, it is possible to determine if that population grew under interface-controlled or diffusion-controlled growth (Hirsch, 2011; Petley-Ragan *et al.*, 2016).

Reduce 3D runs both single scale and scale-dependant statistics. Single scale statistics include the ordering index, clustering index, and impingement index. These statistics do not consider variation in crystal size distribution with distance but represent an average of all data (Hirsch, 2011). The ordering index calculates the ratio between the average observed nearest neighbour distance between crystals in the sample and random simulation. The clustering index compares the observed crystal density to the random distribution, by calculating the average distance between any number of crystal centers and randomly located points. The impingement index uses the location and volume of crystals to calculate the theoretical size the crystals may have grown without impingement. Values greater than that of the random distribution indicate a clustered distribution, while values less than the random distribution indicate an ordered distribution (Petley-Ragan *et al.*, 2016).

Scale dependent statistics consider the spatial distribution of porphyroblasts over various test distances (figure 3.4.1) and include the L'function, pair correlation function, and the mark covariance function (Hirsch, 2011). The L'function is a spatial statistic that calculates the average number of crystal centers present in a sphere surrounding each crystal. This sphere is defined by distance r , which increases each model run. The pair

correlation function (PCF) calculates the number of crystal centers in a spherical shell surrounding every crystal. The distance of this shell from the crystal center increases with every model run, and the thickness of the shell is determined by an algorithm in Reduce 3D. The mark covariance function (MCF) is similar to the pair correlation function, but takes into account another measurement. In this case the radius was used as the mark value. The mean radius value for every two crystals is compared to the mean radius of the entire crystal population. Each of these described spatial statistics is run for both the observed crystal distribution and the randomly generated crystal distribution. The random distribution creates a null hypothesis envelope. If the observed crystal population falls within this envelope, it has a random distribution. If the observed population falls above the envelope, there is a greater number of crystal centers than expected at that distance (L'function and PCF) or larger crystal sizes than expected (MCF), indicating a clustered distribution. However, if the observed population falls below this envelope and there are less crystal centers than expected or smaller crystal sizes, this indicates an ordered distribution (Petley-Ragan *et al.*, 2016).

Reduce 3D simulations were run with default settings as suggested in the software. With these settings 100 simulations are run on the random distribution population, and a 96% confidence interval is implemented on all statistics (Hirsch, 2011). The radius of each garnet porphyroblast was used as the mark value. The statistics were calculated for both a sphere-normalized radius and the semi-major axis length.

Figure 3.4.1: Schematic of the scale-dependent (3D) statistics used by Reduce3D to characterize a crystal distribution. r = radius (Petley-Ragan *et al.*, 2016).

3.5 Phase Equilibrium Modeling

Rock specific phase diagrams and isopleths for the garnet endmembers (almandine, grossular, pyrope, and spessartine) were calculated using THERIAK-DOMINO software (de Capitani and Brown, 1987; de Capitani and Petrakakis, 2010). This was done using the MnO-Na₂O-CaO-K₂O-FeO-MgO-Al₂O₃-H₂O-TiO₂ model system and the internally consistent database of Holland and Powell (1998). In addition, the plagioclase solid solution is modeled according to Newton *et al.* (1980), and garnet was modeled as a quaternary solid solution from Connolly (2005). The chlorite solution model is as described by Gaidies *et al.* (2008A). Staurolite is modeled with the database of Holland and Powell (1998) but has been extended to include Mn-solutions. White mica is modeled as a quaternary solid solution as described at <http://www.esc.cam.ac.uk/astaff/holland/ds5/muscovites/mu.html>. Two amphibole solution models are used, from Dale *et al.* (2005) and Holland and Powell (1998). Melt is

modeled according to White *et al.* (2007). An H₂O fluid was used due to a negligible amount of carbon present in the studied samples. SiO₂ and H₂O are considered to be in excess for all calculations, and all iron is considered as FeO. The thermodynamic database and mineral specific solution models can be found in appendix A.5.

Phase equilibrium modeling is based on the premise that metamorphic mineral assemblages continuously evolve to remain thermodynamically stable at different P-T conditions (Brown, 2014; Tinkham and Ghent, 2005). THERIAK-DOMINO calculates rock specific phase equilibria based on Gibbs energy minimization using a specific bulk rock composition and a thermodynamic database (de Capitani and Petrakakis, 2010). The most stable mineral assemblage at any given point in P-T space is that which has the lowest Gibbs energy (Best, 2012). A simplified representation of this is shown in figure 3.5.1. THERIAK-DOMINO calculates all of the stable mineral assemblages in a defined P-T range, and determines the Gibbs energy of each phase. Mineral reactions occur where there is a change in the equilibrium mineral assemblage, and are shown as lines on the phase diagram. By comparing the observed equilibrium mineral assemblage to the phase diagram it is possible to determine the peak P-T experienced by the rock during metamorphism (de Capitani and Petrakakis, 2010).

Metamorphic P-T conditions at the onset of garnet growth can be determined by garnet isopleth thermobarometry (i.e. Brown, 2014; Evans, 2004; Gaidies *et al.*, 2006). The compositional zoning of garnet reflects changes in P, T, and effective bulk rock chemistry (Borghi *et al.*, 2002). Therefore, the P-T conditions at the onset of garnet growth can be determined using the chemistry of the center of the oldest garnet, provided that it has not been modified by later diffusion (Gaidies *et al.*, 2006; Gaidies *et al.*, 2014).

Figure 3.5.1: Simplified schematic view of how a Gibbs free energy minimization is used in phase equilibrium modeling. P and composition (X) are constants and T is variable. In this example, at lower T, phase assemblage 2 is stable as it has a lower Gibbs free energy. At higher T, phase assemblage 1 is stable. At the point when one assemblage stabilizes or destabilizes a phase reaction occurs.

THERIAK-DOMINO creates plots of compositional isopleths, or lines of constant chemistry, for major garnet endmembers (Ca^{2+} , Fe^{2+} , Mn^{2+} , Mg^{2+}) within P-T space (de Capitani and Petrakakis, 2010; Tinkham and Ghent, 2005). In order to best utilize this method, garnet chemistry must be obtained from the core of the oldest, and largest garnet crystal (Gaidies *et al.*, 2006). In this study, this was accomplished by locating garnet both in thin section and using XR- μ CT and centrally sectioning these crystals.

3.6 Garnet Crystallization Modeling

A simulation of garnet growth was done with THERIA_G software (Gaidies *et al.*, 2008A) for sample 12PBA-27A. A brief introduction to this method is presented below. For a complete description of both this method and the software program see Gaidies *et al.* (2008A). All input files for Theria_G can be found in appendix A.5.

THERIA_G is numerical modeling software that simulates garnet growth zoning of major elements (Fe^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+}) along any specified P-T-t path in a defined rock volume. By comparing the observed garnet growth zoning to that predicted by THERIA_G it is possible to infer a relative P-T-t path experienced by the observed sample during metamorphism. The inputs to THERIA_G include a thermodynamic database, defined P-T-t path, and the observed crystal size distribution (CSD) (Gaidies *et al.*, 2008A). The thermodynamic database used for THERIA_G simulations is the same as earlier defined for phase equilibrium modeling.

THERIA_G works with two models to simulate garnet growth. Firstly, a Gibbs energy minimization model is used to determine equilibrium phase relations within the rocks and the composition of successive shells during prograde garnet growth. Secondly, a multi-component diffusion model for spherical garnet is used to simulate major element diffusion through garnet and the resulting modifications to the original prograde growth zoning (Gaidies *et al.*, 2008A).

The entire garnet population is simulated according to the CSD. Garnet growth begins with the discrete nucleation of every garnet contained within the largest crystal size class. Garnet growth is then simulated by the addition of successive shells of a defined thickness to these nuclei. Each successive shell corresponds to a P-T step in the

simulation. The shell thickness is the same for each garnet crystal and is independent of crystal size, meaning all simulated garnet crystals have the same radial growth rate. Thus, as garnet crystals become larger a greater volume of material is needed to form these shells (Gaidies *et al.*, 2008A). For this study a uniform shell thickness of 5 μm was used. To account for chemical fractionation of the effective bulk rock chemistry during garnet growth, the material used to grow garnet at each step is removed modifying the effective bulk rock composition. The effect of this fractionation becomes increasingly prominent with greater volume of garnet (Evans, 2004; Gaidies *et al.*, 2008A). The CSD and the radial range of each size class control the nucleation of garnet crystals. Once the first generation of garnet reaches the maximum radial range of the bin, the entirety of the next generation of garnet crystals is nucleated. This allows for the software to predict the compositional zoning of garnet for each size class as defined by the CSD. The rate of garnet growth is determined by the input P-T-t path (Gaidies *et al.*, 2008A). THERIA_G predicts equilibrium phase relations using THERIAK-DOMINO software (de Capitani and Petrakakis, 2010) and a defined thermodynamic database. With this method, changes to the equilibrium mineral assemblage during garnet growth is recorded (Gaidies *et al.*, 2008A). The initial position of the P-T path was determined in this study by garnet isopleth thermobarometry, and the peak P-T by the equilibrium mineral assemblage predicted by THERIAK-DOMINO.

The initial prograde garnet growth zoning calculated by THERIA_G is being constantly modified by intracrystalline diffusion within garnet and intercrystalline diffusion between garnet and the rock matrix (Gaidies *et al.*, 2008A). THERIA_G utilizes kinetic diffusion parameters for major elements in garnet as defined by

Chakraborty and Ganguly (1992). Diffusion in garnet becomes increasingly efficient with high T and longer time (Gaidies *et al.*, 2008B). Thus, diffusion of major elements within garnet may be used to infer the rate of metamorphism (McCarron, 2013). With regard to major elements within garnet, Ca^{2+} is the slowest and Mn^{2+} is the quickest to diffuse through garnet. As a result, the zoning of Ca^{2+} within garnet is the least likely to have been significantly modified by diffusion and would give the best record of prograde growth zoning (Chakraborty and Ganguly, 1992; Gaidies *et al.*, 2015; Loomis *et al.*, 1985). Therefore the Ca^{2+} zoning was used as a proxy to determine the P-T path of prograde garnet growth. As Mn^{2+} is the fastest diffusing element through garnet, the chemical zoning of Mn^{2+} was used to infer the heating and cooling rate during garnet growth and metamorphism.

There are several inherent assumptions in simulations done with THERIA_G. The first is that there is a thermodynamic and chemical equilibrium maintained between the rim of each garnet crystal and the rock matrix during the entire period of garnet growth. THERIA_G also assumes that there is no delay in the transport of elements through the rock matrix to the rim of the growing garnet crystal (Gaidies *et al.*, 2008A). This means that the garnet crystals grow by interface-controlled growth (Gaidies *et al.*, 2008A; Hirsch, 2011). Finally, the simulations also assume a homogeneous rock matrix with respect to effective bulk rock chemistry, as well as that the rock volume is a closed chemical system (Gaidies *et al.*, 2008A).

3.7 Geochronology

The timing of metamorphism was determined by in-situ monazite geochronology. Monazite grains were located in thin section using a Zeiss EVO 50 scanning electron microscope at the Geological Survey of Canada in Ottawa, ON. A population of representative monazite grains was chosen for analysis, and included monazite grains in the matrix as well as included in garnet. The monazite age dating was done using a Cameca SX ultrachron electron microprobe at the University of Massachusetts in Amherst, MA. The electron microprobe was chosen for this analysis as monazite grains included in garnet are too small (ca. 4 – 5 μm in diameter) to be analysed by other methods (i.e. SHRIMP, LA-ICP-MS). A brief introduction to U-Th-Pb dating by microprobe is offered below. For a complete description of this analytical method see Jercinovic *et al.* (2008) and Williams *et al.* (2007). A summary of monazite age results can be found in tables 4.11.1 and 4.11.2, and all monazite spot analysis data can be found in Appendix A.3.

Monazite geochronology was done using the uranium-thorium-lead (U-Th-Pb) system. The basis for U-Th-Pb geochronology is the radiogenic decay of U and Th to Pb over a set period of time. These unstable parent isotopes undergo alpha decay at a constant rate through a series of intermediate isotopes to a final stable daughter product (Faure and Mensing, 2005). The two radiogenic U isotopes, ^{238}U and ^{235}U will decay to ^{206}Pb and ^{207}Pb respectively (Heaman and Parrish, 1991), and radiogenic Th, ^{232}Th , decays to ^{208}Pb . The simplified age equation is shown below; where P is the parent, D is the daughter, t is time, and λ is the decay constant (Faure and Mensing, 2005).

$$(D/P) = e^{\lambda t} - 1$$

Traditional geochronology uses isotope dating, which yields four separate ages for the U-Th-Pb system; $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, $^{208}\text{Pb}/^{232}\text{Th}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ (Faure and Mensing, 2005). Monazite U-Th-Pb geochronology via EPMA utilizes chemical dating, as the microprobe is unable to differentiate the different isotopes of U and Pb. In other words, an age determined by EPMA gives an age reflective of the direct concentrations of U-Th-Pb in the monazite (Williams and Jercinovic, 2002; Williams *et al*, 2006). Once these concentrations are known, age can be calculated using the following equation, where Pb, Th, and U concentrations are in parts per million, age is in years, and λ is the decay constant for each species of U and Th (Williams *et al.*, 2007).

$$\text{Pb} = \left[\frac{\text{Th}}{232} (e^{\lambda^{232}t} - 1) \right] 208 + \left[\frac{\text{U}}{238} 0.9928 (e^{\lambda^{238}t} - 1) \right] 206 + \left[\frac{\text{U}}{235} 0.0072 (e^{\lambda^{235}t} - 1) \right] 207$$

There are two major assumptions related to the chemical dating of monazite by EPMA. The first is that it assumes a negligible amount of common Pb (^{204}Pb). Secondly, it assumes that the only changes to the U-Th-Pb amounts present in the monazite are due to radioactive decay (Goncalves *et al.*, 2005; Williams and Jercinovic, 2002).

Monazite analyses are done in-situ in order to preserve textural relationships within the sample. Prior to analysis, thin sections were double-coated first in 250 μm Al and then a layer of C. Microprobe operating conditions were an accelerating voltage of 15 kV and a beam current of 20 nA. Selected monazite grains were mapped for U, Th, Y, and Ca, prior to detailed spot analysis in order to visualize the chemical variation in these

elements across the grains. Then 2 - 6 spot analyses were done per grain, and the average of these analyses determines the age. The first of these spots is a background analysis that is used to correct for background effects on later spots in that grain. Each spot analysis is approximately 0.5 μm in diameter. Sets of spot analyses are constrained, as best possible, to domains of uniform chemical composition. Count times were 1400 s for Pb, 500 s for U, 400 s for Th, and 100 s for Y. Other major and rare earth elements (P, S, Ca, Si, Sr, La, Ce, Nd, Pr, Gd, Eu, Sm, Tb, Dy, Er, Tm, Yb, Ho, and As) were measured for 20 – 60 s. A Cameca PAP matrix correction (Pouchou and Pichoir, 1985) was used to correct for matrix effects on the analyses and a time dependant intensity (TDI) correction was used for accurate estimation of initial intensities for U, Th, and Pb. Moacyr monazite (ca. 508 Ma) was used as a consistency standard, and was analyzed periodically during each session.

Chapter 4: Results

4.1 Whole-Rock Chemistry

As described in section 3.1, samples were analyzed for 10 major elements. These results are provided in table 4.1.1. Two separate chemical analyses were completed for 12PBA-27A, in order to determine the extent of chemical heterogeneity within the sample. These analyses show little variation in most major element concentrations (i.e. 2.34 – 2.22 wt% MgO, 15.81 – 16.43 wt% Al₂O₃). The largest exception to this is in MnO, where the two analyses yielded 0.05 and 0.11 wt%. A small variation can also be seen in CaO, with analyses of 1.08 and 1.41 wt%. The first chemical analysis for 12PBA-27A was used for all thermodynamic modeling in this study, as this analysis is thought to be more representative of the effective bulk rock chemistry of the modeled sample as the rock sample used for chemistry is macroscopically similar to that used for petrographic analysis. C and S analysis on several samples indicates a low concentration of these components, and thus they were not considered in any of the thermodynamic calculations. Bulk rock chemistry was plotted in both AFM and ACF ternary diagrams, following the technique as described by Spear (1993) (figure 4.1.1). The data from this study are plotted against an average metapelite composition defined by Symmes and Ferry (1991).

The AFM diagram (figure 4.1.1-A) indicates that all of the studied samples contain little Mg relative to Fe and Al, as most samples plot along a roughly linear trend from F to A. Sample 14PBA-43B is an outlier to this population, plotting along the F – M axis. This is due to a higher K₂O and MgO content, yielding lower A/F and A/M ratios.

Garnet bearing samples (12PBA-27A, 12PBA-27A (2), 14PBA-94A, 14PBA-99A-A, 14PBA-99A-B) cluster near the F end of the linear grouping, near the average pelite composition. In general, these garnet-bearing samples have a higher FeO/Fe₂O₃ concentration than the non garnet-bearing samples that plot closer to the A end of the linear grouping. The ACF plot (figure 4.1.1-B) also shows the sample population plotting along a roughly linear trend from A – F. A low CaO concentration across all of the studied samples yields low C/F and C/A ratios. Similar to the AFM diagram garnet-bearing samples group together near the F end of the rough linear trend. The non-garnet bearing samples group near the A end of the trend near the average pelite composition.

Table 4.1.1: Bulk Rock Chemistry

Sample	SiO ₂	Al ₂ O ₃	MnO	MgO	Fe ₂ O ₃	FeO	CaO	Na ₂ O	K ₂ O	TiO ₂	LOI	C	S	Total
12PBA-27A	60.85	16.43	0.05	2.34	3.87	7.60	1.08	0.80	3.53	0.55	2.98			100.08
12PBA-27A (2)	60.90	15.81	0.11	2.22	2.15	8.70	1.41	1.05	3.42	0.53	2.36	0.11	0.13	98.66
14PBA-43B	54.28	19.51	0.05	4.52	2.02	5.30	0.81	3.53	6.46	0.68	2.31			99.47
14PBA-67A	62.11	20.50	0.05	2.30	0.74	4.40	0.73	0.80	4.87	0.63	3.01	0.08	0.05	100.14
14PBA-85A	55.73	24.47	0.05	2.63	1.39	4.90	0.28	0.32	4.68	0.83	3.02	0.02	0.04	98.30
14PBA-94A	61.82	13.73	0.27	2.22	2.52	13.50	5.05	0.14	0.64	0.42	0.15			100.46
14PBA-97A	47.58	26.83	0.08	3.00	1.36	6.30	1.53	1.77	4.95	0.95	3.97	<0.01	0.06	98.32
14PBA-99A-A	65.98	15.16	0.07	1.92	0.86	7.60	4.78	0.33	2.21	0.44	0.84			100.19
14PBA-99A-B	67.23	14.16	0.17	1.90	1.78	7.00	4.22	0.21	1.99	0.41	0.83			99.90
14-PBA-100	60.26	25.07	0.04	1.93	0.66	3.20	0.10	0.30	4.31	0.73	2.15	<0.01	<0.01	98.75
Average Pelite	59.77	16.57	0.07	2.62	5.88*		2.17	1.73	3.53					92.34

All values reported in wt% oxide.

Average pelite from Symmes and Ferry (1991).

* All iron reported as FeO

Figure 4.1.1: Bulk-rock geochemical plots for all studied samples (A) AFM (B) ACF. Average pelite composition from Symmes and Ferry (1991). The AFM diagram has axes defined by $A = \text{Al}_2\text{O}_3 - 3\text{K}_2\text{O}$, $F = \text{FeO}$, and $M = \text{MgO}$. Axes for the ACF diagram follow $F = \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - (\text{K}_2\text{O} + \text{Na}_2\text{O})$, $C = \text{CaO}$, and $F = \text{FeO} + \text{MnO} + \text{MgO}$ (Spear, 1993).

4.2 Petrography

This section discusses the 8 samples used in this study; their locations are given in table 2.4.1. 14PBA-43B is from the upper Montresor group and the remaining 7 samples are part of the lower Montresor group. Sample sections are randomly oriented. Modal percentages are determined using volume estimation from petrographic and XR- μ CT data. The notation of S1 defines the main foliation of the rock, and S0 defines a planar fabric seen as linear inclusions within some porphyroblasts. Mineral abbreviations are after Whitney and Evans (2004) and are defined in appendix A.1.

14PBA-43B

Sample 14PBA-43B (figure 4.2.2-F) contains an assemblage of quartz (20 - 30%), biotite (20 - 30%), muscovite (10 - 20%), plagioclase (10 - 20%), and alkali feldspar (10 - 20%). Accessory minerals include tourmaline, zircon, rutile, monazite, and opaques. A strong foliation (S1) is defined by biotite and muscovite. Matrix biotite, plagioclase, muscovite, and quartz are fine grained and potassium feldspar porphyroblasts are 1 – 2 mm in diameter. These potassium feldspar porphyroblasts are rarely twinned, except in some grains where faint crosshatched twinning can be seen. This indicates that the alkali feldspar may be microcline. The potassium feldspar also contains abundant inclusions of quartz, biotite, and muscovite. These inclusions appear to be randomly oriented and do not define a linear trend or fabric.

12PBA-27A

This sample contains an assemblage of garnet (2 - 5%), biotite (20 - 30%), quartz (20 - 30%), plagioclase feldspar (10 - 20%), muscovite (2 - 5%), and chlorite (1 - 2%) (figure 4.2.1-A, B). Large, fine-grained, sericite-rich clusters comprise another 10 - 20%. Accessory minerals include ilmenite, pyrite, pyrrhotite, tourmaline, zircon, and monazite. Chlorite is seen both in the matrix and along grain boundaries and cracks within garnet and biotite. Chlorite within garnet and biotite grains is inferred to be part of a retrograde assemblage. A well-defined foliation (S1) is defined by biotite. This foliation is commonly wrapping both garnet and the large sericite-rich clusters. These elongate, irregularly shaped, sericite-rich clusters are up to 5 cm in diameter and contain abundant inclusions of quartz, plagioclase, and biotite. These clusters are interpreted to be sericite pseudomorphs after andalusite based on grain morphology and phase assemblages seen in the other samples in this study. Muscovite in the rock matrix is seen crosscutting the main biotite foliation (S1) at random orientations. Garnet crystals are <2 mm in diameter and are commonly embayed. Garnet contains abundant inclusions of quartz and plagioclase, ilmenite, pyrite, pyrrhotite, zircon, and monazite. These inclusions define straight to weakly curved inclusion trails within the crystals (S0) that run at an oblique angle to the main foliation (S1). Many garnet crystals also contain roughly parallel fractures approximately perpendicular to S1, which are commonly filled with biotite and/or chlorite. Straight grain boundaries are observed between biotite, garnet, and the sericite pseudomorphs after andalusite.

14PBA-67A

This sample (figure 4.2.1-C) contains an assemblage of quartz (40 - 50%), biotite (10 - 20%), muscovite (5 - 10%), plagioclase (10 - 20%), and andalusite (2 - 5%).

Accessory minerals include tourmaline, zircon, and opaques. Chlorite seen at the edges of biotite grains is inferred to be part of a retrograde assemblage. The main foliation (S1) is defined by fine-grained biotite and muscovite. This foliation weakly wraps andalusite porphyroblasts that measure up to 2 cm in diameter. Inclusions within andalusite are comprised primarily of quartz and biotite, with rare plagioclase and muscovite.

14PBA-85A

14PBA-85A is composed of an assemblage of biotite (10 - 20%), muscovite (20 - 30%), quartz (20 - 30%), plagioclase (5 - 10%), and andalusite (10 - 20%) (figure 4.2.1-D). Accessory minerals include zircon, monazite, and opaques. Chlorite present at the edges of biotite grains is inferred to be part of a retrograde assemblage. A strong foliation (S1) is defined by biotite and muscovite. Andalusite porphyroblasts up to 2 cm in diameter are irregularly shaped and randomly distributed. The andalusites contain abundant inclusions of quartz, plagioclase, biotite, and muscovite. These inclusions follow a random orientation. The main foliation (S1) wraps the andalusite porphyroblasts.

14PBA-94A

This sample contains an assemblage of garnet (5 - 10%), quartz (20 - 30%), biotite (20 - 30%), plagioclase (20 - 30%), amphibole (1 - 2%), and chlorite (2 - 5%) (figure 4.2.2-A). Observed accessory minerals include ilmenite, pyrite, zircon, and other

opaques. A weak foliation (S1) is defined by biotite and chlorite. Chlorite is present both in the matrix and at the edges of biotite, amphibole, and garnet crystals. Chlorite at the edge of grains is interpreted to be retrograde. Two different amphibole compositions are present (figure 4.3.1-A, B), with one amphibole seen partially surrounding the other. Garnet is strongly clustered in areas up to 2 mm in diameter (figure 4.2.1-E, F). These clusters are composed of many small (<0.2 mm), subhedral to angular fragments of garnet. Rare large garnets are also seen (>1 mm). These generally show some partially preserved crystal faces and a highly embayed garnet core. This area, formerly taken up by the larger garnet, can be defined by a weakly preserved wrapping of main foliation (S1) around the area.

14PBA-97A

14PBA-97A (Figure 4.2.2-B) contains an assemblage of quartz (20 - 30%), biotite (10 - 20%), muscovite (10 - 20%), plagioclase (10 - 20%), and andalusite (10 - 20%). Chlorite observed at the rims of biotite grains is inferred to be part of a retrograde assemblage. Accessory minerals include tourmaline, zircon, pyrite, and opaques. Biotite and muscovite form a well-defined matrix foliation (S1) that wraps the porphyroblasts. Andalusite porphyroblasts of 2 - 3 cm contain inclusions of quartz, plagioclase, biotite, and muscovite. The inclusions are randomly oriented within the andalusite. Grain boundaries and cracks within the andalusite porphyroblasts are replaced by very fine-grained muscovite. Andalusite porphyroblasts show sericite alteration along the crystal faces and along fractures. Approximately 50% of the original andalusite volume has been altered to sericite.

Figure 4.2.1: Representative thin section photos. (A) and (B) 12PBA-27A, (C) 14PBA-67A, (D) 14PBA-85A, (E) and (F) 14PBA-94A.

14PBA-99A

Sample 14PBA-99A shows layering defined by variation in mineral proportions. This variation is most noticeable in garnet volume, and thus the sample was divided into a garnet-rich and a garnet-poor subsample. These subsamples were analyzed separately (see figure 4.4.2-B) and are referred to as 14PBA-99A-A and 14PBA-99A-B.

14PBA-99A-A, the garnet-rich subsample, contains a mineral assemblage of garnet (5 - 10%), biotite (20 - 30%), quartz (30 - 40%), plagioclase (10 - 20%), and rare muscovite (1 - 2%) and chlorite (1 - 2%) (figure 4.2.2-C). Accessory minerals include tourmaline, zircon, monazite, ilmenite, and opaques. Chlorite is observed along edges and cracks within garnet and biotite grains and is interpreted to be part of a retrograde assemblage. Rare muscovite appears corroded. The main foliation (S1) is defined by biotite, which wraps garnet porphyroblasts. Garnets have a maximum diameter of approximately 2 mm. Larger crystals commonly display moderately to highly resorbed crystal faces and contain abundant inclusions of quartz, plagioclase, and rare biotite. Smaller garnets are noticeably less resorbed and contain little to no inclusions. Garnet commonly occurs in clusters up to a few cm in diameter.

14PBA-99A-B is the garnet-poor subsample. This sample consists of garnet (1 - 2%), biotite (30 - 40%), quartz (30 - 40%), plagioclase (10 - 20%), and rare muscovite (1 - 2%) and chlorite (1 - 2%) (figure 4.2.2-D). Accessory minerals include tourmaline, monazite, zircon, ilmenite, pyrite, and other opaques. Some chlorite is seen at the edges of biotite and garnet and is inferred to be retrograde. The main foliation (S1) in this sample is defined by biotite and weakly wraps garnet porphyroblasts. Garnet grains have a maximum diameter of just over 0.5 mm. These crystals are typically resorbed.

Quartz and plagioclase are present as inclusions within garnet crystals. Garnet crystals in this subsample do not appear to have a clustered distribution.

14PBA-100

This sample (figure 4.2.2-E) contains a mineral assemblage of quartz (30 - 40%), muscovite (20 - 30%), biotite (10 - 20%), plagioclase (5 - 10%), and andalusite (10 - 20%). Rare retrograde chlorite is seen replacing the edges of some of the matrix biotite grains. Accessory minerals include tourmaline, zircon, pyrite, and other opaques. Muscovite and biotite define the main foliation (S1), which wraps andalusite porphyroblasts that are up to 3 cm in diameter. Andalusite porphyroblasts contain randomly oriented inclusions of quartz, plagioclase, biotite, and muscovite.

Figure 4.2.2: Representative thin section photographs. (A) 14PBA-94A (B) 14PBA-97A, (C) 14PBA-99A-A, (D) 14PBA-99A-B, (E) 14PBA-100, (F) 14PBA-43B.

4.3 Mineral Composition

Mineral compositions were determined by electron probe micro-analysis (EPMA) for minerals of interest. A full analysis of representative mineral chemistry was completed for sample 12PBA-27A. The dataset for 12PBA-27A, containing biotite, chlorite, plagioclase, and muscovite analyses, is provided in table A.2.3. EPMA analysis was also done in order to characterize the two different amphibole compositions present in 14PBA-94A. Garnet compositions for samples 12PBA-27A, 14PBA-94A, and 14PBA-99A are discussed in detail in the next section.

EPMA mineral analysis for sample 12PBA-27A yields approximately homogenous compositions across each mineral population. Analyses on both the core and rim of biotite indicate homogenous chemistry with a $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of 0.71. The composition of chlorite is also homogeneous with a $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of 0.68. Plagioclase also displays homogenous composition from core to rim of the grains. The plagioclase has a X_{Ab} content of 0.57 and an A_{An} content of 0.42. Little K is present as shown by a X_{Or} content of 0.01. Analysis on the white mica in this sample shows no discernable difference between analyses on the fine-grained white mica pseudomorphing the andalusite and the larger grains within the matrix. This composition of this white mica has a $\text{K}/(\text{Ca}+\text{Na}+\text{K})$ ratio of 0.92 – 0.95. Analyses also show some MgO (0.33 – 0.51 wt%) indicating that the white mica is likely muscovite. The remainder of the total is composed of Na, as almost no Ca is present.

Sample 14PBA-94A contains two amphiboles with distinctly different compositions, referred to as amphibole 1 and amphibole 2 (figure 4.3.1). Partial EPMA chemical analyses were done on these minerals; K_2O and Na_2O were not measured, as the

instrument was not calibrated for these elements at the time of analyses. However, EDS measurements on the amphiboles indicate minor amounts of K_2O and Na_2O . The resulting amphibole compositions are presented in table 4.3.1. Amphibole nomenclature is after Hawthorne *et al.* (2012). Analyses on amphibole 1 indicate a high proportion of Fe and Mg, with little Al, Mn, and Ca. A generalized chemical formula using the average of the four EPMA analyses gives $Ca_{0.1}Fe_2(Mg, Fe, Al)_{4.9}Si_8O_{22}(OH)_2$. This suggests a ferro-anthophyllite endmember composition. Amphibole 2 shows a high proportion of Al, Fe, and Ca. A generalized chemical formula using an average of the four EPMA analyses gives $Ca_{1.9}(Mg, Fe, Al)_{5.3}Al_{1.5}Si_{6.5}O_{22}(OH)_2$, as well as minor Na and K shown by the EDS spectrum. This suggests a ferro-tschermakite endmember composition.

Figure 4.3.1: (A) and (B) Backscattered electron (BSE) images showing the distribution of two amphibole compositions (Amp1 and Amp2), and chlorite in sample 14PBA-94A.

Table 4.3.1: Chemistry of two amphiboles in sample 14PBA-94A compared to amphibole chemistry predicted by THERIAK at two P-T points within the stable assemblage field.

Spot	Amphibole 1						Amphibole 2					
	1	2	3	4	Pr1	Pr2	1	2	3	4	Pr1	Pr2
SiO ₂	51.20	51.56	51.83	51.44			39.97	40.02	41.21	41.26		
TiO ₂	0.03	0.03	0.03	0.07			0.03	0.11	0.00	0.05		
Al ₂ O ₃	0.85	0.84	0.84	0.81	P (bar)	P (bar)	18.65	18.46	17.64	17.09	P (bar)	P (bar)
FeO	32.90	32.48	32.23	32.76	2500	3500	22.64	21.33	21.49	21.64	2500	3500
K ₂ O	-	-	-	-			-	-	-	-		
MnO	0.24	0.25	0.30	0.30	T (°C)	T (°C)	0.06	0.11	0.06	0.08	T (°C)	T (°C)
MgO	10.67	11.18	10.88	10.82	500	550	3.28	3.80	4.02	4.18	500	550
CaO	0.61	0.61	0.60	0.56			11.29	11.29	11.72	11.42		
NaO	-	-	-	-			-	-	-	-		
Total	96.50	96.97	96.72	96.75			95.93	95.13	96.16	95.73		
Cations	15	15	15	15	15	15	13	13	13	13	13	13
Si	7.96	7.95	8.02	7.97	7.93	7.83	6.05	6.09	6.22	6.25	6.80	6.48
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.16	0.15	0.15	0.15	0.15	0.34	3.33	3.31	3.14	3.05	1.92	2.51
Fe3+	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe2+	4.28	4.19	4.17	4.24	6.16	5.34	2.87	2.71	2.72	2.74	3.10	2.34
K	-	-	-	-	0.00	0.00	-	-	-	-	0.00	0.00
Mn	0.03	0.03	0.04	0.04	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00
Mg	2.47	2.57	2.51	2.50	0.73	1.46	0.74	0.86	0.91	0.94	1.19	1.68
Na	-	-	-	-	0.00	0.00	-	-	-	-	0.51	0.60
Ca	0.10	0.10	0.10	0.09	0.03	0.03	1.83	1.84	1.90	1.85	1.99	1.97

All iron is reported as FeO.

- No probe data for K₂O and NaO. EDS spectrum indicates low concentrations of these elements.
Pr values are predicted by THERIAK for the noted P-T points.

4.4 X-Ray Micro Computed Tomography (XR- μ CT)

XR- μ CT was used to characterize the garnet porphyroblast distribution in samples 12PBA-27A, 14PBA-94A, and 14PBA-99A. Representative reconstructed cross sections through the scanned cores of these samples are shown in figure 4.4.1. In these images different minerals are identified based on their x-ray attenuation, as represented by grey values. Iron oxides are the highest attenuating phases and appear brightest. The second highest attenuating phase is garnet, followed by biotite, and then the lower attenuating phases; white mica, quartz, and plagioclase. In all the garnet-bearing samples, the x-ray attenuation of garnet and biotite appears to be uniform across the area of the porphyroblast. A grouping or clustering distribution of garnet crystals is prominently displayed in 14PBA-94A (Figure 4.4.1-B). A less prominent clustered distribution of garnet porphyroblasts is also seen in 14PBA-99A-A (Figure 4.4.1-C).

Garnet was segmented from the rest of the sample, on the basis of its grey value in the XR- μ CT data, in order to visualize and quantify its size and distribution within the rock. 3D reconstructions of garnet within the scanned cores for samples 12PBA-27A and 14PBA-99A are shown in figure 4.4.2. The reconstruction of sample 14PBA-99A shows an uneven distribution of garnet throughout the core, with the top portion showing a much higher number of garnets than the lower portion. Due to this inhomogeneous distribution of garnet the sample was divided into two subsamples, 14PBA-99A-A (garnet-rich subsample) and 14PBA-99A-B (garnet-poor subsample). The areas of high and low garnet concentrations appear to be layered. The approximate division of these two subsamples is shown in figure 4.4.2-B. Sample 12PBA-27A shows a more uniform

Figure 4.4.1: Representative reconstructed XR- μ CT cross sections of garnet bearing samples. (A) 12PBA-27A, (B) 14PBA-94A, (C) 14PBA-99A-A, (D) 14PBA-99A-B. Two white mica pseudomorphs after andalusite are outlined in sample 12PBA-27A, although others can also be seen in this cross section. The dark grey values of the matrix in all samples is representative of a combination of quartz, feldspar, and white mica.

Figure 4.4.2: 3D visualization of the distribution of garnet porphyroblasts in cylindrical cores scanned by XR- μ CT. (A) 12PBA-27A. (B) 14PBA-99A showing the division of the sample into garnet-rich (14PBA-99A-A) and garnet-poor (14PBA-99A-B) subsamples.

distribution of garnet throughout the sample volume, although there may be an area of clustered garnets towards the center of the drill core.

Segmentation of garnet in sample 12PBA-27A yielded 451 crystals. Only crystals that do not intersect with the edges of the rock cylinder are included for analyses. Garnet constitutes approximately 3% of the volume of this sample. The crystal size distribution (figure 4.4.5-A) for this sample shows a right-skewed unimodal distribution. Garnet crystals were divided into 22 size classes, with the largest observed garnet having a radius of 1.1 mm. The calculated radius shown is slightly smaller than the true radius of the observed garnets, as embayments observed along the edges of the grains are not accounted for when radius is calculated from garnet volume. Garnet porphyroblasts have an average aspect ratio of 1.26. There appears to be no correlation between the aspect ratio and volume of garnet (figure 4.4.5-B). Smaller garnets show a slightly greater range in aspect ratio than larger garnets. Stereographic projections of the long and short axes of the garnet porphyroblasts define planes of 171/46 SW and 265/83 NW respectively (figure 4.4.3). These planes are relative to the position of the samples in the XR- μ CT scanner. The plane defined by the long axes of garnet crystals is estimated to be roughly parallel to the main matrix foliation.

Figure 4.4.3: Stereographic projection of the long axis (A) and short axis (B) of 451 garnet crystals from sample 12PBA-27A. Axis directions are relative to the orientation of the sample in the XR- μ CT scanner.

Using the XR- μ CT data set of sample 14PBA-99A-A (garnet-rich subsample) it was possible to numerically segment the garnets from the rock matrix, which constitutes ca. 5% of the sample volume. However, due to the highly clustered and intergrown nature of the porphyroblasts (figure 4.4.4), it was not possible to segment individual grains. Segmentation of the garnet porphyroblasts in 14PBA-99A-B resulted in 568 crystals, which represent 0.8% of the total volume of the subsample. The crystal size distribution for garnet shows a right-skewed unimodal normal distribution (figure 4.4.5-C). The reported radius is slightly smaller than observed in thin section, as the embayments on the

edges of garnet crystals are not considered in the calculation of radius from measured volume.

Garnet crystals in the XR- μ CT dataset of sample 14PBA-94A (figure 4.4.1-B) could not be segmented from the rock matrix with the software used. This is due to the greyscale value of garnet in this sample. In the other garnet-bearing samples, the greyscale range of garnet falls between 140 - 180. In 14PBA-94A, the greyscale range for garnet is 110 - 140. As this range overlaps with the greyscale range for matrix biotite, it was not possible to separate them and isolate garnet. This lower greyscale value observed in garnet is a result of the composition of the garnet, where garnet in sample 14PBA-94A has a significantly higher grossular content and lower almandine content compared to the other three garnet-bearing samples (see tables 4.4.1 and 4.6.1).

Figure 4.4.4: Two examples (A) and (B) of the highly clustered and intergrown garnet porphyroblasts in 14PBA-99A-A (garnet-rich subsample) that did not allow for segmentation of individual garnet crystals.

Figure 4.4.5: (A) Crystal size distribution for 12PBA-27A. Crystal size classes are shown on top of the columns. (B) Volume to aspect ratio plot for 12PBA-27A (C) Crystal size distribution for 14PBA-99A-B (garnet-poor subsample).

4.5 Statistical Analysis of Garnet Distribution

The single scale and scale dependant statistics for the distribution of garnet crystals in 12PBA-27A is shown in figure 4.5.1. The mark value used in the statistics is (A) sphere-normalized radius calculated from volume and (B) the semi-major axis or half of the maximum axis length. The semi-major axis length was taken into account to visualize any effects of elongate porphyroblast geometry, should they differ from the sphere-normalized radius and the general assumption of a spherical crystal shape for garnet porphyroblasts. Considering the elongation of porphyroblasts in this type of statistical analysis has proven useful in other studies (Petley-Ragan *et al.*, 2016). The sample population contained 451 garnet crystals that were segmented from the XR- μ CT data with Blob3D software. Any crystals cut by the edge of the core were omitted from the dataset. The pink shaded region represents a 96% confidence envelope for a simulated random crystal distribution. The blue bar represents the average nearest neighbour distance of garnet crystals to two standard deviations.

The single scale statistics show a clustering index and impingement index that falls within the null hypothesis envelope for both mark values, indicating that the sample garnet population follows a random distribution. Although the null hypothesis envelope for the ordering index does not appear in the diagram, it falls above the sample garnet population. This indicates that there are fewer garnet crystals than expected, suggesting an ordered distribution.

The scale dependant statistics, L'function and pair correlation function (PCF), for both the radius calculated from spherical volume and semi-major axis show an observed garnet population that falls above the null hypothesis envelope at length scales

approximately equal to and larger than the average nearest neighbour distance of 0.1 - 0.2 cm. This indicates that there are more crystal centers than expected, suggesting a clustering of garnet crystal centers at all test distances greater than the average nearest neighbour distance. The L' function for a sphere-normalized radius shows the observed population falling below the null hypothesis envelope at test distances less than the average nearest neighbour distance. This signal is due to crystals being unable to nucleate within the space already taken up by another crystal (Hirsch, 2000). With sphere-normalized radius as the mark value, the mark covariance function (MCF) falls below the 96% null hypothesis envelope at length scales less than the average nearest neighbour distance. This is attributed to the Strauss hard-core process, a positive correlation between the size of two crystals and the distance between their centers where they can only become closer to each other if their size decreases (Illian *et al.*, 2008). The observed garnet population falls within the null hypothesis envelope at test distances corresponding to the average nearest neighbour distance to approximately 15 mean radii, suggesting a random distribution. At test distances greater than 15 mean radii the statistic falls slightly above the null hypothesis envelope indicating that there are larger crystal sizes than expected at those test distances and suggesting a clustered distribution of garnet. The MCF statistics calculated from the semi-major axis shows a random distribution at most scales, with most values falling within the 96% null hypothesis envelope. Some values fall slightly above the null hypothesis envelope, suggesting clustering of garnet porphyroblasts at test distances of 13 - 14 and greater than 17 mean radii.

Figure 4.5.1: Reduce 3D results for garnet in 12PBA-27A using radius calculated from volume (sphere-normalized radius) (A) and the semi-major axis (B) as the mark value.

4.6 Garnet Composition

EPMA traverses were done on garnet porphyroblasts in samples 12PBA-27A and 14PBA-99A. In sample 12PBA-27A traverses were performed on close to central sections of the two largest garnet porphyroblasts as identified by XR- μ CT. Inspection of the XR- μ CT data indicates that the sections of garnets 1 and 2 are approximately 30 - 90 μ m away from the centers of the porphyroblasts. Figure 4.6.1 shows a comparison between the crystal centers as identified by XR- μ CT and a microprobe image of the resulting thin section for garnet 1. Additional traverses were done on garnet porphyroblasts belonging to other size classes as identified in thin section and do not represent central sections. Traverses were performed on the largest representative garnet porphyroblasts in 14PBA-99A-A and -B as identified in thin section. Spot analyses were done on representative garnets from sample 14PBA-94A. Garnet EPMA traverses report $X_{\text{Alm}} = (\text{Fe}^{2+}/\text{Ca}+\text{Mg}+\text{Fe}^{2+}+\text{Mn})$, $X_{\text{grs}} = (\text{Ca}/\text{Ca}+\text{Mg}+\text{Fe}^{2+}+\text{Mn})$, $X_{\text{Prp}} = (\text{Mg}/\text{Ca}+\text{Mg}+\text{Fe}^{2+}+\text{Mn})$, and $X_{\text{Sps}} = (\text{Mn}/\text{Ca}+\text{Mg}+\text{Fe}^{2+}+\text{Mn})$. Y is reported in weight% Y_2O_3 . The location of each traverse is shown as a dashed line on the figure referenced in the text. Garnet core compositions are reported in table 4.6.2 and spot analysis on 14PBA-94A in table 4.6.1

Figure 4.6.1: Comparison between (A) an EPMA scan of the thin section containing the largest garnet in 12PBA-27A and (B) the XR- μ CT image of the ideal central section through that garnet. The thin section cut is approximately 30 - 90 μ m away from the center of the grain.

Table 4.6.1: Mineral composition for spot analysis on garnets in 14PBA-94A. Corresponding locations for the spot analysis are shown in figure 4.6.10-F and 4.6.8-A.

Spot	1	2	3	4	5	6	7	8	9	10	11	12
X_{alm}	0.76	0.76	0.74	0.73	0.72	0.76	0.74	0.74	0.74	0.73	0.78	0.74
X_{sps}	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
X_{prp}	0.08	0.07	0.07	0.07	0.06	0.08	0.07	0.07	0.07	0.07	0.07	0.07
X_{grs}	0.14	0.15	0.16	0.17	0.20	0.14	0.17	0.16	0.16	0.17	0.12	0.16
Y_2O_3	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 4.6.2: Core composition of garnet porphyroblasts of various size classes from 12PBA-27A and the largest garnets identified in thin section from 14PBA-99A-A and-B.

	12PBA-27A							14PBA-99A-A		14PBA-99A-B
Garnet	1	2	3	4	5	6	7	1	2	1
SiO ₂	36.63	36.43	37.12	36.77	36.64	39.31	37.05	36.86	37.24	36.38
TiO ₂	0.01	0.01	0.04	0.03	0.05	0.00	0.04	0.05	0.03	0.01
Al ₂ O ₃	20.85	20.82	20.46	21.15	21.07	20.05	20.91	21.18	21.06	20.95
FeO	35.26	34.48	34.73	35.87	36.30	34.97	35.91	34.35	34.67	35.32
MnO	4.35	3.71	3.68	3.17	2.43	2.79	2.59	2.87	2.99	2.12
MgO	1.21	1.52	1.42	1.64	1.77	1.48	1.75	1.94	1.85	1.83
CaO	1.96	2.08	2.42	1.96	1.85	1.76	2.28	3.51	2.92	2.62
Y ₂ O ₃	0.17	0.37	0.03	0.02	0.10	0.04	0.01	0.01	0.00	0.28
Total	100.27	99.05	99.87	100.59	100.11	100.36	100.53	100.77	100.76	99.51
Oxygen	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00
Si	5.97	5.98	6.05	5.96	5.96	6.30	5.99	5.94	5.99	5.95
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Al	4.00	4.03	3.93	4.04	4.04	3.79	3.99	4.02	3.99	4.04
Fe ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ²⁺	4.81	4.74	4.73	4.86	4.94	4.69	4.86	4.63	4.67	4.83
Mn	0.60	0.52	0.51	0.44	0.34	0.38	0.36	0.39	0.41	0.29
Mg	0.29	0.37	0.35	0.40	0.43	0.35	0.42	0.47	0.44	0.45
Ca	0.34	0.37	0.42	0.34	0.32	0.30	0.40	0.61	0.50	0.46
Fe/(Fe+Mg)	0.94	0.93	0.93	0.92	0.92	0.93	0.92	0.91	0.91	0.91
Mg/(Fe+Mg)	0.06	0.07	0.07	0.08	0.08	0.07	0.08	0.09	0.09	0.09
X _{alm}	0.80	0.79	0.79	0.80	0.82	0.82	0.80	0.75	0.77	0.80
X _{sps}	0.10	0.09	0.08	0.07	0.06	0.07	0.06	0.07	0.07	0.05
X _{prp}	0.05	0.06	0.06	0.07	0.07	0.06	0.07	0.08	0.07	0.08
X _{grs}	0.06	0.06	0.07	0.06	0.05	0.05	0.07	0.10	0.08	0.08

All iron is reported as FeO.

12PBA-27A

Garnet 1 (size class 1: 1.05 – 1.1 mm)

Two garnets from sample 12PBA-27A were centrally sectioned and analyzed. The largest garnet (figure 4.6.2-A), with a radius of 1.24 mm, shows an overall trend of increasing X_{alm} and X_{prp} , and decreasing X_{sps} and X_{grs} from core to rim. X_{alm} values range from 0.78 in the core to 0.83 in the rim. Repeating peaks or spikes in X_{alm} values as high as 0.82 near the core correspond to zones adjacent to cracks in the garnet. X_{prp} shows values of 0.05 in the core rising slightly to 0.07 in the rim. X_{prp} values decrease to 0.03 adjacent to fractures. A sharp decrease in X_{prp} values is seen within 50 μm of the rim. X_{grs} decreases to 0.05 adjacent to cracks in the garnet. The zoning of X_{grs} is also modified by the presence of cracks, with values in the core dropping from 0.07-0.05 near the core. A strong example of the modification of garnet zoning of X_{alm} , X_{prp} , and X_{grs} in proximity to a crack is shown at approximately 1100 μm . The zoning of X_{sps} reaches 0.10 in the core and smoothly drops to 0.05 in the rim. A sharp increase within 50 μm of the rim brings X_{sps} up to 0.06. Y_2O_3 shows two peaks near the garnet core with values between 0.2-0.4, dropping off a diameter of 600 and 1400 μm to <0.1 . X_{sps} and Y_2O_3 values do not appear to be affected by fractures in the garnet.

The qualitative chemical map of garnet 1 (figure 4.6.3) shows concentric chemical zonation of X_{alm} , X_{prp} , X_{grs} , and X_{sps} . The X_{grs} chemical map clearly displays the lower X_{prp} in the vicinity of the parallel cracks running through the garnet. Changes to the chemical zoning near cracks can also be seen in the X_{alm} and X_{grs} chemical maps, with the zone of chemical modification extending up to ca. 20 μm away from the fractures. The

Figure 4.6.2: EPMA compositional profiles across garnet porphyroblasts of different size classes in sample 12PBA-27A. (A) and (B) size class 1, (C) size class 2, (D) size class 7. Traverses were performed at a resolution of 10 μm.

Figure 4.6.3: EPMA element distribution maps for sample 12PBA-27A Garnet 1 (size class 1). (A) Backscattered electron (BSE) image showing location of an EPMA compositional profile (figure 4.6.2-A). (B) Ca (C) Mg (D) Fe (E) Mn (F) Y.

X_{sps} content does not appear to be modified adjacent to the cracks. A 600 μm wide area of high Y is seen at the garnet core, as well as a ring of elevated Y concentration within 50 - 100 μm of the rim.

Garnet 2 (size class 1: 1.05 – 1.1 mm)

The second centrally sectioned garnet (figure 4.6.2-B) from the first size class shows a pattern of increasing X_{alm} and X_{prp} , and decreasing X_{sps} and X_{grs} from core to rim. X_{alm} values range from 0.79 in the core to between 0.82 - 0.84 in the rim on either side of the traverse. A few cracks in the garnet crystal correspond to anomalous peaks in X_{alm} values, bringing core values near cracks up to 0.81. X_{prp} shows values of 0.05-0.06 in the core that gently increase to 0.07 at the rim. A sharp decline in X_{prp} occurs within 200 μm of the rim at the start of the traverse. X_{grs} values range from 0.05 - 0.06 in the core to 0.04 - 0.05 in the rim. Some decreases in X_{grs} values correspond to cracks in the garnet. X_{sps} values follow a smooth path with values of 0.09 in the core and 0.05 in the rim. The X_{sps} zoning does not appear to be affected by fractures in the garnet. Y_2O_3 shows a peak in the core of the garnet with values reaching 0.4 that drop off steeply to 0.1. Two smaller peaks between 0.1 - 0.2 are seen at approximately 600 and 1700 μm . Y_2O_3 drops off to 0.0 - 0.1 at the rim.

Chemical mapping of this garnet (figure 4.6.4) also shows concentric X_{alm} , X_{prp} , X_{grs} , and X_{sps} zoning. This zoning is truncated where the crystal faces of garnet are embayed. Similar to the other garnet from size class 1, there is a 500 μm wide Y high in the core and a Y high ring within 100 μm of the rim.

Figure 4.6.4: EPMA element distribution maps for sample 12PBA-27A Garnet 2 (size class 1). (A) Backscattered electron (BSE) image showing location of an EPMA compositional profile (figure 4.6.2-B). (B) Ca (C) Mg (D) Fe (E) Mn (F) Y.

Garnet 3 (size class 2: 1.0 – 1.05 mm)

One garnet in size class 2 (figure 4.6.2-C and 4.6.10-A) was analyzed from sample 12PBA-27A. The zoning pattern in this garnet shows increasing X_{alm} and X_{prp} and decreasing X_{sps} and X_{grs} from the core to the rim. Core X_{alm} values between 0.79 - 0.80 increase to rim values of 0.83. There is slight variation (<0.02) in the X_{alm} zoning near inclusions. X_{prp} increases from 0.055 - 0.07 moving from core to rim. Similar to X_{alm} , there is some variation in the zoning pattern around inclusions. X_{prp} values drop sharply near the rim. X_{grs} values range from 0.06 - 0.07 in the core decreasing to 0.05 at the rim. X_{sps} measures 0.09 in the core dropping off to 0.05 in the rim. Y_2O_3 values range from 0 – 0.06 with no discernable zoning pattern.

Garnet 4 (size class 7: 0.75 – 0.8 mm)

The garnet in size class 7 (figure 4.6.2-D) shows core to rim zoning of increasing X_{alm} and X_{prp} and decreasing X_{sps} and X_{grs} . X_{alm} values range from between 0.79-0.80 in the core to 0.83 at the rim. Similar to the grains, X_{alm} increases to 0.82 adjacent to fractures in the garnet. X_{prp} values rise from 0.06 in the core to 0.07 at the rim before a sharp decrease within 40 μm of the rim. X_{prp} values are affected by cracks in the garnet, with values falling to below 0.06 near fractures. At the garnet core X_{grs} measures 0.07, with values dropping to 0.05 at the rim and adjacent to fractures. Core X_{sps} values of 0.075 smoothly drop to rim values of 0.05. X_{sps} zoning does not appear to be affected by the cracks in the garnet. Background Y_2O_3 measures 0 – 0.03 with peaks of 0.06 in the core and 0.08 within 50 μm of the rim.

12PBA-27A Garnet 4

Figure 4.6.5: EPMA element distribution maps for sample 12PBA-27A Garnet 4 (size class 7). (A) Backscattered electron (BSE) image showing location of an EPMA compositional profile (figure 4.6.2-D). (B) Ca (C) Mg (D) Fe (E) Mn (F) Y.

Chemical mapping of garnet 4 (figure 4.6.5) shows concentric chemical zonation of X_{alm} , X_{prp} , X_{grs} , and X_{sps} that has been partially truncated by embayments of the edges of the crystal. X_{prp} is shown to decrease along fractures in the garnet. Similar to the larger size class, Y zoning displays a high in the center and a ring near the rim of the garnet crystal.

Garnet 5 (size class 10: 0.6 – 0.65 mm)

A single size class 10 garnet (figure 4.6.6 –A and 4.6.10-B) from sample 12PBA-27A was analyzed. This garnet shows zoning with increasing X_{alm} , decreasing X_{sps} and X_{grs} , and uniform X_{prp} from core to rim. X_{alm} values range from 0.81 in the core to 0.83 at the rim. X_{alm} rises to 0.82 adjacent to fractures in the garnet. Sharp decreases in X_{prp} values are seen within 50 μm of the rim. X_{prp} values are consistently at 0.07 from core to rim. Some sharp decreases to 0.05 are seen adjacent to cracks. These decreases correspond to peaks in X_{alm} values. X_{grs} values range from 0.065 in the core to 0.05 in the rim, with values near the cracks falling as low as 0.05. Zoning of X_{sps} shows core values of 0.06 that fall gently to 0.05 at the rim. A Y_2O_3 peak of 0.06 is seen at the core of the garnet before falling sharply to values of 0.0 - 0.03. A slight increase in Y_2O_3 (up to 0.4) occurs within 40 μm of the rim.

Garnet 6 (size class 12: 0.5 – 0.55 mm)

This garnet (figure 4.6.6-B and 4.6.10-C) shows a zoning pattern of increasing X_{alm} , decreasing X_{sps} and X_{grs} , and uniform X_{prp} from the core to the rim. X_{alm} range from 0.81 in the core to 0.83 at the rim, with peaks adjacent to fractures in the garnet.

Figure 4.6.6: EPMA compositional profiles across garnet porphyroblasts of different size classes in sample 12PBA-27A. (A) size class 10 (B) size class 12, (C) size class 13. Traverses were performed at a resolution of 10 μm.

X_{prp} values are consistently at a value of 0.07 from core to rim. A sharp decrease is seen adjacent to cracks and within 50 μm of the rim. X_{grs} shows flat zoning with values of 0.06 to within 200 μm of the rim where values drop off to 0.05. The X_{sps} zoning shows a shallow gradient of 0.06 at the core dropping slightly to 0.05 at the rim. Y_2O_3 shows a peak at the garnet core with values nearing 0.2. This peak drops off to values below 0.1 before rising again within 50 μm of the rim to 0.15.

Garnet 7 (size Class 13: 0.45 – 0.5 mm)

This garnet is from the smallest size class (figure 4.6.6-C) analyzed from sample 12PBA-27A. A well defined zoning pattern in this sample with increasing X_{alm} , decreasing X_{sps} and X_{grs} , and uniform X_{prp} from core to rim. X_{alm} has a core value of 0.81 that increases to 0.83 in the rim. X_{prp} zoning is uniform from core to rim with values around 0.07 before dropping off steeply within 50 μm of the rim. X_{grs} measures 0.07 at the core and decreases to 0.05 at the rim. X_{sps} drops slightly from 0.06 at the core to 0.05 at the rim. A high Y ring is seen within 50 μm of the garnet rim.

The chemical zoning of X_{alm} , X_{prp} , X_{grs} , and X_{sps} in this sample (figure 4.6.7) is concentric and truncated by embayments in the garnet. Modification of the chemical zoning is seen along cracks, which is especially evident in X_{prp} . A ring of elevated Y is seen near the garnet rim.

Figure 4.6.7: EPMA element distribution maps for sample 12PBA-27A Garnet 7 (size class 13). (A) Backscattered electron (BSE) image showing location of an EPMA compositional profile (figure 4.6.6-C). (B) Ca (C) Mg (D) Fe (E) Mn (F) Y.

14PBA-94A

A chemical map was prepared of a large garnet from sample 14PBA-94A (figure 4.6.8). This garnet is highly corroded in the core, although remnants of the crystal faces are preserved. Across the area of the garnet a slight trend of increasing X_{grs} and X_{alm} and decreasing X_{prp} from core to rim can be seen. X_{sps} is uniform from core to rim. Within the corroded portion of the large grain, small, irregularly shaped fragments of garnet crystals are seen. These small crystals also appear to be chemically zoned with respect to X_{alm} , X_{prp} , and X_{grs} , with the zonation reflecting the position of the fragment within the core of the larger grain. No pattern in Y is observed. Y highs in the image are due to inclusions in the garnet. Spot analyses were performed across the garnet (figure 4.6.8-A), and results are presented in table 4.6.1. The spot analyses indicate a trend reminiscent of chemical zoning with increasing X_{alm} and X_{prp} , decreasing X_{grs} , and uniform X_{sps} from the core to the rim of the garnet. X_{alm} increases from approximately 0.72 near the core to 0.76 at the rim. Similarly, X_{prp} increases from 0.06 near the core to 0.08 at the rim. X_{grs} decreases slightly from a core value of 0.2 to a rim value of 0.14. X_{sps} content stays at a uniform 0.03 across the garnet. Very little Y_2O_3 is present with only a single analysis at the center of the garnet yielding a value greater than 0.

Additional spot analyses were done on 3 smaller garnets towards the center of a large garnet cluster (figure 4.6.10-F). The first two garnets (spots 8 - 10) show approximately uniform values for all endmembers in the core and rim measurements, with X_{alm} at 0.73 - 0.74, X_{prp} at 0.07, X_{grs} at 0.16 - 0.17, and X_{sps} at 0.03. In contrast, the third garnet (spots 11 - 12) shows a more pronounced change in endmember composition

Figure 4.6.8: EPMA element distribution maps for a garnet porphyroblast in sample 14PBA-94A. (A) Backscattered electron (BSE) image showing locations of EPMA spot analyses (table 4.3.1). (B) Ca (C) Mg (D) Fe (E) Mn (F) Y.

between the core and rim analyses. X_{alm} decreases from 0.78 in the core to 0.74 in the rim. X_{grs} increases from 0.12 to 0.16 from core to rim. Uniform X_{sps} (0.03) and X_{prp} (0.07) contents are observed across the garnet. No Y_2O_3 is detected in any of the three analyzed garnet crystals.

14PBA-99A-A

Garnet 1

The first garnet from a cluster in 14PBA-99A-A (Figure 4.6.9-A and 4.6.10-E) shows a pattern of increasing X_{alm} , decreasing X_{grs} and X_{sps} , and uniform X_{prp} from core to rim. A X_{alm} content of 0.75 in the core rises to 0.77 in the rim. X_{grs} content falls from slightly below 0.1 in the core to 0.085 in the rim. A consistent X_{prp} content of approximately 0.08 is observed from core to rim. Weak zoning in X_{sps} is observed with core values of approximately 0.065 falling slightly to 0.06 at the rim. No discernable zoning pattern is seen in Y_2O_3 , with most values falling slightly above 0.

Garnet 2

An analysis on a second garnet from 14PBA-99A (Figure 4.6.9-B and 4.6.10-E) shows X_{alm} decreasing and X_{grs} increasing from core to rim. Core X_{alm} values of 0.78 fall to 0.76 at the rim. X_{grs} rises from just above 0.08 in the core to 0.11 in the rim. A constant X_{prp} value of 0.08 is seen across the diameter of the garnet. X_{sps} content decreases slightly from 0.07 in the core to 0.055 in the rim. No pattern in Y_2O_3 is observed. Garnet 2 displays an opposite zoning pattern in X_{alm} and X_{grs} than what is observed in garnet 1.

Figure 4.6.9: EPMA compositional profiles across the largest representative garnet porphyroblasts as identified in thin section from sample 14PBA-99A (A) and (B), and 14PBA-99A-B (C). Traverses were performed at a resolution of 10 μm .

14PBA-99A-B

Chemical zoning in the largest garnet located in thin section from sample 14PBA-99A-B (figure 4.6.9-C and 4.6.10-D) shows relatively uniform zoning of X_{alm} , X_{grs} , X_{prp} , and X_{sps} from core to rim. X_{alm} values consistently range from 0.80 - 0.81 across the garnet. X_{prp} zoning shows values ranging between 0.07 - 0.08 across garnet before a decrease within 50 μm of the rim. X_{grs} also shows values of 0.65 - 0.75 from core to rim. Slight zoning is seen in X_{sps} values, with values in the core of 0.05 that fall slightly to 0.45 at the rim. There is a Y_2O_3 peak at the core with values of 0.3, falling to values below 0.1 within 30 μm the rim.

Figure 4.6.10: BSE (back scattered electron) images showing locations of EPMA compositions profiles (dashed lines) for (A) 12PBA-27A Garnet 3 (B) 12PBA-27A Garnet 5 (C) 12PBA-27A Garnet 6 (D) 14PBA-99A-B Garnet 1 (E) 14PBA-99A-A Garnet 1 and Garnet 2 (F) location of garnet spot analyses in 14PBA-94A (table 4.3.1).

4.7 Phase Equilibrium Modeling

Phase equilibrium diagrams were calculated over a P-T range of 300 - 600°C and 1000 - 7000 bar for lower-grade samples and 400 - 700°C for higher-grade samples. Both equilibrium assemblage diagrams and garnet isopleths were calculated using the bulk rock chemistry provided in table 4.1.1. The observed mineral assemblage for each sample is highlighted in dark grey. The predicted stability fields for garnet-bearing assemblages are highlighted in light grey. No evidence for melting was observed in any of the studied samples and is not considered in the phase diagrams in this section. 2(Pl) refers to the separation of plagioclase into separate albite-rich and anorthite-rich phases. Garnet core chemistry is shown in table 4.6.2. As this value may not be reflective of the overall zoning pattern for each endmember, primarily due to modification of the garnet zoning along cracks, representative core composition values were chosen from the overall trend of the garnet compositional profile.

14PBA-43B

This lower-grade sample from the upper Montresor group contains an observed mineral assemblage of quartz + biotite + muscovite + plagioclase + microcline. Rutile is present as an accessory mineral. This observed mineral assemblage is predicted to be stable over a P-T range of 355 - 455°C and <4200 bar (figure 4.7.1).

Figure 4.7.1: Equilibrium phase diagram for sample 14PBA-43B. The observed mineral assemblage is highlighted in dark grey. The stability field of garnet bearing assemblage is shown in light grey. 1=Pl Chl Ph Spn Mc 2=Pl Chl Ph Spn Mc Rt.

12PBA-27A

Sample 12PBA-27A from the lower Montresor group contains an observed mineral assemblage of quartz + plagioclase + garnet + andalusite + biotite + chlorite + ilmenite. The large sericite clusters observed in 12PBA-27A are inferred to be muscovite pseudomorphs after andalusite, based on their shape, size, and overall similarity to fresh and partially sericitized andalusite in other lower Montresor group samples in this study. While andalusite porphyroblasts are completely pseudomorphed by muscovite, it is still interpreted to be part of the stable mineral assemblage. Muscovite is not interpreted to be

Figure 4.7.2: Sample 12PBA-27A. Calculated phase equilibrium diagram (A), garnet isopleths (B - E) for almandine (X_{Alm}), grossular (X_{GrS}), pyrope (X_{Prp}), and spessartine (X_{Sps}), and garnet isopleth intersection (F). The observed mineral assemblage is highlighted in dark grey and the stability field of garnet bearing assemblages is shown in light grey. 1=Pl Ilm Chl Bt And 2 = Pl Ilm grt Chl Bt And 3=Pl Ilm Grt St Bt And 4=Pl Chl Cz Spn Pa

part of the stable assemblage as it is only observed in these pseudomorphs and as individual grains in the matrix that lie at an angle to the main foliation (S1). The observed mineral assemblage is predicted over a range of P-T space from 520 - 550°C and 1000 - 2500 bar (figure 4.7.2-A). A garnet isopleth intersection calculated using the core composition of the largest garnet gives a P-T estimate of 540°C and 3500 bar (figure 4.7.2-F). This intersection falls 5 - 10°C above the garnet-in reaction in the stability field of quartz + plagioclase + ilmenite + garnet + muscovite + biotite + chlorite + staurolite.

14PBA-67A

This sample from the lower Montresor group contains an observed mineral assemblage of quartz + muscovite + biotite + plagioclase + andalusite + ilmenite. This assemblage is predicted at P-T conditions of 500 - 640°C and <4000 bar (figure 4.7.3-A).

14PBA-85A

Sample 14PBA-85A contains an observed mineral assemblage of quartz + biotite + muscovite + plagioclase + andalusite + ilmenite. This assemblage is predicted over a range of P-T space from 500 - 640°C and <4000 bar (figure 4.7.3-B).

14PBA-94A

The observed mineral assemblage of 14PBA-94A contains plagioclase + quartz + garnet + chlorite + biotite + ilmenite + two amphiboles. This assemblage defines a P-T stability field of 475 - 580°C and 1000 - 4500 bar (figure 4.7.4-A). The two amphiboles

Figure 4.7.3: Equilibrium phase diagrams for non-garnet bearing samples. (A) 14PBA-67A; 1=(2)Pl Chl Ph Spn Rt 2=Pl Ilm Chl Ph Bt St 3=Pl Chl Ph Czo Rt Pg 4=Pl Chl Ph Czo Rt Pg 5=Pl Ilm Chl Ph Czp Rt (6) Pl Ilm St Ph Bt Sil. (B) 14PBA-85A; 1=Pl Ilm Ph Bt St 2=Pl Ilm Grt Chl Ph St 3=Pl Ilm Ph Bt St Grt 4=Pl Ilm Grt Ph Bt St Sil. (C) 14PBA-97A; 1=(2)Pl Chl Ph Rt 2=Pl Chl Ph Rt 3=Pl Ilm Chl Ph Pg Rt 4=Pl Ilm Chl Ph Czo Pg Rt 5=Pl Ilm Chl Ph St 6=Pl Ilm Grt Chl Ph St 7=Pl Ilm Ph Bt And Crd Sa. (D) 14PBA-100; 1=Pl Ilm Chl Ph And Rt 2=Pl Ilm Chl Ph And St 3=Pl Chl Ph St And Rt 4=Pl Ilm Ph Bt And Sa 5=Pl Chl Ph St Ru 6=Pl Ph Bt St Ky Ru 7=Pl Ph Grt Bt St Ky Rt. The observed mineral assemblage in each sample is highlighted in dark grey. The stability field of garnet bearing assemblages is shown in light grey.

Figure 4.7.4: Sample 14PBA-94A. Calculated phase equilibrium diagram (A), garnet isopleths (B - E) for almandine (X_{Alm}), grossular (X_{Grs}), pyrope (X_{Prp}), and spessartine (X_{Sps}). The observed mineral assemblage in each sample is highlighted in dark grey and the stability field of garnet bearing assemblages is shown in light grey. 1=Pl Chl Ph Amp1 Cz Spn 2=Pl Ilm Grt Bt Chl Amp1 Ath 3=Ilm Chl Ph Amp1 Cz Spn 4=Ilm Grt Chl Ph Amp1 Cz Ma 5=Pl Ilm Grt Ph Chl Amp1

observed in this sample are differentiated based on their composition (table 4.3.1). The amphibole composition predicted by THERIAK for two P-T points within the stable assemblage field for the sample appears to be representative of the observed amphiboles. The petrographic relationship of the two amphiboles shows amphibole 2 surrounding amphibole 1, possibly indicating that amphibole 2 began to grow after amphibole 1. Both amphiboles are thought to be part of the equilibrium mineral assemblage, as neither shows petrographic evidence of breaking down. These observations suggest a P-T path that moves through the amphibole 1 stability field into a stability field containing both amphibole 1 and amphibole 2. No isopleth intersection was calculated for this sample as the composition of garnet is interpreted to be modified by later processes.

14PBA-97A

This sample contains an observed mineral assemblage of quartz + biotite + muscovite + plagioclase + andalusite + ilmenite. This sample also contains partial fine-grained muscovite pseudomorphs after andalusite. This muscovite is interpreted to be late and not a part of the stable mineral assemblage. Muscovite within the main foliation (S1) is part of the stable mineral assemblage. This sample is predicted over a P-T range of 500 - 640°C and <4000 bar (figure 4.7.3-C).

14PBA-99A-A

Sample 14PBA-99A-A (the garnet-rich subsample of 14PBA-99A-A) contains an observed mineral assemblage of plagioclase + quartz + muscovite + biotite + chlorite + garnet + ilmenite. This assemblage is predicted over a P-T range of 440 - 560°C and 2500

- 7000 bar (figure 4.7.5-A). Two separate garnet isopleth intersections were calculated for this sample, for two neighboring garnet crystals that show distinct differences in chemical zoning in their representative EPMA compositional profiles (figure 4.6.9-A, B). Garnet 1 shows a broad isopleth intersection over a range of P-T space from approximately 540 - 570°C and 4400 - 6000 bar (figure 4.7.6-A). Garnet two shows a tighter isopleth intersection in P-T space from 550 - 560°C and 4000 - 5400 bar (figure 4.7.6-B). Both sets of isopleths intersect in the stability field defined by the observed mineral assemblage, approximately 40 - 50°C above the garnet-in curve.

14PBA-99A-B

The observed mineral assemblage in 14PBA-99A-B (the garnet poor subsample of 14PBA-99A) includes plagioclase + quartz + muscovite + biotite + chlorite + garnet + ilmenite. This mineral assemblage is predicted over a range of P-T space from 450 - 560°C and 1000 - 7000 bar (figure 4.7.7-A). A garnet isopleth intersection was calculated using the representative core composition of the largest garnet located in thin section gives a P-T estimate of 550 - 575°C and 2500 - 4000 bars (figure 4.7.7-F). This intersection falls over the stability fields of quartz + plagioclase + ilmenite + garnet + biotite + staurolite + chlorite and quartz + plagioclase + ilmenite + garnet + biotite + staurolite. This intersection occurs approximately 100°C above the garnet-in reaction.

Figure 4.7.6: Sample 14PBA-99A-A. Calculated garnet isopleth intersection for garnet 1 (A) and garnet 2 (B). The area of isopleth intersections is shown in dark grey. The stability field of garnet bearing assemblages is shown in light grey.

14PBA-100

Sample 14PBA-100 contains an observed mineral assemblage of quartz + muscovite + biotite + plagioclase + andalusite + ilmenite. This assemblage is predicted over a P-T range of 500 - 630°C and <4000 bar (figure 4.7.3-D).

Figure 4.7.7: Sample 14PBA-99A-B. Calculated phase equilibrium diagram (A), garnet isopleths (B - E) for almandine (X_{Alm}), grossular (X_{Grs}), pyrope (X_{Prp}), and spessartine (X_{Sps}), and garnet isopleth intersection (F). The stability field of garnet bearing assemblages is shown in light grey. The observed mineral assemblage in (A) and the area of isopleth intersection in (F) are highlighted in dark grey.

4.8 Garnet Crystallization Modeling

Garnet crystallization was modeled for sample 12PBA-27A in order to determine a metamorphic P-T-t path. 12PBA-27A was chosen for garnet crystallization modeling as it contains the most well preserved garnet porphyroblasts of the studied samples. Garnet crystallization modeling was done with THERIA_G software (Gaidies *et al.*, 2008A).

The crystallization of a garnet population was modeled along various P-T-t paths to replicate the observed zoning. A modified garnet CSD (see appendix A.5) containing 20 size classes was used to correct for the effects of garnet resorption in the observed population, as this is not taken into consideration by THERIA_G. Four of these garnet size classes (1, 2, 7, and 13) were used to represent the garnet population in 12PBA-27A in this model. These were chosen as they provide the most well defined garnet zoning, as their compositions are the least modified adjacent to fractures and inclusions. The effect of modified zoning along fractures and inclusions in garnet 1 is shown in figure 4.8.1.

Three different scenarios were modeled in order to investigate the effects of various processes on the resulting growth zoning. The first model is presented with no modification to the input parameters other than the CSD. The second scenario investigates the effects of preventing staurolite from growing in the simulations. A third scenario shows the effect of an effective bulk rock chemistry change by late K influx, in an attempt to simulate the effects of K-metasomatism. The P-T paths that provided the most accurate representation of the observed garnet zoning for each of these scenarios are presented below.

Figure 4.8.1: Visualization of the modification of garnet growth zoning along fractures (dotted line) and inclusions (solid line) for endmember compositions almandine (A), grossular (B), pyrope (C), and spessartine (D). Retrograde zoning (dashed line) at the garnet rim is also shown.

4.8.1 Scenario 1: No Changes

Scenario 1 utilizes an unmodified effective bulk-rock chemistry and the thermodynamic database of Holland and Powell (1998) (see appendix A.5). The phase diagram and isopleth intersections for this sample are shown in figure 4.6.2. The P-T path that yielded the best match between the observed and predicted garnet chemical zoning is provided in table 4.8.1 and figure 4.8.2. This P-T path is shown with three constant heating/cooling rates (HR/CR) of 10°C/Ma, 1°C/Ma, and 0.5°C/Ma, giving total times for the P-T-t paths of 8.5 Ma, 85 Ma, and 170 Ma. Predicted stable mineral assemblages along the P-T path are also provided in table 4.8.1. Phase relations before and after garnet growth are shown in figure 4.8.2. Garnet growth begins at 526.0°C and ends at 565.9°C, with a period of no growth from 526.6°C to 551.4°C. Garnet is predicted to grow within a stable mineral assemblage of plagioclase + ilmenite + chlorite + muscovite + biotite + quartz + water for the first period of growth and then plagioclase + ilmenite + biotite + staurolite + andalusite + quartz + water for the second period of growth. Model results are shown in figures 4.8.3 and 4.8.4.

Size Class 1

Garnet size class 1 displays a good fit between the predicted and observed garnet radius, with the predicted radius approximately 50 µm larger. The almandine profile (figure 4.8.3-A) displays a predicted core composition 2 mol% lower than the observed. This trend continues to the rim, where there is a good match between the predicted and the observed profiles. Grossular (figure 4.8.3-B) shows a good match between the observed and predicted zoning at both the core and rim of the grain. A fall of 1 mol% in

Table 4.8.1: P-T-t path with variable HR/CR's and predicted stable mineral assemblages for garnet growth for scenario 1.

Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:			Size Class 1 radius (µm)	Temperature range (°C)	Stable Mineral Assemblage
		10°C/Ma	1 °C/Ma	0.5 °C/Ma			
525.00	2840.00	0.00	0.00	0.00	0 - 260	526.0 - 526.6	Pl Ilm Grt Chl Ph Bt Qtz H ₂ O
530.00	2860.00	0.50	5.00	10.00	-	526.6 - 535.4	Pl Ilm Chl Ph Bt St Qtz H ₂ O
535.00	2900.00	1.00	10.00	20.00	-	535.4 - 544.7	Pl Ilm Ph Bt St Qtz H ₂ O
537.00	2930.00	1.20	12.00	24.00	-	544.7 - 551.4	Pl Ilm Bt St And Qtz H ₂ O
550.00	2955.00	2.50	25.00	50.00	260 - 1206	551.4 - 565.9	Pl Ilm Grt Bt St And Qtz H ₂ O
560.00	2940.00	3.50	35.00	70.00	-	565.9 - 533.0	Pl Ilm Bt St And Qtz H ₂ O
570.00	2932.00	4.50	45.00	90.00	-	533.0 - 530.0	Pl Ilm Chl Bt St And Qtz H ₂ O
560.00	2800.00	5.50	55.00	110.00			
550.00	2740.00	6.50	65.00	130.00			
530.00	2600.00	8.50	85.00	170.00

Figure 4.8.2: Phase relations before (A) and after (B) garnet growth for scenario 1. P-T path is shown by the dotted line. The stability field of garnet bearing assemblages is highlighted in grey. 1-Pl Ilm Bt Chl And St.

the predicted composition occurs at 300 - 350 μm . A slight mismatch also occurs at 500 - 1000 μm with the predicted composition falling 0.5 - 1 mol% below the observed. The pyrope profile (figure 4.8.3-C) shows a predicted core composition falling 1 mol% below the observed. A jump of 2 mol% occurs at 300 μm . The predicted pyrope values are above the predicted up to the rim, which is <0.5 mol% above the observed. The predicted spessartine content is 3 mol% higher than the observed at the core of the garnet (figure 4.8.3-D). This trend continues until the rim, where there is a good match between the predicted and the observed. The slight rise observed at the rim is attributed to late diffusion during cooling. The predicted chemical gradients generally display steeper chemical gradients than the observed. The jump in the predicted almandine, grossular, and pyrope profiles is attributed to the period of time where garnet is predicted not to grow. The variable HR/CR's (10°C/Ma, 1°C/Ma, 0.5°C/Ma) do not have a significant effect on the predicted chemical profiles. Minor changes such as slight smoothing of the predicted profiles along the jumps, and a slight lowering of spessartine content near the core are observed at the slowest HR/CR.

Size Class 2

The predicted garnet radius for size class 2 is approximately 50 μm larger than the observed radius. Almandine (figure 4.8.3-E) shows a predicted profile with a core composition 3 mol% below the observed and a good match at the rim. There is also a good fit between the predicted and observed core grossular contents (figure 4.8.3-F). A 1 mol% jump in composition is seen at 250 μm . From 250 μm to the garnet rim the predicted grossular content falls 0.5 - 2 mol% below the observed, with a 0.5 mol%

Figure 4.8.3: Scenario 1 garnet crystallization modeling results for size class 1 (A - D) and 2 (E - H).

mismatch at the rim. Pyrope (figure 4.8.3-G) shows a predicted core composition 1.5 mol% lower than the observed. A jump in pyrope at 250 μm brings the predicted composition 0.5 mol% above the predicted. A good match is seen at the rim with the observed pyrope only slightly higher than the predicted. The spessartine profiles (figure 4.8.3-H) show a predicted core content 4 mol% higher than the observed, lowering to a good fit between the predicted and observed profiles at the rim. Steeper chemical gradients are seen in the predicted profiles. Similar to size class 1, the variation in HR/CR's has little effect on the profiles, with the only differences being slight smoothing of the profiles along the compositional jumps and a slight lowering in the spessartine core content at slower rates.

Size Class 7

Size class 7 predicts a garnet radius approximately 100 μm larger than the observed. The predicted almandine profile (figure 4.8.4-A) shows a core composition 5 mol% lower than the observed, rising to a good match at the rim. It is difficult to judge the fit of the grossular profile (figure 4.8.4-B) for this size class, as the observed profile is highly variable by about 2 mol% due to cracks. However, the predicted chemical profile falls within the range of the observed composition, with good matches at the core and rim of the garnet. Pyrope (figure 4.8.4-C) also shows a good match between predicted and observed composition from core to rim. The drop-off in the observed pyrope is attributed to retrograde zoning. Spessartine (figure 4.8.4-D) shows a large mismatch of 7 mol% between the predicted and observed composition at the garnet core, trending to a good match at the rim. The variable HR/CR's have no effect on the predicted grossular and

pyrope profiles. At slower HR/CR's the predicted almandine core composition varies by <0.5 mol% between 10°C/Ma and 0.5°C/Ma. Similarly, at the slowest HR/CR the core spessartine content drops by approximately 1 mol%.

Size Class 13

The predicted radius for this size class is approximately 100 µm larger than observed. The predicted almandine profile (figure 4.8.4-E) shows a mismatch between the predicted and observed core compositions of 3 - 5 mol% for HR/CR's of 0.5°C/Ma and 10°C/Ma. For all HR/CR's a steeper predicted chemical gradient is seen. There is a good match between the predicted and observed garnet composition at the rim. The predicted grossular (figure 4.8.4-F) content at the garnet core falls 1 mol% below the observed profile. This trend continues across the grain until the rim, where there is a good match between the predicted and observed compositions. The predicted profile shows a shallower chemical gradient than the observed. There is a good match between the predicted and observed pyrope contents (figure 4.8.4-G) from the core to the rim of the crystal. The predicted spessartine content (figure 4.8.4-H) gives a core composition 4 - 6 mol% above the observed for HR/CR's of 0.5°C/Ma and 10°C/Ma respectively, with a good match seen at the garnet rim. Variations in the HR/CR of garnet do not have an effect on the grossular and pyrope profiles. At slower HR/CR's the predicted almandine content is slightly raised and the spessartine content is slightly lowered, both by approximately 2 mol%.

Figure 4.8.4: Scenario 1 garnet crystallization modeling results for size class 7 (A - D) and 13 (E - H).

4.8.2 Scenario 2: No Staurolite

In scenario 1, staurolite is predicted to grow with garnet for the entirety of the second portion of garnet growth along the predicted P-T path. This predicted mineral assemblage is not representative of the sample, as there is no evidence for staurolite in 12PBA-27A. Due to this, it appears that staurolite may be estimated to begin growing at too low a P-T in the simulations. In scenario 2, the effect of a possible overestimation of staurolite stability is tested. This is accomplished by removing staurolite from the thermodynamic database, thus preventing it from crystallizing during the model run. There is no change to the effective bulk rock chemistry of the sample considered in scenario 2.

The equilibrium assemblage diagram and garnet isopleth intersection were calculated using the altered thermodynamic database. The observed mineral assemblage (quartz + garnet + biotite + andalusite + plagioclase + chlorite + ilmenite) gives a P-T estimate of 520 - 545°C and 1000 - 3800 bar (figure 4.8.5-A). A garnet isopleth intersection gives a P-T estimate of 530°C and 3100 bar (figure 4.8.5-F). This intersection occurs approximately 5°C above the garnet-in reaction across the stability fields of plagioclase + ilmenite + chlorite + muscovite + biotite + garnet and plagioclase + ilmenite + chlorite + muscovite + biotite + garnet + chloritoid.

The P-T path that gives the best correlation between the predicted and observed garnet zoning in the garnet crystallization model is presented in table 4.8.2 and figure 4.8.6. The P-T path is shown with three constant HR/CR's of 10°C/Ma, 1°C/Ma, and 0.2°C/Ma, giving total times for the P-T-t paths of 5.37 Ma, 53.68 Ma, and 268.4 Ma. Predicted stable mineral assemblages along the P-T path are also provided in table 4.8.2

and phase relations both before and after garnet growth are provided in figure 4.8.6. Garnet growth begins at 526.0°C and ends at 556.8°C. There were two breaks during garnet growth where the garnet did not grow, from 526.9 - 531.7°C and from 547.3 - 549.2°C. Garnet is predicted to grow in equilibrium with mineral assemblages containing a combination of plagioclase + ilmenite + garnet + chloritoid + muscovite + biotite + andalusite + chlorite + quartz + water. Garnet stops growing in the stability field of plagioclase + ilmenite + garnet + biotite + andalusite + chlorite + quartz + water. Model results are shown in figures 4.8.7 and 4.8.8.

Size Class 1

The predicted radius measures approximately 50 μm larger than the observed. The predicted almandine (figure 4.8.7-A) zoning shows a predicted core composition 2 mol% lower than the predicted composition. A good match between the predicted and observed zoning is seen in the 400 μm adjacent to the rim. Overall grossular (figure 4.8.7-B) shows a good match between the predicted and observed chemical zoning from the core to the rim of the garnet. Minor variations are seen at 400 and 600 μm where the predicted zoning falls 0.5 - 1 mol% above the observed, and the predicted rim composition is 0.5 mol% above the observed. The predicted pyrope (figure 4.8.7-C) core composition is 1 mol% below the observed, and a good match at the rim. Spessartine (figure 4.8.7-D) shows a predicted core content 3 mol% higher than the observed profile. There is a good match observed in the 400 μm adjacent to the garnet rim. Overall, the predicted profiles show steeper chemical gradients than the observed profiles. Variation

Table 4.8.2: P-T-t path with variable HR/CR's and predicted stable mineral assemblages for garnet growth for scenario 2 (no staurolite).

Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:			Size Class 1 Radius (μm)	Temperature range (°C)	Stable Mineral Assemblage
		10°C/Ma	1 °C/Ma	0.2 °C/Ma			
525.00	2840.00	0.00	0.00	0.00	0 - 420	526.0 - 526.9	Pl Ilm Grt Chl Ph Bt Qtz H ₂ O
527.00	2841.00	0.20	2.00	10.00	-	526.9 - 531.7	Pl Ilm CtdChl Ph Bt Qtz H ₂ O
530.00	2900.00	0.50	5.00	25.00	420 - 940	531.7 - 544.5	Pl Ilm Grt Ctd Chl Ph Qtz H ₂ O
540.00	3250.00	1.50	15.00	75.00	940 - 1070	544.5 - 547.3	Pl Ilm Grt Ctd Chl Ph Bt And Qtz H ₂ O
540.50	3300.00	1.55	15.50	77.50	-	544.7 - 547.3	Pl Ilm Chl Ph Bt And Qtz H ₂ O
543.60	3450.00	1.86	18.60	93.00	-	547.3 - 549.2	Pl Ilm Chl Bt And Qtz H ₂ O
550.00	3600.00	2.50	25.00	125.00	1070 - 1220	549.2 - 556.8	Pl Ilm Grt Chl And Qtz H ₂ O
555.00	3600.00	3.00	30.00	150.00	-	556.8 - 535.0	Pl Ilm Chl Bt And Qtz H ₂ O
556.84	3574.85	3.18	31.84	159.20			
556.00	3500.00	3.27	32.68	163.40			
555.00	3400.00	3.37	33.68	168.40			
550.00	3100.00	3.87	38.68	193.40			
535.00	2800.00	5.37	53.68	268.40

Figure 4.8.6: Phase relations before (A) and after (B) garnet growth for scenario 2. P-T path is shown by the dotted line. Garnet stability field is highlighted in grey.

in HR/CR has no effect on the predicted grossular and pyrope profiles. However, almandine and spessartine are slightly affected with the predicted profiles smoothing at the slowest HR/CR.

Size Class 2

The predicted radius for garnet size class 2 is approximately 50 μm larger than the observed. The almandine profile (figure 4.8.7-E) shows a predicted core composition 3 mol% lower than the observed. A good match between the predicted and observed garnet profiles is seen from a radius of 600 μm to the garnet rim. Overall, grossular (figure 4.8.7-F) shows a good match between the predicted and observed profiles from garnet core to rim. Slight mismatches at 300 and 800 μm have the predicted zoning 0.5 mol% below and 1 mol% above the observed. Predicted core pyrope content (figure 4.8.7-G) falls 1.5 mol% below the observed core composition. This trend continues across the garnet to the rim where the predicted profile falls 0.5 mol% below the observed profile. The spessartine profile (figure 4.8.7-H) shows predicted core composition 4 mol% above the observed, lessening towards a good match at the garnet rim. Once again, variation in HR/CR has little effect on the predicted chemical profiles other than slightly smoothing of the almandine and spessartine profiles.

Size Class 7

The model predicts a radius for garnet size class 7 that is approximately 100 μm larger than the observed radius. The predicted core almandine content (figure 4.8.8-A) falls 2 - 4 mol% for HR/CR's of 0.02°C/Ma and 10°C/Ma, respectively. At the rim the

Figure 4.8.7: Scenario 2 garnet crystallization modeling results for size class 1 (A - D) and 2 (E - H).

predicted profile is 0.5 mol% below the observed. The fit of the grossular profiles (figure 4.8.8-B) is difficult to discern due to scatter in the observed compositions. The predicted chemical profile lies towards the upper portion of this scatter at the core, and at the rim the predicted profile is 1.5 mol% above the observed. The predicted pyrope profile (figure 4.8.8-C) falls consistently below the observed profile, with 2 mol% difference in the core and 1 mol% difference at the rim. The spessartine profiles (figure 4.8.8-D) show predicted core content 4 - 6 mol% above the observed profile, for HR/CR's of 0.02°C/Ma and 10°C/Ma respectively. A good match between predicted and observed spessartine profiles is shown at the garnet rim. Spessartine and almandine predicted profiles show steeper chemical gradients than observed.

Size Class 13

Garnet size class 13 shows a predicted radius 100 μm larger than the observed. The predicted profiles in this size class show more variation due to HR/CR than the larger size classes. The predicted almandine profiles (figure 4.8.8-E) show core content falling from 3 - 0.5 mol% below the observed profile for HR/CR's of 0.02°C/Ma and 10°C/Ma respectively. There is a good match between the predicted and observed rim compositions. Grossular (figure 4.8.8-F) shows a good match between the predicted and observed compositions from the garnet core to a radius of 300 μm . From 300 μm to the rim the predicted content falls below the observed, to a 1 mol% difference at the garnet rim. The predicted core pyrope content (figure 4.8.8-G) falls 2 mol% below the predicted profile, continuing across the garnet to a 0.5mol% difference at the rim. The predicted spessartine profiles (figure 4.8.8-H) show core contents 2 - 4 mol% higher than the

predicted profiles, for heating rates of $0.02^{\circ}\text{C}/\text{Ma}$ and $10^{\circ}\text{C}/\text{Ma}$. At the garnet rim there is a good match between the predicted and observed profiles for the $10^{\circ}\text{C}/\text{Ma}$ and $1^{\circ}\text{C}/\text{Ma}$ HR/CR profiles. The $0.02^{\circ}\text{C}/\text{Ma}$ HR/CR profile falls $0.05\text{mol}\%$ below the observed profile. The grossular and pyrope profiles are not as affected by the HR/CR, but show a slight smoothing of the profiles at slower rates. At these slow HR/CR's the core compositions and chemical gradients trend towards the observed profiles for spessartine, but there is still a mismatch of over $2\text{ mol}\%$.

Figure 4.8.8: Scenario 2 garnet crystallization modeling results for size class 7 (A - D) and 13 (E - H).

4.8.3 Scenario 3: K-Metasomatism

Sample 12PBA-27A, as well as other samples from the lower Montresor group, show evidence for late alteration by fluid infiltration. This includes abundant sericite pseudomorphs after andalusite and modification of garnet growth zoning along cracks. In order for muscovite to form after andalusite, a source of K is required. Previous studies have shown that increasing the K⁺ and H⁺ content of a rock will result in the preferential formation of muscovite after aluminosilicate phases (Chinner, 1973). K may be sourced from other minerals within the rock (e.g. biotite) or from an outside source (e.g. fluids). If the K is sourced from an outside fluid, it is likely that the composition of the fluid is out of equilibrium with the rock. Thus when it is added to the rock it may change the effective bulk rock chemistry. Scenario 3 tests the effects of a modification to the effective bulk rock K content after garnet growth. It is assumed in this scenario that the only chemical component to change in concentration within the effective bulk rock chemistry is K, and that all of the K needed to pseudomorph the andalusite in the sample came from an outside source. A simple reaction for the replacement of andalusite by muscovite may be:

This reaction is thought to be a good approximation for this system, as EPMA analysis on the white mica indicates a composition that is 92 - 95% muscovite (see table A.2.3). Petrography and XR- μ CT results indicate approximately 10 volume% sericite pseudomorphs after andalusite in 12PBA-27A. This is similar to the andalusite content

predicted by THERIAK for the maximum P-T conditions determined in scenarios 1 and 2. The amount of K needed to completely replace 10 volume% was done based on a 2000 cm³ rock volume utilized by THERIAK. 10 vol% andalusite in a 2000 cm³ rock volume gives 200 cm³ of andalusite, with 1 mol andalusite corresponding to 52 cm³:

$$(1 \text{ mol And} / 52 \text{ cm}^3) * 200 \text{ cm}^3 = 3.85 \text{ mol And}$$

Showing that 3.85 mol And is present in a rock volume of 200 cm³, and since there are 3 mol andalusite for every 2 mol K:

$$3.85 \text{ mol And} * (2 \text{ mol K} / 3 \text{ mol And}) = 2.56 \text{ mol K}$$

It is calculated that 2.56 mol K is needed to completely replace 10 vol% andalusite in the modeled rock volume. This is rounded to an even 2.5 mol, and when this value is subtracted from the measured bulk rock K content of 4.5 mol% the initial K content of the rock is determined to be ca. 2.0 mol%. This is the value used for the K content in scenario 3. As with scenario 2, staurolite is removed from the thermodynamic database.

The equilibrium assemblage diagram and garnet isopleth intersection were calculated using the altered bulk rock composition and thermodynamic database. The observed mineral assemblage (quartz + garnet + biotite + andalusite + plagioclase + chlorite + ilmenite) yields a peak P-T estimate of 520 - 580°C and 1000 - 4400 bar (figure 4.8.9-A). The calculated garnet isopleth intersection gives a P-T estimate of 530 - 550°C and 3100- 3400 bars (figure 4.8.9-F). This intersection occurs at the garnet-in

Figure 4.8.9: Sample 12PBA-27A. Calculated phase equilibrium diagram (A), garnet isopleths for almandine (X_{Alm}), grossular (X_{Grs}), pyrope (X_{Prp}), and spessartine (X_{Sps}) (B - E), and garnet isopleth intersection (F). The observed mineral assemblage is highlighted in dark grey and the stability field of garnet bearing assemblages is shown in light grey. 1-Pl Ilm Chl Ph Pa Ma 2-Ilm Chl Ph Cz Pa 3-Ilm Grt Ctd Chl Ph Pa Ma 4-Pl Ilm Ctd Chl Ph Grt Ma 5-Pl Ilm Grt Chl Ph Ky Pa 6-Pl Ilm Grt Chl Ph Ky

Table 4.8.3: P-T-t path with variable HR/CR's and predicted stable mineral assemblages for garnet growth for scenario 3 (K- metasomatism).

Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:			Size Class 1 Radius (µm)	Temperature range (°C)	Stable Mineral Assemblage
		10°C/Ma	1 °C/Ma	0.2 °C/Ma			
525.00	3000.00	0.000	0.00	0.00	0 - 1100	538.4 - 541.3	Pl Ilm Grt Ctd Chl Bt And Qtz H ₂ O
527.00	3020.00	0.200	2.00	10.00	1100 - 1200	541.3 - 543.8	Pl Ilm Grt Chl Bt And Qtz H ₂ O
530.00	3052.00	0.500	5.00	25.00	-	543.8 - 538.9	Pl Ilm Grt Chl Bt And Qtz H ₂ O
535.00	3120.00	1.000	10.00	50.00	-	538.9 - 531.0	Pl Ilm Chl Bt And Qtz H ₂ O
540.00	3150.00	1.500	15.00	75.00	-	531.0 - 530.3	Pl Ilm Chl Ph Bt And Qtz H ₂ O
542.00	3120.00	1.700	17.00	85.00	-	530.3 - 529.9	Pl Ilm Ctd Chl Ph Bt And H ₂ O
544.00	3090.00	1.900	19.00	95.00		529.9 - 525.0	Pl Ilm Ctd Chl Ph Qtz H ₂ O
542.00	3000.00	2.100	21.00	105.00			
540.00	2960.00	2.300	23.00	115.00			
530.00	2800.00	3.300	33.00	165.00			
525.00	2750.00	3.800	38.00	190.00

Figure 4.8.10: Phase relations before (A) and after (B) garnet growth for scenario 3. P-T path is shown by the dotted line and the garnet stability field is highlighted in grey.

reaction within the stability field of the assemblage plagioclase + ilmenite + garnet + chloritoid + chlorite + biotite + andalusite + quartz + H₂O.

The model P-T path that gives the best fit between the predicted and observed garnet zoning is presented in table 4.8.3 and figure 4.8.10. This P-T path is shown with three constant HR/CR's of 10°C/Ma, 1°C/Ma, and 0.2°C/Ma, giving total times for completion of the P-T-t paths of 3.8 Ma, 30 Ma, and 190 Ma, respectively. Predicted stable mineral assemblages along the modeled P-T path are provided in table 4.8.3, and phase relations before and after garnet growth are shown in figure 4.8.10. Garnet growth starts at 538.4°C and ends at 543.8°C. There were no breaks in garnet growth with this model, and garnet is predicted to grow in equilibrium with plagioclase + ilmenite + biotite + andalusite + chloritoid + chlorite + quartz + water. Garnet growth terminates in the stability field of plagioclase + ilmenite + garnet + biotite + andalusite + chlorite + quartz + water. Model results are shown in figures 4.8.11 and 4.8.12.

Size Class 1

There is a good fit between the predicted and observed garnet radius for size class 1, with the predicted radius <50 µm larger. Overall, all of the garnet endmembers show a good fit between the predicted and observed compositions from core to rim of the garnet (figure 4.8.11-A to D). Variations from this include a predicted almandine (figure 4.8.11-A) profile that is 1 mol% higher in the core than the observed profile. Pyrope (figure 4.8.11-C) shows a mismatch between the predicted and observed compositions of 0.5 - 2 mol% from a radius of 900 µm to the rim, and a shallower predicted profile. The variable HR/CR's had no discernable effect on the predicted garnet profiles.

Figure 4.8.11: Scenario 3 garnet crystallization modeling results for size class 1 (A - D) and 2 (E - H).

Size Class 2

Similar to size class 1, the predicted radius for size class 2 is approximately 50 μm larger than the observed radius. Almandine (figure 4.8.11-E) and grossular (figure 4.8.11-F) show good fits between the predicted and observed garnet profiles. The predicted core pyrope content (figure 4.8.11-G) provides a good match with the observed, but overall the predicted profile has a shallower chemical gradient than the observed, leading to a rim composition approximately 2 mol% lower than the observed. The spessartine (figure 4.8.11-H) profile shows a predicted core content <0.5 mol% above the observed. The predicted spessartine composition is consistently up to 2 mol% above the observed profile from core to rim. Variation in the HR/CR has no discernable effect on the predicted garnet profiles.

Size Class 7

The predicted radius of garnet size class 7 is 100 μm larger than the observed radius. The predicted almandine (figure 4.8.12-A) and grossular (figure 4.8.12-B) profiles provide a good match with the observed profiles. The predicted and observed pyrope (figure 4.8.12-C) profiles have similar chemical gradients, but the predicted profile falls consistently 1 - 2 mol% below the observed profile from garnet core to rim. The predicted spessartine (figure 4.8.12-D) profile is 2 mol% above the observed profile from the core to rim of the garnet. No significant change to the predicted profiles is observed due to changes in the HR/CR.

Size class 13

The predicted garnet radius is approximately 100 μm larger than the observed. A good fit is seen between the predicted and observed almandine (figure 4.8.12-E) profiles, with a slight mismatch at the core with the predicted almandine content 0.5 mol% below the observed. From the core to 400 μm , the predicted grossular (figure 4.8.12-F) content is consistently 0.5 mol% less than the observed. At a radius larger than 400 μm the predicted composition falls above the observed, to a difference of 1 mol% at the rim. Pyrope (figure 4.8.12-G) shows similar chemical gradients in the predicted and observed profiles, but the predicted profile falls 1.5 mol% below the observed. The predicted core spessartine (figure 4.8.12-H) content falls 3 mol% above the observed profile. A steeper chemical gradient is present in the predicted profile causing the predicted profile to consistently fall above the observed profile. Variable HR/CR's have no effect on the grossular and pyrope profiles. Slight variability can be seen in the almandine and spessartine profiles, where the slowest HR/CR causes slight shallowing of predicted chemical gradients.

Figure 4.8.12: Scenario 3 garnet crystallization modeling results for size class 7 (A - D) and 13 (E - H).

4.9 Heating After Garnet Crystallization

The previous scenarios have shown that it is possible to determine a P-T path for sample 12PBA-27A that predicts the chemical zoning of garnet with some degree of accuracy, especially in the larger size classes. However, a noticeable trend across all three modeled scenarios is the inability of the model to accurately predict the chemical zoning of the two fastest diffusing garnet endmembers, almandine and spessartine, in the smaller garnet size classes. This may suggest that the amount of diffusion that affected the observed garnets cannot be replicated in this model, even at very slow HR/CR's that are unrealistic in duration for the Trans-Hudson orogeny. It has been estimated that the Trans-Hudson orogeny occurred over ca. 120 Ma (Corrigan *et al.*, 2009), and the slowest HR/CR's (0.2 - 0.5°C/Ma) used in the previous three scenarios gave total times for completion of the P-T path of 268 Ma, 170 Ma, and 190 Ma respectively.

The efficiency of cation diffusion in garnet is controlled by three factors; grain size, T, and time. Smaller grain sizes, higher T, and longer timescales lead to a higher efficiency of diffusion across the garnet (Caddick *et al.*, 2010). As the amount of diffusion modeled over reasonable timescales cannot provide a representative model of the observed zoning, there may be another factor that was not considered in this model. If T were to increase after garnet growth, this could allow for increased diffusion within the garnet. Field relationships have shown that the lower Montresor belt is cut by late granodiorite, granite, and pegmatite dykes (Percival *et al.*, 2015A, C). This section investigates the possibility of a secondary heating event, due to contact metamorphism, and the effect of this heating on the compositional zoning of garnet.

The P-T paths determined in the three previous scenarios are unmodified, and a

secondary heating event is added at low P after garnet growth. Garnet growth is modeled using a HR/CR of 10°C/Ma. There are two inherent limits placed on this model. Firstly, there is no second generation of garnet growth observed in sample 12PBA-27A, indicating that secondary heating may have taken place at P below the garnet-in reaction. Secondly, there is no evidence for melt in this sample, indicating that T may have been below the melting curve. In this section, three HR/CR's are used along the secondary heating path of 1000°C/Ma, 100°C/Ma, and 10°C/Ma, with the fastest of these being most realistic of the HR/CR's associated with contact metamorphism (Walther and Wood, 1984).

The calculated phase equilibrium diagram after garnet growth along the P-T path described in scenario 3 is shown in figure 4.9.1-C. This scenario uses modified bulk rock composition with decreased K content. The phase equilibrium diagram indicates that there is no P between 1000 - 4000 bar where it would be possible to model a secondary heating event without the P-T path crossing the garnet-in reaction and creating a second generation of garnet growth. As sample 12PBA-27A shows no evidence for two generations of garnet growth, garnet growth during secondary heating may be unlikely and a model for secondary heating was not done for this scenario. When the effects of an influx of K after garnet growth are taken into consideration by adding the K taken out during garnet growth back into the bulk rock chemistry, the garnet-in reaction moves up P such that a secondary heating pulse could be modeled without crossing the garnet-in reaction (figure 4.9.1-D). However, the presence of biotite and chlorite within garnet fractures suggests that fluid infiltration occurred at greenschist facies during cooling. Thus these fluids, and their associated changes to the effective bulk rock chemistry,

would not have been present before or at the peak T of such a thermal pulse. This is especially important if the source of fluids is attributed to the same plutonism in the lower Montresor belt that may be the heat source for any contact metamorphism.

Revisiting scenario 1

The secondary heating P-T path for scenario 1 is modeled at 1300 bar and reaches a maximum T of 675°C. The P-T paths for garnet growth and secondary heating are provided in table 4.9.1 and figure 4.9.1. Phase equilibrium modeling indicates that melting begins at 675°C - 725°C at 1000 - 4000 bar (figure 4.9.1-A). At the modeled P of 1300 bar, melting is predicted to begin at 700°C. At peak T, the sample is within the stability field of plagioclase + ilmenite + biotite + cordierite + sanidine. Although cordierite and sanidine are predicted at peak P-T conditions, neither is observed in 12PBA-27A. A constant HR/CR of 10°C/Ma is used for garnet growth. This combined with variable HR/CR's of 1000°C/Ma, 100°C/Ma, and 10°C/Ma for secondary heating giving total times along the P-T path of 5.713 Ma, 8.818 Ma, and 39.868 Ma. As the P-T path for garnet growth has not changed from the previous model for scenario 1, the predicted radius for each size class remains the same. Model results are presented in figures 4.9.2 and 4.9.3.

Figure 4.9.1: Phase relations after garnet growth with melting curves for sample 12PBA-27A with modifications pertaining to scenario 1 (A) and scenario 2 (B). Phase relations for scenario 3 after garnet growth are shown without an influx of K (C) and with addition of K (D) to the bulk rock chemistry. See text for discussion. P-T paths are shown by the dotted lines, the stability field of garnet bearing assemblages is highlighted in dark grey, and the melting curve is shown in dark grey.

Table 4.9.1: P-T-t path for garnet growth with a constant heating/cooling rate and secondary heating with variable heating/cooling rates for revisiting scenario 1 (No changes).

	Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:		
			10°C/Ma	10 °C/Ma	10 °C/Ma
Garnet growth	525.00	2840.00	0.00	0.00	0.00
	530.00	2860.00	0.50	0.50	0.50
	535.00	2900.00	1.00	1.00	1.00
	537.00	2930.00	1.20	1.20	1.20
	550.00	2955.00	2.50	2.50	2.50
	560.00	2940.00	3.50	3.50	3.50
	570.00	2932.00	4.50	4.50	4.50
	560.00	2800.00	5.50	5.50	5.50
	550.00	2740.00	6.50	6.50	6.50
	530.00	2600.00	8.50	8.50	8.50
	Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:		
			1000°C/Ma	100 °C/Ma	10 °C/Ma
Secondary heating	520.00	2300.00	8.510	8.600	9.500
	515.00	1700.00	8.515	8.650	10.000
	540.00	1350.00	8.540	8.900	12.500
	675.00	1300.00	8.675	10.250	26.000
	500.00	1200.00	8.850	12.000	43.500

Table 4.9.2: P-T-t path for garnet growth with a constant heating/cooling rate and secondary heating with variable heating/cooling rates for revisiting scenario 2 (No staurolite).

	Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:		
			10°C/Ma	10 °C/Ma	10 °C/Ma
Garnet growth	525.00	2840.00	0.00	0.00	0.00
	527.00	2841.00	0.20	0.20	0.20
	530.00	2900.00	0.50	0.50	0.50
	540.00	3250.00	1.50	1.50	1.50
	540.50	3300.00	1.55	1.55	1.55
	543.60	3450.00	1.86	1.86	1.86
	550.00	3600.00	2.50	2.50	2.50
	555.00	3600.00	3.00	3.00	3.00
	556.84	3574.85	3.18	3.18	3.18
	556.00	3500.00	3.27	3.27	3.27
	555.00	3400.00	3.37	3.37	3.37
	550.00	3100.00	3.87	3.87	3.87
	535.00	2800.00	5.37	5.37	5.37
	Temperature (°C)	Pressure (bar)	time (Ma) for heating/cooling rate:		
			1000°C/Ma	100 °C/Ma	10 °C/Ma
Secondary heating	520.00	2200.00	5.383	5.518	6.868
	522.00	1800.00	5.385	5.538	7.068
	540.00	1600.00	5.403	5.718	8.868
	675.00	1500.00	5.538	7.068	22.368
	500.00	1400.00	5.713	8.818	39.868

Size Class 1

The predicted profiles for garnet size class 1 (figure 4.9.2 A-D) show that at HR/CR's of 1000°C/Ma and 100°C/Ma along the secondary heating path, there is very little difference from the profile predicted solely for garnet growth at 10°C/Ma for all garnet endmembers. When a rate of 10°C/Ma is used along the secondary heating path, some modification of the profiles occurs. In the predicted grossular (figure 4.9.2 B) and pyrope (figure 4.9.2 C) profiles, there is smoothing of the profile along the jumps in composition at 300 - 350 μm . The predicted almandine profile (figure 4.9.2 A) shows an increase of up to 2 mol% from 300 μm to the rim compared to the other profiles. Similarly, the predicted spessartine profile (figure 4.9.2 D) shows a relative decrease of up to 2 mol% from 300 μm to the rim with a HR/CR for secondary heating of 10°C/Ma. The predicted core content for each spessartine profile is 3 mol% above the observed core composition.

Size Class 2

As with size class 1, the predicted profiles for size class 2 (figure 4.9.2 E-H) with secondary HR/CR's of 1000°C/Ma and 100°C/Ma do not display noticeable variation from the profile predicted for just garnet growth. As the HR/CR decreases along the secondary heating path, the grossular (figure 4.9.2-F) and pyrope (figure 4.9.2-G) predicted profiles smooth the jump in composition, with this effect being most noticeable at a rate of 10°C/Ma. At a secondary HR/CR of 10°C/Ma, the predicted almandine profile (figure 4.9.2-E) shows a core content slightly higher (>0.5 mol%) than the other predicted profiles. This remains approximately 3 mol% below the observed

Figure 4.9.2: Revisit to Scenario 1 garnet crystallization modeling results for size class 1 (A - D) and 2 (E - H) with garnet growth followed by secondary heating.

composition. Along the profile from 300 μm to the rim, this profile is up to 2 mol% higher than the other profiles. The predicted spessartine profile (figure 4.9.2-H) at 10°C/Ma shows predicted core content <0.5 mol% lower than the profiles with slower HR/CR's. This core composition is 4 mol% above the observed profile. The spessartine profile for garnet growth only remains up to 2 mol% below the other predicted profiles up until the garnet rim.

Size Class 7

Garnet size class 7 shows no variation in the predicted grossular profile (figure 4.9.3-B) due to the differences in HR/CR. The three remaining garnet endmembers begin to show more variation in the predicted profiles (figure 4.9.3-A-D) at the different HR/CR's along the secondary path. In general, less than a 0.5 mol% spread in the predicted profiles for no secondary heating, and secondary heating at 1000°C/Ma and 100°C/Ma for these endmembers. Pyrope (figure 4.9.3-C) also shows little variation for secondary heating at 10°C/Ma. At a secondary HR/CR of 10°C/Ma the predicted almandine profile (figure 4.9.3-A) rises towards the observed profile, and is now 2 mol% below the observed profile. The predicted spessartine profile (figure 4.9.3-D) shows a similar trend with the predicted core composition lowered from a difference of 6 mol% for most of the predicted profiles to 4 mol% for secondary heating at 10°C/Ma. These trends in almandine and spessartine continue to the rim of the garnet.

Size Class 13

Garnet size class 13 shows the most variation in the predicted garnet profiles for all endmembers (figure 4.9.3 E-H) at the various HR/CR's during the modeled secondary heating event. The predicted almandine profiles (figure 4.9.3-E) for no secondary heating, and heating at 1000°C/Ma and 100°C/Ma show a 1.5 mol% spread at the garnet core, 4 mol% below the observed profile. For 10°C/Ma the predicted profile is nearly horizontal and 2 mol% above the predicted profile at the garnet core. No variation in the predicted profiles for grossular (figure 4.9.3-F) is seen at any HR/CR. The predicted pyrope profiles (figure 4.9.3-G) show a 0.5 mol% variation across all the modeled HR/CR's, with the slower rates corresponding to higher concentrations. A 2 mol% variation is seen in the predicted spessartine profiles (figure 4.9.3-H) for the faster HR/CR's. This results in a core content 5 – 6 mol% higher and an overall steeper chemical gradient than the observed profile. At a secondary HR/CR of 10°C/Ma, the predicted profile is shallower and has a core content 1 mol% below the observed.

Figure 4.9.3: Revisit to Scenario 1 garnet crystallization modeling results for size class 7 (A - D) and 13 (E - H) with garnet growth followed by secondary heating.

Revisiting scenario 2

Scenario 2 with added late heating is modeled at 1500 bar with a maximum T of 675°C. The modeled P-T paths for garnet growth and secondary heating are provided in table 4.9.2 and figure 4.9.1-B. Phase equilibrium modeling shows melting beginning at 675°C - 725°C at P of 1000 - 4000 bar (figure 4.9.1-B). At the modeled P of 1500 bar, melting is predicted to begin at 700°C. At the peak modeled T, the sample is contained within the stability field of plagioclase + ilmenite + biotite + cordierite + sanidine. Although cordierite and sanidine are predicted at peak T, neither is observed in 12PBA-27A. Garnet growth occurs with a constant HR/CR of 10°C/Ma. This is followed by variable HR/CR's of 1000°C/Ma, 100°C/Ma, and 10°C/Ma for the secondary heating path giving total times along the P-T path of 8.85 Ma, 12 Ma, and 43.5 Ma. These are compared to the predicted profile for garnet growth alone at a HR/CR of 10°C/Ma. As the P-T path for garnet growth has not changed from the previous model for scenario 1, the predicted radius for each size class remains the same. Model results are presented in figures 4.9.4 and 4.9.5.

Size Class 1

For HR/CR's of 1000°C/Ma and 100°C/Ma during the modeled secondary heating event, the predicted profiles for all garnet endmembers (figure 4.9.4 A-D) show little to no variation from the predicted profile for garnet growth only at a HR/CR of 10°C/Ma. In addition the predicted grossular (figure 4.9.4-B) and pyrope (figure 4.9.4-C) profiles for secondary heating at 10°C/Ma also display little variation apart from some smoothing of the profiles. The predicted almandine profile (figure 4.9.4-A) shows some

Figure 4.9.4: Revisit to Scenario 2 garnet crystallization modeling results for size class 1 (A - D) and 2 (E - H) with garnet growth followed by secondary heating.

modification at the slowest HR/CR. This increases the predicted core content by 1.5 mol% giving a decent match between the predicted and observed profiles from core to rim. At 10°C/Ma the predicted spessartine profile (figure 4.9.4-D) also shows a decrease in the core content of 1.5 mol%, but this remains 2 mol% above the observed spessartine profile.

Size Class 2

Little to no variation is seen in the predicted grossular (figure 4.9.4-F) and pyrope (figure 4.9.4-G) profiles for any variation in HR/CR for the modeled secondary heating event. Slight smoothing of the profiles is noted in the predicted pyrope profile at slower HR/CR's. The predicted almandine (figure 4.9.4-E) and spessartine (figure 4.9.4-H) profiles for secondary heating at 1000°C/Ma and 100°C/Ma show slight deviations from the predicted profile for solely garnet growth at 10°C/Ma. At secondary HR/CR's of 10°C/Ma more noticeable changes to the predicted profiles are present for these two endmembers. These changes include a shallower chemical gradient and a predicted core chemistry of 1.5 mol% closer to the observed profile.

Size Class 7

Once again the predicted grossular (figure 4.9.5-B) and pyrope (figure 4.9.5-C) profiles show little variation as a result of HR/CR changes, other than slight smoothing of the profiles that is most evident in pyrope. A slight rise in the predicted pyrope core content of 0.5 mol% should also be noted. In this size class, slight variation in the predicted almandine (figure 4.9.5-A) and spessartine (figure 4.9.5-D) can be seen

between the predicted profile for garnet growth and at HR/CR's for secondary heating of 1000°C/Ma and 100°C/Ma of approximately 1 mol% at the garnet core. At 10°C/Ma a good match between the observed and predicted profiles is seen. The slower HR/CR of 10°C/Ma also has a more noticeable effect on the predicted spessartine zoning (figure 4.9.5-D), lowering the predicted core content to 2 mol% above the observed profile and shallowing the predicted chemical gradient.

Size Class 13

Garnet size class 13 shows more variation due to HR/CR during secondary heating than the other size classes. The predicted almandine profile (figure 4.9.5-E) shows variation at all of the secondary heating HR/CR's. At 100°C/Ma the predicted profile is 1 mol% above the profile for solely garnet growth and 1 mol% below the observed profile. At 10°C/Ma the predicted almandine profile is horizontal with a predicted core content 2 mol% above the observed. The predicted grossular profiles (figure 4.9.5-F) show little to no variation due to HR/CR. The predicted pyrope profiles (figure 4.9.5-G) only show deviation from the predicted garnet growth profile at 10°C/Ma at a HR/CR for secondary heating of 10°C/Ma. This raises the predicted core content by 0.5 mol%. The predicted spessartine profiles (figure 4.9.5-H) show a 1.5 mol% variation between the garnet growth profile and the profiles for secondary heating at 1000°C/Ma and 100 °C/Ma, with predicted core content 3 - 4 mol% above the observed profile. Secondary heating at 10°C/Ma causes significant shallowing of the predicted profile and brings the predicted core composition 1 mol% below the observed profile.

Figure 4.9.5: Revisit to Scenario 2 garnet crystallization modeling results for size class 7 (A - D) and 13 (E - H) with garnet growth followed by secondary heating.

4.10 Summary of Modeling Results

Each of the three modeled scenarios yielded differences in the predicted P-T path that gave the best fit between the predicted and observed garnet compositional zoning. Scenario 1 yielded a nearly isobaric prograde P-T path from 525°C and 2840 bar to 566°C and 2938 bar. Garnet growth ceases in a stable assemblage field containing staurolite, which is not observed in this sample. The second scenario, in which staurolite was removed from the thermodynamic database, yielded a best fit prograde P-T path from 526°C and 2840 bar to 557°C and 3575 bar. Garnet growth now terminates within the observed mineral assemblage field. Both of these scenarios fail to replicate the observed almandine and spessartine core compositions in all modeled garnet size classes. A third scenario is modeled to test the effects of K-metasomatism after garnet growth. This scenario yielded a best-fit prograde P-T path from 539°C and 3140 bar to 544°C and 3090 bar. Overall, scenario 3 gives the best fit of all scenarios between the observed and predicted garnet compositional profiles in the largest garnet size class. In the smaller size classes, the core spessartine and almandine compositions cannot be replicated.

In all three scenarios little variation in the predicted profiles is seen with changes to the HR/CR along the P-T path. When a secondary thermal pulse is modeled for scenarios 1 and 2, little variation is seen in the profiles for any of the modeled garnet size classes until a HR/CR of 10°C/Ma, very slow for contact metamorphism, is used.

4.11 Geochronology

In-situ monazite geochronology was done for sample 12PBA-27A. Monazite in this sample proved to be very sparse, with generally less than 20 grains per thin section large enough ($>3\ \mu\text{m}$ in diameter) to be considered for analysis. Monazites contained within garnet were even more rare and generally $3 - 5\ \mu\text{m}$ in diameter. A number of monazite grains could not be analyzed due to a lack of space to place the desired number of spot analyses (≥ 4). In addition, analysis for some grains had to be discarded for bad analysis totals stemming from matrix effects due to the small grain size. In total, 3 monazite grains included in garnet and 10 matrix monazite grains are shown in this study. A summary of the monazite age data for each grain is shown in tables 4.11.1 and 4.11.2. The error on the calculated ages is 1σ .

Three monazite grains included in garnet were analyzed (2b, 19a, 19b). These monazite grains are located towards the core of the garnets (figure 4.11.3), with monazite 2b located within garnet 1. Almost all monazite inclusions are present along cracks through the garnet or in other garnet inclusions, such as apatite or quartz. Grains are generally subhedral. The calculated weighted average for the three samples gives $1829 \pm 24.7\ \text{Ma}$ for monazite 2b, $1905 \pm 29\ \text{Ma}$ for 19a, and $1845 \pm 5.4\ \text{Ma}$ for 19b.

A total of 10 matrix monazite were analyzed, with a variety of grain morphology and composition seen across the monazite population (figure 4.11.1). Seven of these monazite grains show a euhedral to subhedral morphology (monazite 15-core, 17-core, 18-core, 22, 23a, 23b, 23c) and are used to represent the matrix monazite population. Grains 15, 17, and 18 have rims that differ in composition from the core. These were analyzed separately and not included in the same age calculation. The matrix monazite

Figure 4.11.1: Representative elemental distribution maps (Ca, U, Th, Y) showing variation in matrix monazite grain morphology and composition for sample 12PBA-27A. (A - D) Low Y rim, monazite 15 (E - H) high Y rim, monazite 17 (I - L) heterogeneity in Ca and Th, monazite 22 (M - P) Th heterogeneity corresponding to two calculated ages, monazite f25b.

Figure 4.11.2: Monazite geochronology results for 12PBA-27A. Each histogram represents the weighted mean for a set of spot analysis on a single grain, where the length represents the total error in Ma. The width of each histogram is a graphical representation of short-term random error on the calculation (Williams *et al.*, 2005). Results are presented for (A) monazite inclusions in garnet, (B) matrix monazite, (C) monazite core – rim relationships, and (D) altered monazite.

grains commonly display heterogeneous compositions with respect to Ca and Th (i.e. figure 4.11.1 I-L). For example, monazite 15-core shows an analyzed Th content that varies from 21190 – 54862 ppm. U is fairly homogeneous across the grains. The age calculations for single monazite grains show a wide spread in ages (figure 4.11.2-B), from 1837 ± 8.6 Ma to 1870 ± 9.4 Ma. The spread in calculated ages does not appear to correlate with variation in composition. A single weighted average for the seven grains (40 spot analyses total) gives a calculated age of 1864 ± 3.3 Ma.

Chemical mapping of monazite 15 shows an anomalous low Y rim (15-rim, figure 4.11.1 A-D). The low Y rim (approximately 5000 ppm Y) appears homogenous in Y, Ca, Th, and U while the core (ca. 7000 ppm Y) is quite heterogeneous in Th and Ca. This is the only matrix monazite in the studied population to show this compositional feature. Analysis of the low Y rim yields a calculated age slightly younger than the core of the grain (figure 4.11.2-C), with the core giving an age of 1870 ± 12.6 Ma and the rim an age of 1837 ± 8.6 Ma. Chemical mapping of monazites 17 and 18 show narrow ($<5 \mu\text{m}$) high Y rims (17-rim, figure 4.11.1 E-H). Cores of these grains have Y contents of approximately 2000 ppm and the rims have Y contents of approximately 5000 ppm Y. The calculated ages for the high Y rims are slightly younger, but within error of the calculated ages for the monazite cores (figure 4.11.2-C). The core of monazite 17 gives calculated ages of 1853 ± 3.9 Ma for the rim and 1852 ± 21.7 Ma for the core. Monazite 18 yielded slightly older calculated ages with 1870 ± 9.4 Ma for the core and 1866 ± 10.3 Ma for the rim.

Two monazite grains (f25a, f25b) in proximity to a sericite pseudomorph after andalusite differ from the other matrix monazite grains in that they display a highly

corroded morphology with irregular grain boundaries (f25b, figure 4.11.1 M-P). These grains show chemical heterogeneity with respect to Ca, Th and U. The largest chemical variation is with respect to Th, where totals range from approximately 5500 – 19000 ppm. In general, parts of the monazite grain with low Th also yield lower U content. As lower Th content is correlated with younger calculated ages, the spot analyses were divided in order to calculate a weighted average age for the low Th and high Th domains of monazite f25a and f25b. Another monazite grain, f25c, shows a subhedral grain morphology. Analysis of f25c yields a Th content similar to the high Th domains of f25a and f25b as well as a similar age. Calculated ages for the high Th domains of f25a and f25b give ages of 1842 ± 29 Ma and 1836 ± 18.8 Ma (figure 4.11.2-D). A weighted average of ages for the low Th domains from monazites f25a and f25b, and the analysis on f25c (12 spot analyses total), gives an age of 1792 ± 10.1 Ma.

Table 4.11.1: Monazite geochronology data and calculated ages.

Sample	Spot	Y (ppm)	1σ	U (ppm)	1σ	Th (ppm)	1σ	Pb (ppm)	1σ	Age (Ma)	Error (Ma)	Weighted Average of Ages (Ma)	Total Error (Ma)
Monazite inclusions in Garnet													
2b	1	8485	67	1620	26	65780	58	6029	13	1810	7	1829	24.7
	2	8532	67	2292	27	71358	60	6866	14	1851	7		
	3	8951	68	2556	27	74922	61	7156	15	1827	6		
19b	1	6779	62	2190	27	55058	54	5401	13	1841	8	1845	5.4
	2	5481	58	2258	27	48390	51	4908	13	1860	9		
	3	5717	59	2442	27	43767	49	4507	13	1838	9		
	4	5422	58	2155	27	39461	46	4064	12	1844	10		
	5	4657	55	1809	26	46672	50	4576	13	1845	9		
19a	1	6452	61	1966	27	41151	48	3406	12	1909	10	1905	29
	2	4860	56	1621	26	45048	50	4580	13	1925	10		
	3	4430	55	2075	27	45741	50	4793	13	1925	9		
	4	5495	59	1355	26	38029	46	3689	12	1845	11		
Matrix Monazite													
15-core	1	6760	62	4082	28	44086	49	5194	13	1885	8	1870	12.6
	2	7966	66	3881	28	52267	53	5837	13	1882	7		
	3	7973	66	4136	28	54862	54	6125	13	1876	7		
	4	7214	64	2717	27	37642	46	4014	12	1814	10		
	5	8111	66	3395	28	43439	49	4863	13	1867	9		
	6	5971	60	2204	27	21190	37	2551	12	1869	15		
15-rim	1	6232	61	3470	28	44110	49	4924	13	1860	9	1837	8.6
	2	4781	56	4187	28	43798	49	5055	13	1836	8		
	3	4286	54	4329	28	43372	49	5043	13	1830	8		
	4	5386	58	4325	28	44054	49	5098	13	1829	8		
17-core	1	2398	47	2741	27	37810	46	4127	12	1852	10	1853	3.9
	2	2294	47	2882	27	61753	57	6275	13	1864	7		
	3	2143	46	2437	27	31926	43	3502	12	1842	11		
	4	2697	48	3813	28	58970	55	6289	13	1852	7		
	5	2426	47	3337	28	51432	52	5479	13	1849	8		
	6	2221	47	2691	27	43096	49	4561	13	1850	9		
17-rim	1	5935	60	3226	28	48579	51	5296	13	1881	8	1852	21.7
	2	4831	56	3484	28	48224	51	5311	13	1868	8		
	3	4568	55	3307	28	46902	50	5034	13	1833	8		
	4	6311	61	3423	28	47972	51	5139	13	1826	8		
18-core	1	2209	47	2557	27	40317	47	4397	13	1897	10	1870	9.4
	2	2084	46	2219	27	47717	51	4861	13	1870	9		
	3	2151	46	2220	27	48597	51	4922	13	1863	9		
	4	2103	46	2390	27	55703	54	5563	13	1854	8		
	5	2391	47	3240	28	49519	51	5306	13	1856	8		
	6	2462	48	2952	27	45119	49	4932	13	1890	9		
18-rim	1	4590	55	4430	29	50865	52	5858	13	1872	7	1866	10.3
	2	2688	48	2960	27	57125	55	5920	13	1870	7		
	3	7608	64	5177	29	48924	51	5877	13	1857	7		
22	2	1663	45	2761	27	53095	53	5460	13	1855	8	1857	14.4
	3	1656	45	2667	27	46498	50	4796	13	1832	9		
	4	1670	45	2722	27	57471	55	5919	13	1883	7		
	5	1816	46	2405	27	25839	40	2973	12	1843	13		
	6	1968	46	2169	27	22970	38	2646	12	1838	15		
23a	1	1934	46	2806	27	18177	35	2532	12	1902	15	1865	10.4
	2	2507	48	2840	27	19457	36	2593	12	1861	15		
	3	3056	50	3744	28	42237	48	4836	13	1855	9		
	4	2016	46	3933	28	22844	38	3248	12	1867	12		
	5	2077	46	4365	28	20274	36	3152	12	1861	12		
23b	1	2076	46	3051	27	9319	29	1782	11	1860	19	1848	12.7
	2	2320	47	4166	28	15451	33	2628	12	1835	14		
	3	1029	41	3329	27	23951	38	3153	12	1869	12		
	4	2093	46	3345	27	13821	32	2247	11	1847	15		
	5	2028	46	3476	28	14687	33	2325	11	1821	15		

Table 4.11.2: Monazite geochronology data and calculated ages continued.

Sample	Spot	Y (ppm)	1 σ	U (ppm)	1 σ	Th (ppm)	1 σ	Pb (ppm)	1 σ	Age (Ma)	Error (Ma)	Weighted Average of Ages (Ma)	Total Error (Ma)
23c	1	2293	47	5984	29	10201	29	2902	12	1918	13	1873	18
	2	2342	47	7673	31	13125	31	3593	12	1861	10		
	3	2428	48	8531	31	10599	30	3724	12	1893	10		
	4	3252	51	5457	29	2253	22	1914	11	1839	17		
	5	2007	46	2159	26	11970	31	1697	11	1832	20		
	6	1866	45	2180	26	10246	29	1543	11	1818	22		
f25a	1	2473	48	7352	30	16541	34	3784	12	1860	10	1842	29
	2	2462	48	4725	28	11877	31	2470	11	1817	14		
	3	2413	48	4017	28	14200	32	2468	11	1831	14		
	4	3099	50	1962	26	8458	28	1209	11	1676	25	1791	108
	5	2743	49	3875	28	5449	25	1608	11	1765	19		
	6	2945	50	4387	28	8384	28	2125	11	1857	16		
f25b	1	3203	51	7831	31	12554	31	3581	12	1855	10	1836	18.8
	2	2196	47	4527	28	14607	32	2635	11	1814	13		
	3	2272	47	3987	28	19029	35	2890	12	1842	13		
	4	2125	46	2257	26	11465	30	1652	11	1801	20	1801	3.5
	5	3031	50	4729	28	9794	29	2270	11	1799	14		
	6	4256	54	4993	28	7064	27	2130	11	1804	15		
f25c	1	1468	44	1873	26	14281	32	1783	11	1813	19	1790	11.9
	2	2834	49	6182	29	19511	36	3544	12	1807	10		
	3	2901	49	8113	31	21243	37	4275	12	1803	8		
	4	2289	47	5856	29	17476	34	3204	12	1774	11		
	5	2187	47	3247	27	11863	30	1907	11	1735	17		
	6	2879	49	6798	30	15487	33	3336	12	1779	10

Figure 4.11.3: Location of monazite grains included within garnet. (A) monazite 2b (B) monazite 19a & 19b.

Chapter 5: Discussion

5.1 Clustering of Garnet Porphyroblasts

XR- μ CT data for samples 12PBA-27A and 14PBA-99A show distinct clustering of garnet crystals. This is especially evident in the reconstructions of the scanned cores showing only the garnet crystals (figure 4.4.2). These images show that there are distinct sections of the drill cores that contain high and low concentrations of garnet that are defined by roughly parallel banding. Statistical analyses of the garnet distribution in 12PBA-27A also confirm the clustering of garnet crystals. The L'function and pair correlation function (PCF) for both the sphere-normalized radius and semi-major axis show the observed garnet population falling above the null hypothesis envelope for a random distribution at length scales greater than the average nearest neighbour distance. This means that there are more crystal centers in the observed population than expected, and clustering is present at length scales of 0.1 to >1 cm. This is supported by what is seen in the XR- μ CT data, where clusters of garnet are approximately 1 - 3 cm in width. As both the L'function and PCF look at the distribution of crystal centers rather than crystal size, resorption of garnet has no effect on these results.

Unimodal crystal size distributions for the garnet populations in samples 12PBA-27A and 14PBA-99A-B (figure 4.4.5) are indicative of garnet porphyroblast growth during a single metamorphic event (Berger *et al.*, 2011). In addition, preferential alignment of the long axes of garnets in 12PBA-27A, as shown by stereographic projection (figure 4.4.3), suggests crystal growth under similar deformation conditions. The clustering of garnet crystals indicates that there was an inhomogeneous distribution

of energetically preferable nucleation sites for garnet across the volume of the rock. This inhomogeneous distribution may be explained due to chemical heterogeneity in the protolith or nucleation sites clustered on a precursor mineral phase (Denison *et al.*, 1997; Daniel and Spear, 1999; Ketcham *et al.*, 2005). As the clustering of garnet in these samples appear to follow roughly parallel layering, it is thought that the clustering is due to chemical heterogeneity resulting from layering in the sedimentary protolith.

The hypothesis of heterogeneous chemistry across the protolith rock volume is supported by significant chemical variation seen across small volumes of rock. For example, in sample 14PBA-99A two separate bulk rock chemical analyses were done to describe the garnet-poor and garnet-rich areas. The most notable chemical differences between these areas are in MnO (0.07 and 0.17 wt%) and Fe₂O₃ (0.86 and 1.78 wt%). In addition, two chemical analyses on sample 12PBA-27A from a reasonably sized hand sample yielded significant differences in MnO contents (0.5 and 0.11 wt%) (see table 4.1.1). From this it can be suggested that heterogeneity in MnO content played a role in preferential garnet crystallization in these samples. These two samples indicate that there are significant chemical, mineralogical, and textural changes across the approximately 10 cm³ cylinder volume scanned by XR- μ CT used for chemical analysis. This suggests that the chemical equilibrium domain for these rocks may be quite small, and that the rocks are not chemically equilibrated over volumes as small as 10 cm³.

5.2 Variation in Garnet Composition

The pattern of compositional zoning in garnet in this study shows increasing almandine and pyrope coupled with decreasing grossular and spessartine from core to rim. This zoning pattern is most distinctly shown in 12PBA-27A (i.e. figure 4.6.3), and is indicative of garnet growth during prograde metamorphism (Borghi *et al.*, 2002).

Modification to the compositional zoning in proximity to the garnet rim and adjacent to fractures and inclusions is seen by sharp changes to the overall compositional zoning pattern. This is attributed to retrograde zoning and mass transfer reactions with adjacent matrix phases (Borghi *et al.*, 2002; Hurai *et al.*, 2010; Tirone and Ganguly, 2010).

Compositional profiles across garnet porphyroblasts from different size classes in sample 12PBA-27A provide evidence that initial prograde growth zoning has also been modified by late intracrystalline diffusion. The efficiency of intracrystalline diffusion in garnet is directly related to T, garnet size, and time; where higher T, and more time result in more diffusion (Caddick, 2010; Florence and Spear, 1991). Smaller grains are more sensitive to diffusion as there is less distance for components to travel. If diffusion was not present in this system, then the compositional zoning of each garnet size class would be purely a result of the portion of the P-T path where garnet grew (Gaidies *et al.*, 2008A). Instead, it can be seen that spessartine, which is considered to be the fastest diffusing element through garnet and therefore the best proxy for intracrystalline diffusion, shows a miss-match between the compositional zoning profiles of the large and small grains. For example, smaller garnet crystals show a shallower spessartine compositional gradient than larger crystals (figure 5.4.2-D), indicating that there has been some component of intracrystalline diffusion.

Compositional zoning of trace elements such as Y in garnet is useful in determining the history of garnet growth. Y strongly partitions into garnet when it becomes available during metamorphism (Catlos *et al.*, 2002; Lanzirotti, 1995). Due to this, garnets commonly exhibit Y rich cores, similar to what is seen in the cores of the larger garnet size classes from sample 12PBA-27A (i.e. figure 4.6.3-A). Garnet porphyroblasts of all size classes from this sample show a ring of high Y approximately 50 μm away from the rim (i.e. figure 4.6.3-A). Y peaks away from the garnet are commonly attributed to either the breakdown of Y bearing matrix phases (i.e. allanite, xenotime, monazite) or resorption and subsequent regrowth of garnet (Lanzirotti, 1995). As there is no textural evidence in the garnet to suggest resorption and subsequent regrowth, the observed high-Y ring is thought to represent Y release due to the breakdown of a Y bearing accessory mineral.

Two traverses on neighboring garnet crystals in sample 14PBA-99A-A (figure 4.6.10-E) show opposing trends in their almandine and grossular zoning (figure 4.6.9). These differences in almandine and grossular cannot be easily explained. Possibilities for these patterns include fracturing, growth under diffusion-controlled conditions, multiple episodes of garnet growth, and variability in bulk rock composition. Fracturing is an unlikely cause as these grains have subhedral morphology (see figure 4.6.10-E). Diffusion-controlled growth is also thought to be unlikely, as these garnet crystals are quite close together and display symmetrical zoning. If diffusion-controlled growth, where growth is limited by the availability of elements to the growing crystal surface (Daniel and Spear, 1999) was a factor, it is a possibility that the availability of elements to each growing crystal surface would be variable and result in unsymmetrical zoning

patterns. Polyphase garnet growth could explain the observed difference in garnet composition, if the two garnets grew under different P-T conditions. This would imply that garnet grew for a second time such that new grains nucleated and grew without the growth of secondary rims on the older garnet crystals. Polyphase metamorphism is likely not the cause of the observed zoning patterns, as there is no additional evidence in this sample for a second generation of metamorphic mineral growth and a unimodal CSD for 14PBA-99A-B (Figure 4.4.5-C) suggests growth during a single metamorphic event. However, it remains possible that bulk-rock chemistry differences between these two sections of core would allow for a second period of garnet growth in this portion of the rock and not the other. The most likely cause of the differences in compositional zoning may be garnet overgrowing compositional heterogeneities in the protolith.

The single preserved large garnet in sample 14PBA-94A displays fairly homogenous compositional zoning (figure 4.6.8). The grossular chemical map shows slight zoning reminiscent of prograde growth zoning with decreasing grossular content from core to rim of the grain. This trend can also be seen in the small fragments of garnet also included in the area of this map. Spot chemical analysis on several of the smaller grains indicates uniform spessartine and pyrope contents with varying grossular and almandine, similar to what is seen in 14PBA-99A-A. In this case the compositional variation in the small garnet fragments is thought to be a result of mechanical fracturing of larger garnet crystals. Where the preserved zoning in each fragment reflects its original location in the larger garnet crystal.

5.3 The Effect of Fluids on Mineral Composition and Texture

The studied samples show varying degrees of evidence for chemical and textural modification. This evidence includes modification of garnet composition, pseudomorphing of andalusite by sericite, and fracturing or cracking of garnet porphyroblasts. The addition of fluids into a system can have both a catalytic and thermodynamic effect as it may affect both the rate of metamorphic reactions and the effective bulk rock chemistry of a system (Putnis and Austrheim, 2010). The introduction of fluids into a rock has been shown to increase the rate of metamorphic reactions, as well as cause changes to mineral compositions and textures (i.e. Hames and Menard, 1993; Hurai *et al.*, 2010; Jamtveit and Austrheim, 2010; Whitney *et al.*, 1996). This is especially evident during retrograde metamorphism, where there is evidence that the presence of fluid has a greater effect on reactions than a change in P-T conditions (Jamtveit and Austrheim, 2010). The increase in reaction rate is due to the movement of fluids providing a transport mechanism for mass transfer reactions, which allows components to move through a rock significantly faster than reactions reliant on solid-state diffusion (Jamtveit and Austrheim, 2010; Putnis and Austrheim, 2010). The majority of metamorphic reactions are dissolution-precipitation reactions, where phases are broken down into chemical components, which are transported some distance and precipitated into new phases. With this mechanism, the transport rate of these components is often the limiting factor. Thus by increasing the transport rate with fluids, the rates of metamorphic reactions can be increased (Jamtveit and Austrheim, 2010).

When garnet-bearing rocks are subjected to fluids, it commonly results in modification to garnet growth zoning. This occurs along areas where the fluid interacts

with the crystal such as its rims and fractures (Hames and Menard, 1993, Hurai et al., 2010; Whitney *et al.*, 1996). This type of modification of garnet growth zoning is especially evident in sample 12PBA-27A (i.e. figure 4.6.3). Where there are cracks in these garnets, there is clear modification of the chemical zoning in almandine, pyrope, and grossular within approximately 20 μm of these cracks. This is best displayed in the pyrope elemental distribution map (figure 4.6.3-C). The spessartine growth zoning does not appear to show diffusion along the fractures in garnet. As Mn is the fastest diffusing element through garnet (Gaidies *et al.*, 2008A) it is possible that the fluids did cause diffusion of Mn, but this occurred at a fast enough rate that the resulting profile was smoothed. The modification along cracks is due to the fractures providing a conduit for fluid to flow through the rock. These fluids interact with the edges of the crack moving chemical components along with them (Keleman and Hirth, 2012). As the cracks are primarily filled with biotite and chlorite, this suggests that a mechanism for the observed garnet compositional change may be mass-transfer reactions with the biotite and chlorite (Hurai *et al.*, 2010) and/or a reaction between the garnet and fluid to form biotite and chlorite.

Resorption is a dissolution process resulting in the embayment of grains that commonly occurs as a result of the introduction of fluids into a rock (Hames and Menard, 1993; Whitney et al., 1996). Every garnet-bearing sample in this study shows resorption of garnet to varying degrees. Sample 14PBA-94A shows a large garnet porphyroblast with deep embayments suggesting significant resorption (figure 4.6.8), while garnet porphyroblasts in 12PBA-27A and 14PBA-99A show less evidence of resorption along the edges of grains. The higher inferred resorption in 14PBA-94A may indicate a greater

volume of fluids affecting this rock. Resorption can increase the effect of fluid-driven reaction as it increases the surface area on which a reaction can occur (Keleman and Hirth, 2012; Jamtveit and Austrheim, 2010; Putnis and Austrheim, 2010).

When fluids are introduced into a rock one of two processes must take place. There must either be an increase in solid volume to accommodate the fluid volume introduced, or exchange with the surrounding material to maintain a constant rock volume (Jamtveit and Austrheim, 2010). When the introduction of fluids causes the rock volume to increase, the increased P can cause mechanical fracturing of the rock as well as crystals contained within it (Floess and Baumgartner, 2013; Jamtveit and Austrheim, 2010; Keleman and Hirth, 2012). Floess and Baumgartner (2013) attribute the volume increase in a fluid-consuming reaction to the nucleation and growth of sheet silicate minerals, such as biotite and muscovite. Due to an abundance of fracturing observed in some samples as well as the formation of sericite pseudomorphs after andalusite, it is postulated that some of the fluid input was consumed by the rocks rather than exchanged with the surrounding environment. When this fracturing occurs, it creates additional pathways for fluid flow, which has the effect of increasing the rock's porosity. This generally has the effect of increasing both the rate and volume of fluid flow (Keleman and Hirth, 2012; Jamtveit and Austrheim, 2010; Putnis and Austrheim, 2010). However, reactions can also form new mineral phases within the fractures, sealing them and reducing the flow of fluids (Jamtveit and Austrheim, 2010). This is observed in 12PBA-27A where fractures within garnet are commonly filled with biotite and chlorite. This may be explained by a simple reaction where garnet + fluids = biotite + chlorite. The presence of biotite and chlorite within garnet fractures and sericite pseudomorphs after

andalusite suggest the infiltration of fluids occurred at greenschist facies conditions during cooling. Mechanical fracturing of crystals and increased fluid infiltration is common in extensional settings. Lateral extensional stresses cause crystals to break, providing pathways for fluids to travel (Bruhn *et al.*, 1994).

Differences between the amount of fracturing seen in garnet-bearing samples from the study area is attributed to variation in the amount of fluids introduced into the rock as well as potential differences in stresses and P-T conditions. Sample 14PBA-94A shows a high degree of fracturing with small, angular garnet fragments clustered in areas up to 2 mm in diameter (i.e. figure 4.6.10-F). It is possible that compositional differences between garnet fragments reflect the portion of the initially larger grain that the fragment originated from (see table 4.6.1). In comparison, garnet porphyroblasts in sample 12PBA-27A show only parallel cracks in most crystals. The other garnet-bearing sample, 14PBA-99A shows no visible cracking in its garnet porphyroblasts.

Fluids that are added to a rock from an outside source are commonly out of equilibrium, or of a different composition than the rock. This is because at P-T conditions below granulite/eclogite facies where dehydration of minerals can occur, fluid supply to the rocks is generally controlled by an external source (Jamtveit and Austrheim, 2010). Due to this, the introduction of fluids into a rock will affect the bulk rock chemistry. The exact chemistry change due to fluids cannot be quantified without obtaining an unaltered rock sample (Putnis and Austrheim, 2010). However, the relative composition of the fluid can often be determined by looking at the resulting mineralogical and chemical changes to certain minerals. Studies have shown that adding K⁺ and H⁺ bearing fluids will cause preferential replacement of aluminosilicate phases with muscovite (Chinner, 1973). This

process is evident in rocks from the Montresor belt, where andalusite porphyroblasts are pseudomorphed to varying amounts by muscovite, indicating that there was a K⁺ and H⁺ component to the fluid present in these samples. There is a large variation in the amount of replacement from none (14PBA-100, figure 4.2.2-E), partially replaced (14PBA-97A, figure 4.2.2-B), and fully replaced (12PBA-27A, figure 4.2.1-A). These differences are interpreted to be a result of differences in proximity to the fluid source and the amount of fluid added to each rock. Differences in P-T conditions between samples may also account for some of this variation (Whitney et al., 1996).

5.4 Interface vs. Diffusion Controlled Garnet Growth

Porphyroblast growth of any mineral phase during metamorphism can be described as being either interface-controlled or diffusion-controlled (figure 5.4.1). In interface-controlled growth conditions, the rate of garnet growth is limited by the attachment of elements to the growing crystal surface (Daniel and Spear, 1999; Hirsch 2000). This assumes that all chemical components needed for garnet growth move through the matrix faster than they are attached to the growing crystal surface, and that these reactions are faster than changes in P, T, and composition (Daniel and Spear, 1999; Gaidies *et al*, 2008A; Kretz, 1966). In addition, interface controlled growth results in randomly distributed crystals (Daniel and Spear, 1999; Hirsch, 2000). During interface-controlled growth, all garnet porphyroblasts will grow at the same radial rate (Daniel and Spear, 1999; Gaidies *et al.*, 2008A). This implies that their observed composition reflects the portion of the metamorphic P-T path where garnet nucleated and grew, assuming that

Figure 5.4.1: (A) Diffusion controlled garnet growth showing the diffusional gradient surrounding garnet crystals and an ordered distribution of crystals. (B) Interface controlled garnet growth with no diffusional gradient and a random distribution of garnet crystals in the rock volume (after Daniel and Spear, 1999).

this composition has not been modified by intracrystalline diffusion (Gaidies *et al.*, 2008A). Conversely, in diffusion-controlled porphyroblast growth, the rate at which chemical elements move through the rock matrix limits garnet growth. This results in chemical depletion halos surrounding growing crystals, and as a result garnet composition would reflect the availability of elements rather than P-T conditions (Daniel and Spear, 1999; Denison and Carlson, 1997; Hirsch, 2000). Determining whether garnet grew under interface or diffusion controlled conditions is important for crystallization modeling, as THERIA_G assumes interface controlled growth conditions (Gaidies *et al.*, 2008A).

As shown in figure 5.4.2, all garnet porphyroblasts from different size classes in sample 12PBA-27A show similar chemical gradients. As grossular is the slowest diffusing component through garnet (Gaidies *et al.*, 2008A), it is assumed to be the best indicator of the initial chemical gradients. In this sample, the grossular content has been

modified along cracks in the garnet crystal, which obscures this trend. However, it can be seen that similar chemical trends exist across the different garnet size classes for all endmembers. The spessartine chemical profiles show smaller grains with core composition that has dropped below the trend of the larger grains. As spessartine is the fastest diffusing component through garnet (Gaidies *et al.*, 2008A), this trend in the composition is attributed to late modification of the compositional zoning by intracrystalline diffusion. Garnet porphyroblasts from all size classes have approximately equal rim composition, suggesting that all porphyroblasts stopped growing at the same point in P-T-t space. Concentric compositional zoning in major elements can also be used as an indicator for interface-controlled garnet growth. Concentric zoning shows a uniform availability of elements on each growing crystal face. Under diffusion-controlled growth conditions, non-concentric zoning may be expected as a reflection of differences in the availability of elements to different growth surfaces.

Growth conditions can also be shown by statistical analysis of the 3-dimensional distribution of garnet. Interface vs. diffusion-controlled growth is best shown by the mark covariance function (MCF). Garnet porphyroblasts that grow under interface-controlled conditions result in a randomly distributed population of crystals. When garnet grows under diffusion-controlled conditions this leads to an ordered distribution of porphyroblast sizes (Daniel and Spear, 1999; Hirsch, 2000). Statistical analyses of the garnet population in 12PBA-27A using both a sphere-normalized radius and the semi-major axis of garnet show a randomly distributed garnet size over most length scales which falls within the null-hypothesis envelope (Figure 4.5.1), indicating interface-controlled growth. Over some small portions the observed population falls slightly above

Figure 5.4.2: Core to rim chemical compositional profiles for 7 size classes of garnet from 12PBA-27A. (A) Almandine (X_{alm}). (B) Grossular (X_{grs}). (C) Pyrope (X_{prp}). (D) Spessartine (X_{sps}). Garnets 1 and 2 = size class 1, garnet 3 = size class 2, garnet 4 = size class 7, garnet 5 = size class 10, garnet 6 = size class 12, and garnet 7 = size class 13. Garnet size classes are defined in figure 4.4.5-A.

the null-hypothesis envelope, indicating a clustered distribution at those length scales. This is seen at length scales greater than 15 mean radii for a sphere normalized radius and length scales of 13 – 14 and greater than 17 mean radii for the semi-major axis. The observed clustering of garnet porphyroblasts is thought to be a result of chemical heterogeneity in the protolith. It should be noted that the MCF statistic compares crystal sizes at different length scales to calculate this statistic. Garnet porphyroblasts in 12PBA-27A are embayed, which would have reduced the measured crystal size by some amount and is not accounted for in this analysis. Based on petrological observation, it is thought that resorption affected each size class approximately the same amount. Thus, the MCF statistic is considered to be a good indication of garnet growth conditions. Overall the similarity in chemical gradients across crystal size classes, concentric growth zoning, and a statistically random distributed crystal size population shown in the MCF suggest that garnet porphyroblasts in 12PBA-27A grew under interface-controlled conditions. Therefore, simulation of garnet crystallization with THERIA_G is a good model for 12PBA-27A.

5.5 Geochronology

The population of matrix monazite from sample 12PBA-27A gives a range of ages from 1837 ± 8.6 Ma to 1870 ± 9.4 Ma, with a statistical peak at 1864 ± 3.3 Ma. These ages are interpreted to represent growth during peak regional metamorphism in the Montesor Belt during the Trans-Hudson orogeny. The range of monazite ages in 12PBA-27A is interpreted to represent continuous stages of monazite growth during prograde metamorphism from ca. 1870 to 1837 Ma, with peak metamorphic conditions

possibly occurring at 1837 Ma. This would suggest that metamorphism in the Montresor belt reached peak conditions approximately 73 Ma after the earliest estimate for the onset of the Trans-Hudson orogeny at 1.91 Ga. This time lag has previously been interpreted as the time needed for crustal thickening and thermal incubation after collision (Berman, 2010).

This study shows a small population of monazite grains included in garnet, with three analyzed grains. The small population is due to a combination of scarce monazite and small grain sizes. Two of these monazites, 2b and 19b, give similar ages of 1829 ± 24.7 Ma and 1845 ± 5.4 Ma, suggesting garnet growth is coincident with the growth of ca. 1845 Ma monazite. Monazite 19a has a calculated age of 1905 ± 29 Ma. While this age may represent an earlier onset of metamorphism than what the other analyzed monazite grains indicate, there is a large error of 29 Ma on this age making it difficult to constrain exact timing. It is also possible that this is an inherited monazite from an older source. The age may also be due to analytical error, as some spot analyses show elevated Si concentration (see table A.3.1) indicating that there is the possibility of matrix effects due to the surrounding silicates. With one analysis it is difficult to say which of these possibilities accounts for the older age and spread in age data. More analyses on monazite inclusions within garnet would be needed to strengthen age populations, especially with regards to the older age.

Two monazite grains (17 & 18) out of the matrix population show narrow high Y rims. These two grains are less than 1 cm apart in the thin section. Calculated ages for these rims are slightly younger, but within error, of the monazite cores, with calculated core/rim ages of 1853 ± 3.9 Ma and 1852 ± 21.7 Ma for monazite 17 and 1870 ± 9.4 Ma

and 1866 ± 10.3 Ma for monazite 18. It is hypothesized that these high Y rims are due to the breakdown of a Y rich matrix phase (i.e. allanite, apatite, xenotime) that released Y into the rock. These rims may be correlated with the high Y rings seen near the rims of garnet porphyroblasts in the sample (i.e. figure 4.6.3-F). The anomalous low Y rim seen with monazite 15 gave an age of 1837 ± 8.6 Ma. This is younger than the core of the grain at 1870 ± 12.6 Ma. The mechanisms of formation of this low Y rim are not known. There is no clear relationship between the concentration of Y in monazite and timing of garnet growth, as there is little variation in Y concentration across the studied monazite grain population. A more detailed understanding of the monazite composition and the observed Y anomalies may be determined by a study of the monazite trace element composition and detailed phase relationships for monazite forming reactions.

Three monazite grains located on the edge of a large muscovite pseudomorph after andalusite show distinct morphology, chemistry, and calculated ages from the rest of the matrix monazite population. Two of these monazite grains (f25a and f25b) are highly embayed, and show distinct variation in Th concentration across the grain. The Th content is directly correlated with calculated age, with high Th domains giving ages of 1842 ± 29 Ma and 1836 ± 18.8 Ma, and low Th domains giving ages of 1791 ± 108 Ma and 1801 ± 3.3 Ma. An experiment by Williams *et al.* (2011) has shown that in the presence of fluids, monazite can undergo significant compositional changes at T well below its estimated closure T of 675 - 730°C (Parrish, 1990). At experimental conditions of 450°C and 4500 bar, altered monazite domains became depleted in U, Th, and Pb leading to a complete resetting of the age. Unaltered monazite domains retained their original age (Williams *et al.*, 2011). Resetting of monazite ages in the presence of fluids

has also been observed in other studies (i.e. Tartèse *et al.*, 2011). It is interpreted that the low Th domains of monazite f25a and f25b represent altered domains that became reset at the time of fluid infiltration. The high Th domains are within error of the age calculated for the matrix monazite population and as a result are thought to have been unaffected by the fluids. Another monazite grain in proximity to the pseudomorph, f25c, differs in its subhedral morphology and high Th content. This monazite gives a calculated age of 1790 ± 11.9 Ma. Based on these factors, this monazite is interpreted to have grown during the fluid infiltration event. Monazite f25c and the low Th domains of f25a and f25b provide evidence for a fluid mediated monazite growth and alteration event at 1792 ± 10.1 Ma. This age is interpreted to represent the age of emplacement of granitic and pegmatitic dykes in the lower Montresor group, thought to be the source of these fluids.

5.6 Pressure-Temperature Estimates

Several non-garnet bearing samples were studied from the lower Montresor group, including samples 14PBA-67A, 14PBA-85A, and 14PBA-100. These samples are very similar with respect to their mineral composition, containing assemblage of quartz + andalusite + biotite + muscovite + plagioclase in variable abundance. The chlorite in these samples replaces biotite, and is interpreted to have formed after peak conditions during cooling. Phase equilibrium modeling for these samples yields peak P-T estimates of 500 - 630°C and <4000 bar. The similarity in P-T results for these samples is due to little variation in bulk rock composition and mineral assemblages. P-T estimates for these samples are interpreted to be representative of the peak conditions during the Trans-

Hudson orogeny for the lower Montresor belt, as these samples show no evidence of alteration.

Sample 14PBA-97A contains the same peak mineral assemblage as those mentioned above, containing quartz + andalusite + biotite + muscovite + plagioclase. However, in this sample, andalusite porphyroblasts are partially altered to sericite. Sericite is restricted to the edges of the grains and along cracks, and commonly constitutes 30 - 50% of the porphyroblasts. The sericite replacing andalusite is interpreted to have formed during cooling after peak conditions, as the random orientation indicates growth during static conditions. In contrast, muscovite within the matrix is aligned with the main foliation, indicating that it grew during prograde conditions. The presence of sericite after andalusite in this sample indicates potential for fluids and related modifications to the rock's effective bulk rock composition. A peak P-T estimate of 500 - 640°C and <4000 bar for this sample is similar to the P-T estimates for samples with unaltered andalusite. This suggests that the presence of fluids in this sample did not have a significant enough impact on the effective bulk rock composition to affect the P-T estimate.

Peak P-T estimates obtained through phase equilibrium modeling for garnet bearing samples (12PBA-27A, 14PBA-94A, and 14PBA-99A) are derived with the assumption that the affect of garnet fractionation on the effective bulk rock chemistry does not have a significant impact on the location of the predicted stable assemblage fields in P-T space. Results for 14PBA-94A and 14PBA-99A, are discussed in this section. Sample 12PBA-27A was used for more extensive analysis and thermodynamic modeling and is discussed in detail in the following section.

Sample 14PBA-94A contains a mineral assemblage of quartz + biotite + plagioclase + chlorite + garnet + amphibole 1 + amphibole 2. Phase equilibrium modeling yields a peak P-T estimate of 525 - 580°C and <4500 bar, falling within the range predicted by the non-garnet bearing samples from the lower Montresor group. This sample shows highly embayed and intensely fractured garnets, providing evidence for fluid infiltration. Garnet resorption and fracturing is interpreted to have occurred during cooling. While a change to the effective bulk rock composition due to fluids cannot be ruled out for this sample, as the predicted P-T falls within the range predicted for other lower Montresor group samples, it is thought that this did not significantly affect the predicted peak P-T. As the garnet crystals in this sample are highly modified by late processes, as shown by embayments and fractures, a garnet isopleth intersection was not calculated. Two amphiboles in this sample are characterized by their composition. Petrographic relationships show amphibole 2 surrounding amphibole 1, indicating that amphibole 1 was overgrown by amphibole 2. This suggests a P-T path that moved from an assemblage field containing solely amphibole 1 to a field containing both amphiboles. As the assemblage field containing plagioclase + ilmenite + garnet + biotite + chlorite + amphibole 1 occurs within a large area of P-T space, a well-defined P-T path cannot be defined for moving from one assemblage field to the other. It can be said that the reaction to involve amphibole 2 in the stable assemblage occurred during prograde metamorphism with increasing T. The rough P-T path defined by the amphiboles in this sample agrees with the P-T paths modeled for sample 12PBA-27A using garnet growth zoning.

14PBA-99A consists of relatively garnet-rich and garnet-poor layers on a cm scale. It shows a mineral assemblage of garnet + biotite + quartz + plagioclase + chlorite

+ muscovite, with variation in the amount of garnet in the two subsamples due to heterogeneous bulk rock composition with respect to MnO. Alteration of the muscovite and partial alteration of biotite and garnet rims to chlorite is interpreted to have occurred during cooling. Phase equilibrium modeling yields P-T estimates of 440 - 560°C and 2500 - 7000 bar for the garnet-rich subsample and 450 - 560°C and <7000 bar for the garnet-poor subsample. Despite the differences in MnO content and garnet abundance, the two P-T estimates overlap. This may confirm that the observed differences in effective bulk rock composition between the two subsamples are primary and not a result of late fluid modification to the bulk rock composition. Two garnet isopleth intersections for the garnet-rich subsample yield P-T estimates of 540 - 570°C and 4400 - 6000 bar and 550 - 560°C and 4000 - 5400 bar. While the origin of the differences in the zoning patterns in these two grains is unknown, the two intersections yield nearly the same P-T estimate. An isopleth intersection for the garnet-poor subsample gives a P-T estimate of 550 - 575°C and 2500 - 4000 bar. The calculated garnet isopleths for this sample all intersect 50 - 100°C above the garnet-in reaction, due to diffusional relaxation of garnet zoning and non-central sectioning. An average isopleth intersection for the three garnet crystals from 14PBA-99A gives a P-T estimate of 550 - 560°C at 4000 bar.

As no structural discontinuities were observed between the lower Montresor group samples, they are interpreted to have experienced the same metamorphic history. Given this, an estimate of the metamorphic conditions experienced by the lower Montresor belt during regional metamorphism associated with the Trans-Hudson orogeny may be given by the overlap of the stable assemblage fields for all studied samples. The combination of data from all lower Montresor group samples is shown in figure 5.6.1-A.

It can be seen that the mineral assemblage fields for the garnet bearing samples 14PBA-94A and 14PBA-99A do not overlap with those of 12PBA-27A and the non-garnet bearing samples. This may be due to the effects of chemical fractionation during garnet growth, which is not accounted for in the phase diagrams for 14PBA-94A and 14PBA-99A. The overlap between the assemblage fields of 12PBA-27A and the non-garnet bearing samples yields a P-T estimate of 500 - 580°C and <4000 bar. A comparison of the isopleth intersections of all garnet-bearing lower Montresor samples is shown in figure 5.6.1-B. It is noted that the isopleth intersections for 14PBA-94A and 14PBA-99A cover a wider range of P-T space and yield higher P-T estimates further away from the garnet-in reaction than the intersections for 12PBA-27A. This may be due to 14PBA-94A and -99A being randomly oriented slices through the largest garnet observed in thin section, meaning the composition likely does not represent the garnet core. This highlights how central sections of the oldest garnet porphyroblast can yield better P-T estimates for the onset of garnet growth.

A single sample from the lower grade upper Montresor group containing a mineral assemblage of quartz + biotite + muscovite + plagioclase + alkali feldspar gives a P-T estimate of 355 - 455°C and <4200 bar. This is ca. 50 - 200°C lower than the T estimates for the lower Montresor group. The difference in P-T between the lower and upper Montresor group is attributed to differences in crustal level during metamorphism.

Figure 5.6.1: Comparison of observed mineral assemblage fields for all lower Montresor group samples (A), isopleth intersections of garnet-bearing samples (B), and observed mineral assemblage fields for 12PBA-27A before and after garnet growth, showing the effects of chemical fractionation during garnet growth and the model parameters of each scenario, on the location of the observed mineral assemblage fields in P-T space (C).

5.7 Pressure-Temperature-Time Path

Sample 12PBA-27A contains a mineral assemblage of quartz + plagioclase + garnet + andalusite + biotite + chlorite + ilmenite. The andalusite is fully pseudomorphed to muscovite, but andalusite is still considered part of the equilibrium assemblage at peak metamorphic conditions. Muscovite in the pseudomorphs and in the matrix displays random orientations and is interpreted to have grown under static conditions during cooling. Each of the three modeled scenarios yielded slight differences in the predicted peak P-T estimate. Scenario 1, with no modifications to the thermodynamic database or to the bulk rock composition, gives a peak P-T estimate of 520 - 550°C and 1000 - 2500 bar. When staurolite was removed from the thermodynamic database, the predicted peak P-T is 520 - 545°C and 1000 – 3800 bar. The main outcome of removing staurolite is that the stable assemblage field becomes stable at higher P, rising from 2500 to 3800 bar. This change allows for garnet to grow along the modeled P-T path without the prediction of staurolite. When K was removed from the modeled bulk rock composition to account for the potential effects of K-metasomatism after garnet growth, a peak P-T of 520 - 580°C and 1000 - 4400 bar is calculated. It should be noted that all three of the peak P-T estimates calculated for 12PBA-27A overlap with the 500 - 580°C and <4000 bar estimate from the other lower Montresor group samples in this study (figure 5.6.1-A). The effect of chemical fractionation during garnet growth on the predicted P-T of the observed mineral assemblage fields is shown in figure 5.6.1-C.

Garnet crystallization was modeled for each of the three scenarios to determine a P-T-t path. As the modeled growth zoning is a direct representation of the chosen P-T path, any variations in path would lead to changes of the predicted zoning patterns. The

P-T paths presented in this study represent the best fit path that could be determined for each of the three scenarios. An average HR/CR for regional metamorphism has been estimated to be around 10°C/Ma (Wood and Walther, 1984). In this study, this rate, along with two slower rates, were used in modeling the P-T path. This was done in order to see the highest possible effects of intracrystalline diffusion in the sample.

The best-fit P-T path for scenario 1 is nearly isobaric, with a total P change from 2840 – 2955 bar during prograde metamorphism. However peak P and peak T do not correspond to the same point. A peak P of 2955 bar occurs at 550°C, followed by a slight decrease in P to 2932 bar at 570°C. At this point there is a sharp decrease in both P and T. Initial garnet growth occurs in the stability field of plagioclase + ilmenite + garnet + chlorite + muscovite + biotite from 526 – 526.6°C. This is followed by a period with no garnet growth up until 551.4°C. During this time the P-T path crosses a number of reactions, where chlorite and muscovite are removed from the assemblage and andalusite is added. This gap in garnet growth leads to the jump in grossular and pyrope content seen in the predicted profiles (figure 4.8.3-F, G). No jump in composition is not seen in the observed profiles, indicating that a break in garnet growth did not occur in the sample or that diffusion was efficient enough to relax the zoning so it is no longer seen. The rim of garnet is modeled to grow from 551.4 – 565.9°C in the stability field of plagioclase + ilmenite + garnet + biotite + staurolite + andalusite. Overall, there is a good fit between the predicted and observed rim compositions in all size classes, and grossular and pyrope show decent fits from core to rim in all models. All size classes show discrepancy between the predicted and observed spessartine and almandine profiles at the core, indicating that the model does not replicate the amount of diffusion that is observed. In

this model, staurolite is predicted with garnet for the entirety of the modeled P-T path. This is unrealistic as no staurolite is observed in the sample, and suggests that staurolite may be estimated to come into the assemblage at too low a P-T in the simulations.

To test the possibility of an overrepresentation of staurolite in scenario 1, a model was created with staurolite removed from the thermodynamic database preventing it from crystallizing in the modeled P-T space (scenario 2). The removal of staurolite has noticeable effects on the resulting P-T path, steepening the P gradient to an overall change during prograde metamorphism of 2840 – 3600 bar. The predicted P-T path shows approximately 7°C of heating after the peak P, moving from 550°C and 3600 bar to 556.8°C and 3574.89 bar. Garnet growth along the P-T path is intermittent, with two breaks in garnet growth from 526.9 - 531.7°C and from 547.3 - 549.2°C. These gaps are seen in the predicted garnet profiles as small jumps in composition at approximately 400 μm and 1100 μm . The garnet core grows in equilibrium with plagioclase + ilmenite + garnet + chlorite + muscovite + biotite + quartz. Following the first break in garnet growth chloritoid is added, followed by andalusite. This reaction of garnet growth followed by andalusite, or growth of garnet and andalusite at the same time, is supported by observations of andalusite surrounding garnet (figure 4.2.1-A). Garnet growth terminates in the observed stable assemblage field of plagioclase + ilmenite + garnet + chlorite + andalusite + quartz. Similar to size class 1, grossular shows a good fit in all size classes, and all endmembers show a good fit in rim composition between predicted and observed compositions. Core compositions in almandine, pyrope, and spessartine cannot be replicated in the model.

Consistent in both scenarios 1 and 2 is the lack of variability in the predicted garnet zoning as a result of changes to the heating/cooling rate. Almost no discernable variation is seen in the larger garnet size classes. Predictably, the smallest garnet size class shows the most variation, with almandine and spessartine showing approximately a 2 mol% variation in core content between HR/CR of 10°C/Ma and 0.2 or 0.5°C/Ma. However, it can be seen that the amount of diffusion in the model is not enough to replicate the core composition observed in the sample, even in the fastest diffusing garnet endmembers. This suggests that diffusion is very inefficient at the modeled crystal sizes and T. Florence and Spear (1991) predict that peak metamorphic T must be above 600°C in order for intracrystalline diffusion to have a significant effect on the chemical gradients of garnet, while peak T in these models reach 570°C and 556.8°C. This lack of diffusion is evident even at timescales that are unreasonable in duration for the Trans-Hudson orogeny. The slowest HR/CR used in these scenarios give total times of 170 Ma and 268 Ma, where the estimated total time for the Trans-Hudson is 120 Ma (Corrigan *et al.*, 2009). These garnet crystallization models prove unable to determine a plausible HR/CR for garnet growth. This result indicates that there must be another factor, unconsidered in these models that accounts for the discrepancy between the observed and predicted zoning patterns.

A third garnet crystallization model was run to test the effects of K-metasomatism after garnet growth (scenario 3). This model assumes a simple scenario where the only change to the effective bulk rock composition as a result of fluids is the addition of the amount of K needed to completely pseudomorph all andalusite with muscovite. The lower Montresor belt is cut by granodiorite, granite, and pegmatitic dykes (Percival *et al.*,

2015A, C), and these are proposed as the source of K-bearing fluids. Staurolite is prevented from growing in this model. The effect of lower K content on the phase equilibrium models is that the garnet-in reaction is moved slightly up T and the stable assemblage field becomes larger and remains in equilibrium to a T ca. 30°C higher than the other scenarios. Garnet is modeled to grow continuously from 538.4 – 543.8°C. Garnet nucleates in the stability field of plagioclase + ilmenite + garnet + chloritoid + chlorite + biotite + andalusite. At 541°C the chloritoid-out reaction is crossed and chloritoid leaves the stable mineral assemblage. Garnet growth is terminated in the observed equilibrium assemblage field. The resulting P-T path is nearly isobaric, with only a slight P increase during prograde metamorphism. Overall, this scenario has yielded the best result in matching the observed and predicted chemical profiles, especially with regard to almandine and grossular. Pyrope loses its match at the garnet rims and in smaller crystal sizes. The predicted spessartine profile provides a good match in the largest crystal size, but as the sizes decrease, the amount of mismatch in the garnet cores increases. As with the other scenarios, diffusion is found to be inefficient in this model as no discernible difference in the chemical zoning of any of the garnet endmembers, in any size class, is seen between any of the modeled heating/cooling rates from 0.2 - 10°C/Ma. Thus, a heating/cooling rate cannot be determined in this model.

The three garnet crystallization models for 12PBA-27A yielded three distinct P-T paths (figure 5.7.1). The first scenario gave an approximately isobaric ‘hairpin’ prograde P-T path at ca. 2900 bar from 525 – 570°C. When staurolite is removed from the assemblage, the prograde path steepens with P rising from 2800 – 3600 bar and a maximum T of 556.8°C is reached. In both of these scenarios garnet begins to grow at

Figure 5.7.1: Comparison of the best fit P-T paths for the three garnet crystallization models for sample 12PBA-27A. The lighter line represents the entire modeled P-T path and the darker sections represents the portions of the P-T paths where garnet grows.

approximately the same P-T conditions of 526°C and 2800 bar. With the modification to the K content in scenario 3, the total P-T path becomes noticeably shorter. This P-T path differs in that the onset of garnet growth occurs at a higher P-T of 538.4°C and >3100 bar. Garnet also grows along a much shorter P-T path to a peak T of 543.8°C and a peak P of 3150 bar. Scenario 1 shows that peak P-T is reached at the same point; while scenarios 2 and 3 show slight (<10°C) heating after peak P is reached. The peak P-T range predicted by the other lower Montresor group samples in this study is 500 - 580°C and <4000 bar; so the predicted peak P-T's in scenario 1 at 570°C and 2940, scenario 2 at 560°C and 2955 bar, and scenario 3 at 544°C and 3150 bar fall in this predicted range.

5.8 Low-Pressure High-Temperature Metamorphism and Regional Context

The P-T estimates obtained in this study from phase equilibria and garnet crystallization modeling of samples from the lower Montresor group indicate this area experienced peak metamorphic conditions of 500 - 580°C and <4000 bar. This is consistent with peak P estimates of 5000 bar for the Trans-Hudson orogeny in the northwestern Rae Province (Berman, 2010). Low pressure – high temperature (LP-HT) metamorphism has been defined as occurring at P less than the aluminosilicate triple point at ca. 4000 bar and at T between 500 - 750°C (De Yoreo *et al.*, 1991; Lux *et al.*, 1986; Scrimgeour *et al.*, 2001). These P estimates mean that total crustal thickness in LP-HT metamorphic terranes must not have exceeded 40 - 55 km (Sandiford and Powell, 1991), which is similar to what is estimated for the Trans-Hudson orogeny where peak crustal thickness has been estimated at 52-58 km (Corrigan *et al.*, 2009).

In collisional events such as the Trans-Hudson orogeny, the LP-HT metamorphic conditions cannot be solely a result of crustal thickening (White, 2005; Sandiford and Powell, 1991). This is based on models that have shown that if the amount of heat in LP-HT metamorphism is attributed to crustal thickening then the Moho T would exceed the liquidus at the base of the crust (Sandiford and Powell, 1991). As a result of this, LP-HT metamorphism in orogenic settings has been attributed to high heat flow at the base of the crust and advection of heat within the crust via plutonism and fluid circulation. Thus, orogenic LP-HT terranes are often associated with syn- to post-tectonic plutonic activity (De Yoreo *et al.*, 1991; Lux *et al.*, 1986; Sandiford and Powell, 1991; Stüwe *et al.*, 1993). Syn- to post-tectonic plutonism is observed in the Trans-Hudson orogeny, with the emplacement of the ca. 1845 – 1795 Ma Hudson suite as an example (Van Breemen *et*

al., 2005). Plutons associated with LP-HT metamorphism are sourced from the base of the crust, where crustal thickening combined with high heat flow causes melting of crustal material. The resulting plutons are commonly granitic in composition and contain no mantle components (White, 2005). It is estimated that melting at the base of the crust begins 10 – 40 Ma after the onset of crustal thickening (De Yoreo *et al.*, 1991). This may be demonstrated by the time difference between the onset of the Trans-Hudson orogeny at ca. 1.91 Ga (Berman, 2010) and the earliest age estimate of the associated Hudson suite at ca. 1845 Ma (Van Breemen *et al.*, 2005).

There is some debate as to whether plutons associated with LP-HT metamorphic events are a driving heat source for metamorphism or a reflection of high heat flow at the base of the crust (De Yoreo *et al.*, 1991). Monazite geochronology in this study indicates that peak metamorphism in the Montresor belt occurred at ca. 1837 Ma. This is synchronous with the emplacement ages of the Hudson granitoids at ca. 1845 – 1795 Ma (Van Breemen *et al.*, 2005). These ages demonstrate that magmatic activity occurred with peak metamorphic conditions, suggesting syn-metamorphic plutonism might have been a driving source of heat during regional metamorphism.

In addition, altered monazite provides evidence for a fluid mediated alteration event at 1792 ± 10.1 Ma. This age is also inferred to represent the age of emplacement for granitic and pegmatitic dykes cross-cutting lower Montresor belt and/or the timing of extension in the Montresor belt. It is probable that these dykes were emplaced with the younger end of the Hudson suite. Extension may have also been a factor, as extension may provide sufficient stress for crystals to break, providing pathways for fluids to travel (Bruhn *et al.*, 1994). LP-HT metamorphism can also be attributed to extensional regimes,

where crustal thinning moves hot mantle rocks closer to the surface (De Yoreo *et al.*, 1991). However, the difference in metamorphic grade between the upper and lower Montesor groups suggest that extension and movement along the detachment fault occurred some time after peak metamorphic conditions. Late stage folding within the central Rae associated with the Trans-Hudson is estimated to have occurred at ca. 1780 Ma (Sanborn-Barrie *et al.*, 2014). This folding event is believed to have formed the synclinal structure observed in the Montesor belt. This suggests that extension and movement along the detachment fault separating the upper and lower Montesor groups must have occurred between ca. 1837 Ma (peak metamorphic conditions) and ca. 1780 Ma (late-stage folding).

LP-HT metamorphism commonly displays clockwise, nearly isobaric P-T paths associated with rapid T increase and metamorphic crystallization (De Yoreo *et al.*, 1991). This is reflected in the models for sample 12PBA-27A, which yield relatively shallow, clockwise P-T paths. The P-T paths also show that peak P and peak T were reached at approximately the same point along the metamorphic P-T path (within 10°C). This is unlike typical regional metamorphic P-T paths, where the initial P increase is followed by decompression and significant increase in T before cooling. The increase in T after peak P is due to the generally slow thermal conductivity of the rocks (England and Thompson, 1984). Thus, while a heating/cooling rate could not be determined by garnet diffusion modeling in this study, the shape of the resulting P-T path suggests that metamorphism occurred with relatively rapid heating and constant P, as is characteristic of LP-HT terranes.

Geothermal gradients were calculated for sample 12PBA-27A at the P-T point of the garnet isopleth intersection for each of the three modeled scenarios. This sample was used for these calculations as its isopleths are not thought to be as modified by intracrystalline diffusion as the other garnet bearing samples. Gradients were calculated assuming an average crustal density of $2.7 - 3.1 \text{ g/cm}^3$, where 10 km depth is approximately equal to 3500 bar (Spear, 1993). Calculated geothermal gradients for each of the three scenarios are 54°C/km , 59.8°C/km , and 58.3°C/km (average = 57.4°C/km). These high geothermal gradients are typical of LP-HT metamorphic terranes, where geothermal gradients can range from $60\text{-}150^\circ\text{C/km}$ (De Yoreo *et al.*, 1991). The three calculated geothermal gradients for 12PBA-27A correspond to depths of 10 km, 8.85 km, and 9.3 km (average = 9.4 km) for metamorphism of the lower Montresor Belt. A late to post metamorphic low angle detachment fault with a vertical offset of several km, to account for the juxtaposition of amphibolite and greenschist facies rocks, separates the upper and lower Montresor belt. Assuming a linear geothermal gradient at depth during metamorphism of 57.4°C/km , the depth of metamorphism for two T points within the predicted peak P-T field (figure 4.7.1) were calculated. A T of 400°C corresponds to a depth of 7.0 km and 450°C at a depth of 7.8 km. These estimates suggest a vertical offset on the order of 1.6 – 2.4 km between the upper and lower Montresor belt after the metamorphic peak.

The monazite ages and peak P-T conditions determined in this study is similar to what was previously determined for metamorphism in the Montresor belt. Davis *et al.* (2014) report in-situ U-Th-Pb monazite ages of 1861 ± 7 and 1844 ± 6 Ma. These ages are within the range of ca. 1870 – 1837 Ma monazite ages in this study. Berman *et al.*

(2015) predicted peak P-T conditions for the lower Montresor group of 575°C and 3300 bar. This overlaps with the P-T estimate obtained in this study from the overlap of the assemblage fields of 12PBA-27A and the non-garnet bearing samples of 500 - 580°C and <4000 bar. The peak P-T estimate obtained from the best fit P-T path from the garnet crystallization modeling (544°C, 3092 bar) is slightly lower in both P and T than the estimate by Berman *et al.* (2015).

The P-T-t results from this study for the Montresor belt are also similar to the metamorphic conditions predicted for the Trans-Hudson orogeny across the Rae Province. The Committee Bay group (ca. 200 km east) shows greenschist to amphibolite facies metamorphism occurring at 1.86 – 1.82 Ga (Sanborn-Barrie *et al.*, 2014). Similarly to the lower Montresor group, the Woodburn Lake group (ca. 200 km south) saw peak metamorphic conditions of 540 – 560°C at ca. 1834 ± 5 Ma (Pehrsson *et al.*, 2013). These P-T-t conditions have been attributed to the Snowbird phase of the Trans-Hudson orogeny and the resulting collision of the Rae, Hearne, and Meta-Incognita microcontinent at ca. 1870 Ma which drove crustal thickening (Berman *et al.*, 2010; Sanborn-Barrie *et al.*, 2014).

5.9 Potential for Polyphase Metamorphism

In HT-LP metamorphic terranes it can often be difficult to discern the number of metamorphic events, due to the associated emplacement of syn- to post- tectonic plutons. The emplacement of plutons and the resulting metamorphism may be episodic in nature (De Yoreo *et al.*, 1991; Stüwe *et al.*, 1993). As the lower Montresor belt contains crosscutting granodiorite, granite, and pegmatite dykes (Percival *et al.*, 2015A, C), it is

thought that these dykes had the potential to cause episodic contact metamorphism during their emplacement. The emplacement of these dykes in the lower Montresor group may be dated by altered monazite that indicate a fluid-mediated alteration event ca. 45 Ma after peak P-T conditions. Thus, it possible that plutonism occurred after garnet growth.

Garnet crystallization modeling of sample 12PBA-27A showed that it is possible to determine a P-T path and predict the chemical zoning in the largest garnet size class. However it is consistent across all three modeled scenarios that the core contents of almandine and spessartine, the fastest diffusing garnet endmembers, cannot be predicted in the smaller garnet crystals. As the observed diffusional relaxation cannot be replicated in the models by increasing time, an increase in peak T may have been a contributing factor. Modeling used the same P-T path determined for garnet growth with the addition of a secondary thermal pulse, to replicate the effects of pluton emplacement and coincident contact metamorphism after garnet growth.

This study models the secondary thermal pulse at 1000°C/Ma, 100°C/Ma, and 10°C/Ma, with the fastest HR/CR being the most realistic of contact metamorphism (Wood and Walther, 1984). The slower HR/CR's aim to replicate the effect of multiple thermal pulses, rather than a single prolonged event. Garnet growth is modeled at 10°C/Ma. The rate chosen for garnet growth does not have a significant impact on the results of the model, as variation in the HR/CR during growth has been shown to have a negligible effect on the predicted zoning patterns. As there is no evidence of melt seen in any of the samples, any thermal pulse must have occurred at a T below the melting curve. For 12PBA-27A melting is estimated to begin at 675 - 725°C. In order to see the greatest effects of a secondary thermal pulse, heating was modeled to a peak T of 675°C. As

diffusion in garnet becomes efficient at T above 600°C (Florence and Spear, 1991), thus a thermal pulse above this T may allow for the garnet to become open to diffusion. In order to prevent garnet from growing for a second time, the thermal peak was modeled to take place after decompression at P below the garnet-in curve. It was not possible to model a thermal pulse below the garnet-in reaction when K-metasomatism was considered.

Garnet growth combined with secondary heating at 1000°C/Ma, 100°C/Ma, and 10°C/Ma gave total times of 5.713 Ma, 8.818 Ma, and 39.868 Ma for scenario 1 and 8.85 Ma, 12 Ma, and 43.5 Ma for scenario 2. These timescales are within the estimated 120 Ma duration of the Trans-Hudson orogeny (Corrigan *et al.*, 2009). Both of the two scenarios modeled with this pulse show similar modifications to the predicted garnet zoning patterns. As expected, the effects of a thermal pulse are seen most strongly in the smaller garnet crystal sizes, with the slowest modeled heating/cooling rate of 10°C causing the predicted almandine and spessartine profiles to become nearly horizontal. The slow rate also has a small effect on the predicted profile of the larger grains, with the main effect of smoothing the profiles rather than changing the predicted core composition. At the fast heating/cooling rates typical of a single thermal pulse, almost no variation is seen from the profile predicted without this pulse. An exception to this is in the smallest crystal size class, where slight relaxation of the predicted garnet profiles is observed.

Petrographic study of sample 12PBA-27A shows no textural or chemical evidence for a second generation of garnet or other mineral phases during a contact metamorphic event. The peak P-T point for the modeled thermal pulse ends in the stability field of plagioclase + ilmenite + biotite + cordierite + sanidine. No cordierite or sanidine is

observed in the sample. This does not support the theory of a contact metamorphic event. It may be possible that heating took place too quickly for new mineral growth to occur, but this is an untestable hypothesis. As well, the effects of plutonism may have been different across the lower Montresor belt, as a result of variation in T based on the proximity to the emplaced dykes as well as the number of thermal pulses experienced. The model results indicate that a thermal pulse does have the potential to increase the amount of diffusional relaxation seen in garnet. However based on the slow HR/CR's needed to predict significant modification to the predicted zoning, coupled with the lack of new mineral growth from a secondary event seen in the sample, it is thought that the likelihood of such a thermal pulse being a significant contributor to the observed garnet zoning patterns is slim.

5.10 Limitations in Thermodynamic Modeling

In order to evaluate the applicability of the results obtained in this study through phase equilibrium and garnet crystallization modeling, it is important to discuss possible limitations. THERIA_G predicts the chemical zoning for grossular, almandine, and spessartine well for each of the modeled scenarios for 12PBA-27A, with the exception of the amount of diffusional relaxation seen in the core. In scenario 1 the pyrope zoning is also well represented. However in scenarios 2 and 3, the model fails to accurately predict the pyrope compositions. This is more evident in the smaller grains, where the predicted pyrope profiles fall noticeably below the predicted profile. Some of the discrepancy seen in the predicted pyrope profiles may be due to the nature of the pyrope isopleths that display a wide spacing across the P-T range considered, compared to the other garnet

endmembers. The wide spacing means that pyrope is the most effected by any errors in the model. These errors may be a result of a number of factors, including uncertainty in the thermodynamic data and the bulk rock composition.

A theoretical CSD was used for garnet crystallization modeling in order to best replicate the observed crystal sizes and chemical gradients. When the observed CSD was used for the model, the predicted grain sizes were significantly smaller and had steeper chemical gradients than observed. This is likely due to the effects of abundant inclusions and embayments in the garnet, the volume of which are not accounted for by THERIA_G. However, a predicted radius 50 – 100 μm larger than the observed is predicted by THERIA_G across all size classes, indicating that the theoretical CSD used in the simulations is not a perfect representation of the sample. THERIA_G models garnet growth by the nucleation of distinct groups of garnet based on their size class as defined by the input CSD (Gaidies *et al.*, 2008A). Once the garnet-in curve is crossed the first generation of garnet is nucleated and grows until the size of the bin is reached, at which point the second generation of garnet is nucleated. Growth of every garnet, regardless of size, grows at the same radial rate. This means that if diffusion is not considered, the predicted size and compositional zoning of each garnet size class is simply a reflection of where that garnet nucleated along the P-T path. Changing the CSD and the relative abundance of garnet in each size class may impact where each generation of garnet nucleates along the P-T path, and consequently the predicted core composition and crystal size (Gaidies *et al.*, 2008A). If the later generations of garnet are predicted to nucleate too early along the P-T path, this may explain why the core chemistry of the smaller garnets cannot be predicted in the simulations.

Perhaps the main discrepancy seen in the garnet crystallization modeling is the prediction of staurolite in the model that is not seen in the sample. The results suggest that staurolite may be over represented and predicted to come into the model at too low a P and/or T. While the effects of an over representation of staurolite can be mitigated by removing it from the thermodynamic database and preventing its growth in P-T space, the prediction of staurolite suggests a problem with one or more of the model parameters. The possibility exists that staurolite stability may be overestimated within the thermodynamic dataset. Staurolite is a complex mineral, and experimental data and/or solution models may not be an adequate representation. It remains that all thermodynamic data is a simplification of the natural systems, as not all phases and compositions are present in the datasets and some systems may be poorly defined (de Capitani and Petrakakis, 2010; Worley and Powell, 2000). The presence of staurolite may also be due to the bulk rock composition used in the model not being representative of the natural system. This could be due to an unconsidered change to the effective bulk rock chemistry due to fluids, or errors stemming from sampling bias in the bulk rock chemical analysis. Other studies have also found staurolite to be problematic in determining reliable P-T estimates (i.e. Pattison *et al.*, 1999; Pigage and Greenwood, 1982).

This study attempts to model the effects of bulk rock compositional changes due to late fluid infiltration. The model presents a simple scenario of chemical modification where the only change with fluids is the addition of K. This is thought to be a good representation of the system based on chemical analysis of the sericite yielding 92 - 95% muscovite. However, it remains possible that other chemical changes also occurred during fluid infiltration. The model also estimates the amount of K added to the rock to

be enough to completely replace the volume of andalusite by sericite. The true change to the K content of the rock is unknown, as some of the K may have been sourced from the breakdown of minerals already present in the rock. Any unconsidered or over represented chemical changes to the bulk rock composition in this model have the potential to affect the phase equilibria calculations and affect the location of stable assemblage fields in P-T space.

The addition of fluids has also been shown to increase the rate of metamorphic reactions by providing a mechanism for mass-transfer reactions, which allows for chemical components to move through the rock significantly faster than by solid-state diffusion (Jamtveit and Austrheim, 2010; Putnis and Austrheim, 2010). The effects of this can be seen in the compositional garnet maps and profiles for sample 12PBA-27A where there is clear modification of the almandine, pyrope, and grossular growth zoning along cracks in the garnet. This is not seen in the spessartine profile, but as spessartine is the fastest diffusing garnet endmember, it is thought that diffusion may be efficient enough for homogenization across the volume of the grain. This implies that the amount of diffusional relaxation seen in the observed garnet profiles is a result of two mechanisms; solid-state intracrystalline diffusion and fluid-assisted diffusion. THERIA_G only considers the effects of solid-state diffusion on the garnet endmembers as a function of crystal size, T, and time (Gaidies *et al.*, 2008A). This is a potential explanation as to why the amount of diffusion observed in the sample cannot be replicated in the model, even for very long timescales. It may also be possible that the diffusion along cracks is a result of exchange between garnet $\pm$ biotite $\pm$ chlorite $\pm$ fluids, and there was no place for Mn in the biotite and chlorite forming in the cracks, so no diffusion took place.

Chemical and textural analysis of garnet bearing samples from the lower Montresor group indicate that these rocks may have a very small equilibrium volume and may not be chemically equilibrated even over volumes as small as 10 cm³. This heterogeneity is shown most strongly in MnO concentrations, where two analyses on 12PBA-27A yield 0.05 and 0.11 wt% and two analyses on 14PBA-99A yield 0.07 and 0.17 wt%. A noticeable trend in the studied samples is a higher volume% of garnet correlating with higher bulk MnO values, suggesting that bulk MnO concentration affected garnet nucleation and growth. Due to the variation in MnO concentrations across a small rock volume it is difficult to determine an effective bulk rock composition that is representative of the modeled sample. Variations in bulk rock composition affect phase equilibria models by shifting the location of stable assemblage fields in P-T space, thus affecting P-T estimates (Palin *et al.*, 2015). In particular, MnO concentration is important in thermodynamic modeling as MnO stabilizes garnet and as a result strongly affects the T at which garnet is predicted to come into the stable mineral assemblage. Increasing the MnO concentration causes garnet to crystallize at lower T (Symmes and Ferry, 1992). This has a noticeable effect in garnet crystallization modeling as spessartine isopleths are closely spaced parallel to the garnet-in curve. Thus moving the garnet-in reaction slightly up or down T would have a significant effect on the predicted spessartine core content. This has important implications when garnet crystallization modeling is used to determine a rate of metamorphism by modeling diffusional relaxation. Spessartine is the most sensitive to diffusion and is used as the primary indicator of metamorphic rate, so any variation to the initial core composition would directly impact this result.

The modeled P-T paths for each of the three scenarios show variations in the shape, peak P, and peak T. This shows how much of an effect variations in the composition and thermodynamic data can have on the model outputs. For example, by removing staurolite from the database, the shape of the P-T path changes from nearly isobaric to one with increasing P, and gives a difference in peak P from 2955 bar to 3600 bar at similar T. Despite the variation in P-T paths, the peak P-T estimates are thought to be good representations for 12PBA-27A as they fall into the same P-T range predicted for the other lower Montresor group samples, including those interpreted to be unaltered. The consistency in the P-T data between phase equilibrium and garnet crystallization modeling across different samples suggests that the garnet crystallization modeling results were able to somewhat successfully replicate the P-T conditions regardless of potential uncertainty in bulk rock compositions and staurolite thermodynamic data.

Chapter 6: Conclusions

The Montresor belt was deposited between 2.19 – 1.92 Ga (Percival *et al.*, 2015A) and subsequently metamorphosed to amphibolite facies during the Trans-Hudson orogeny. The lower Montresor belt achieved peak metamorphic P-T conditions of 500 - 580°C and <4000 bar, shown by mineral assemblages of quartz, biotite, muscovite, chlorite, garnet, and andalusite. In some rocks, andalusite porphyroblasts were completely pseudomorphed by sericite during cooling. In-situ monazite geochronology dates peak metamorphism in the lower Montresor belt to ca. 1837 ± 8.6 Ma. A single sample from the upper Montresor belt gives a peak P-T estimate of 355 - 455°C and 1000 - 4200 bar at 1847 ± 15 Ma (Percival *et al.*, 2015A). The differences in P-T estimates between the upper and lower portions of the Montresor belt suggest a vertical offset of ca. 1.6 - 2.4 km after the metamorphic peak.

Abundant evidence for fluid infiltration is observed in the lower Montresor belt rocks, including sericite pseudomorphs after andalusite, mechanical fracturing of garnet crystals, diffusional modification of garnet composition within ca. 20 μm of fractures and inclusions in garnet, and alteration of monazite. The presence of biotite and chlorite within garnet fractures suggests that fluid infiltration occurred at greenschist facies after the metamorphic peak. Altered monazite domains with depleted U-Th-Pb provide evidence for a fluid-mediated alteration event at ca. 1792 ± 10.1 Ma. This age is also thought to reflect the emplacement of dykes within the lower Montresor group, as well as regional extension and displacement along the detachment fault separating the upper and lower Montresor groups. Late folding created the observed synclinal structure.

Garnet compositional profiles show zoning patterns typical of prograde growth with increasing almandine and pyrope and decreasing grossular and spessartine from core to rim. Statistical analysis of the distribution of garnet in 12PBA-27A suggests a clustered distribution and growth under interface-controlled conditions, with clustering attributed to heterogeneity in MnO in the original sedimentary layering. Garnet crystallization modeling of a garnet population from 12PBA-27A was done in an attempt to constrain a metamorphic P-T-t path. Scenario 1 predicted garnet growth from 526 – 565.9°C and 2840 – 2930 bar. However, staurolite was predicted to occur at peak conditions, and is not present in the sample suggesting it may be overestimated in the simulation. To correct for this, staurolite was removed from the thermodynamic database and is prevented from growing in P-T space and garnet is predicted to grow from 526 – 556.7°C and 2840 – 3575 bar. When 2.5 mol K was removed from the modeled bulk rock composition to account for the effect of a modification to the bulk rock composition by post-metamorphic fluids, the garnet-in reaction moves up T and garnet is predicted to grow over a smaller P-T range from 538.5 – 543.8°C and 3140 – 3092 bar, giving the best fit between the observed and predicted chemical zoning of garnet in the larger garnet size classes. The simulations yielded clockwise, nearly isobaric P-T paths with little to no heating occurring after peak P. Differences in the predicted P-T paths for each of the models shown in this study highlight the effects of small variations in bulk rock composition and thermodynamic data on the resulting P-T-t estimates. Garnet crystallization modeling is unable to predict a rate of metamorphism, as the amount of diffusion in the sample cannot be replicated in the simulations. This is due to the use of a theoretical CSD affecting where each garnet size class nucleates along the P-T path, and

increased diffusion due to the presence of fluids that is not accounted for in the simulation.

A geothermal gradient of 57.4°C/km was calculated for the lower Montessor group, and is interpreted to be due to advection of heat within the crust via plutonism and the emplacement of the Hudson suite during the Trans-Hudson orogeny. Garnet diffusion models suggest that the effects of any late contact metamorphism associated with the emplacement of plutons is unlikely to have had a major effect on the garnet zoning. This hypothesis could be better constrained by obtaining crystallization ages on the pegmatitic dykes to strengthen the pegmatite-metamorphism-fluids link.

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Appendix A.1: Mineral abbreviations (after Whitney and Evans, 2004)

Afs	Alkali Feldspar
Alm	Almandine
Amp	Amphibole
And	Andalusite
Ath	Anthophyllite
Bt	Biotite
Chl	Chlorite
Cld	Chloritoid
Cam	Clinoamphibole
Crd	Cordierite
Czo	Clinoziosite
Ep	Epidote
Fsp	Feldspar
Grt	Garnet
Grs	Grossular
Ilm	Ilmenite
Kfs	Potassium Feldspar
Ky	Kyanite
Mc	Microcline
Mnz	Monazite
Ms	Muscovite
Mrg	Margarite
Oam	Orthoamphibole
Ph	Phengite
Pl	Plagioclase
Pg	Paragonite
Prp	Pyrope
Qz	Quartz
Rt	Rutile
Sa	Sanidine
Sil	Sillimanite
Spn	Sphene
Sps	Spessartine
St	Staurolite
Tr	Tremolite
Zo	Zoisite
Zrn	Zircon

Appendix A.2: Trace Element Geochemistry and EMPA Mineral Chemistry

Table A.2.1: Bulk-Rock Trace element geochemistry for selected samples.

Sample	Sc	Be	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr
12PBA-27A	12.0	2.0	92.0	110.0	12.0	40.0	60.0	80.0	21.0	2.1	<5.0	173.0	90.0	13.6	165.0
14PBA-67A	18.0	4.0	122.0	150.0	16.0	70.0	<10.0	70.0	27.0	2.0	34.0	196.0	116.0	15.4	112.0
14PBA-85A	23.0	3.0	157.0	190.0	20.0	90.0	30.0	80.0	32.0	2.2	46.0	202.0	56.0	19.8	122.0
14PBA-97A	25.0	6.0	169.0	210.0	17.0	70.0	20.0	110.0	37.0	2.3	19.0	269.0	191.0	24.1	192.0
14PBA-100	15.0	2.0	95.0	150.0	17.0	60.0	<10.0	90.0	32.0	1.8	41.0	243.0	22.0	12.1	223.0

Sample	Nb	Mo	Ag	In	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd
12PBA-27A	7.3	2.0	0.6	<0.1	3.0	<0.2	18.3	390.0	28.2	53.4	5.6	18.9	3.3	0.9	2.5
14PBA-67A	9.1	3.0	<0.5	<0.1	4.0	0.7	16.7	790.0	54.9	108.0	11.6	40.9	6.7	1.5	4.6
14PBA-85A	10.1	3.0	<0.5	<0.1	4.0	0.8	11.8	727.0	47.9	94.7	10.6	39.3	6.7	1.4	5.0
14PBA-97A	12.0	4.0	0.6	<0.1	7.0	0.6	22.7	934.0	41.7	86.6	9.9	37.2	7.0	1.2	5.5
14PBA-100	10.4	9.0	0.6	<0.1	8.0	0.5	10.7	816.0	28.0	59.2	6.8	25.5	4.5	0.7	3.3

Sample	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U
12PBA-27A	0.4	2.5	0.5	1.5	0.2	1.5	0.2	4.2	0.7	1.8	1.1	22.0	0.2	9.7	2.4
14PBA-67A	0.6	3.4	0.6	1.7	0.2	1.6	0.2	2.8	1.1	5.2	1.0	19.0	0.6	13.2	3.2
14PBA-85A	0.7	4.1	0.8	2.2	0.3	2.2	0.3	3.2	1.2	5.9	1.0	16.0	0.5	17.1	3.7
14PBA-97A	0.8	4.6	0.9	2.6	0.4	2.5	0.4	4.8	1.4	3.7	1.6	22.0	0.4	19.0	5.6
14PBA-100	0.5	2.5	0.5	1.5	0.2	1.7	0.3	5.5	1.4	9.9	1.3	23.0	0.6	18.4	6.1

Table A.2.2: Example calculation of garnet chemical formula based on 24 oxygen.

Oxide	Anlalysis (wt%)	Molecular weight of oxide	Molecular Proportion of Oxides	Molecular Proportion of oxygen	Number of anions	Number of cations	Endmember
SiO2	36.63	60.08	0.61	1.22	11.94	5.97	
Al2O3	20.85	101.96	0.20	0.61	6.01	4.00	
TiO2	0.01	79.87	0.00	0.00	0.00	0.00	
FeO	35.26	71.84	0.49	0.49	4.81	4.81	0.80
MnO	4.35	70.94	0.06	0.06	0.60	0.60	0.10
MgO	1.21	40.30	0.03	0.03	0.29	0.29	0.05
CaO	1.96	56.08	0.03	0.03	0.34	0.34	0.06
Total	100.27		1.43			16.01	
Oxygen factor = 16.77				X site total = 6.04			
Oxygen Factor = (24/Molecular proportion of oxygen)							
X site total = Fe + Ca + Mg + Mn							

A.2.3: Representative mineral chemistry for 12PBA-27A.

Biotite						Chlorite				Plagioclase					White Mica				
C1	C2	C3	R1	R2		C1	C2			Spot	C1	C2	R1	R2	Spot	C1	P1	P2	
SiO2	33.30	33.43	33.43	31.57	33.88	SiO2	24.11	24.40		SiO2	58.39	59.17	58.77	58.86	SiO2	47.05	46.18	47.18	
Al2O3	19.57	19.58	19.41	18.58	19.62	Al2O3	21.96	22.51		Al2O3	26.93	27.32	27.11	27.06	Al2O3	36.58	36.83	36.31	
Cr2O3	0.05	0.04	0.05	0.04	0.05	Cr2O3	0.03	0.04		Cr2O3	0.00	0.00	0.00	0.00	Cr2O3	0.02	0.03	0.01	
TiO2	1.66	1.64	1.57	1.50	1.58	TiO2	0.08	0.24		TiO2	0.00	0.00	0.00	0.00	TiO2	0.34	0.19	0.11	
FeO	25.28	25.62	25.31	25.86	24.56	FeO	32.87	32.14		FeO	0.02	0.12	0.06	0.04	FeO	0.89	2.01	1.23	
MnO	0.07	0.07	0.02	0.05	0.01	MnO	0.12	0.13		CaO	8.75	8.67	8.68	8.60	MnO	0.00	0.01	0.01	
MgO	5.81	5.89	5.98	5.99	5.65	MgO	8.32	8.61		Na2O	6.69	6.65	6.72	6.58	MgO	0.33	0.51	0.38	
CaO	0.00	0.00	0.00	0.01	0.00	CaO	0.02	0.01		K2O	0.07	0.08	0.07	0.06	CaO	0.00	0.14	0.00	
Na2O	0.00	0.01	0.04	0.04	0.06	Na2O	0.00	0.00		BaO	0.00	0.00	0.00	0.00	Na2O	0.60	0.47	0.42	
K2O	8.85	8.54	8.40	7.72	8.96	K2O	0.04	0.44		Total	100.85	102.01	101.41	101.20	K2O	10.34	10.30	10.69	
BaO	0.10	0.12	0.13	0.04	0.07	BaO	0.03	0.02		Oxygen	8.00	8.00	8.00	8.00	BaO	0.36	0.18	0.12	
Cl	0.01	0.02	0.01	0.01	0.01	Total	87.59	88.54		Si	2.60	2.59	2.59	2.60	Total	96.53	96.83	96.47	
F	0.14	0.06	0.10	0.07	0.15	Oxygen	14.00	14.00		Al	1.41	1.41	1.41	1.41	Oxygen	11.00	11.00	11.00	
Total	94.84	95.04	94.45	91.47	94.58	Si	2.65	2.65		Cr	0.00	0.00	0.00	0.00	Si	3.09	3.03	3.10	
Total -O=F,Cl	94.69	94.96	94.34	91.38	94.43	Al	2.85	2.88		Ti	0.00	0.00	0.00	0.00	Al	2.83	2.85	2.81	
Oxygen	11.00	11.00	11.00	11.00	11.00	Cr	0.00	0.00		Fe3+	0.00	0.00	0.00	0.00	Cr	0.00	0.00	0.00	
Si	2.63	2.63	2.64	2.59	2.67	Ti	0.01	0.02		Fe2+	0.00	0.00	0.00	0.00	Ti	0.02	0.01	0.01	
Al	1.82	1.82	1.81	1.80	1.82	Fe3+	0.00	0.00		Ca	0.42	0.41	0.41	0.41	Fe3+	0.00	0.00	0.00	
Cr	0.00	0.00	0.00	0.00	0.00	Fe2+	3.03	2.91		Na	0.58	0.57	0.58	0.56	Fe2+	0.05	0.11	0.07	
Ti	0.10	0.10	0.10	0.10	0.10	Mn	0.01	0.01		K	0.01	0.01	0.01	0.01	Mn	0.00	0.00	0.00	
Fe3+	0.00	0.00	0.00	0.00	0.00	Mg	1.37	1.39		Ba	0.00	0.00	0.00	0.00	Mg	0.03	0.05	0.04	
Fe2+	1.67	1.69	1.67	1.78	1.62	Ca	0.00	0.00		Xan	0.42	0.41	0.41	0.42	Ca	0.00	0.01	0.00	
Mn	0.01	0.01	0.00	0.00	0.00	Na	0.00	0.00		Xalb	0.57	0.58	0.58	0.57	Na	0.08	0.06	0.05	
Mg	0.68	0.69	0.71	0.73	0.66	K	0.01	0.06		Xorth	0.01	0.01	0.01	0.01	K	0.87	0.86	0.90	
Ca	0.00	0.00	0.00	0.00	0.00	Fe/(Fe+Mg)	0.69	0.68							Ca/(Ca+Na+K)	0.00	0.01	0.00	
Na	0.00	0.00	0.00	0.01	0.01	Mg/(Fe+Mg)	0.31	0.32							Na/(Ca+Na+K)	0.08	0.06	0.05	
K	0.89	0.86	0.85	0.81	0.90										K/(Ca+Na+K)	0.92	0.92	0.95	
Fe/(Fe+Mg)	0.71	0.71	0.70	0.71	0.71														
Mg/(Fe+Mg)	0.29	0.29	0.30	0.29	0.29														

Spots labeled ‘C’ refer to analyses in the center of a grain while those labeled ‘R’ refer to analyses near the rim of grains. ‘P’ refers to the analyses of muscovite pseudomorphing andalusite, in order to differentiate from an analysis on matrix muscovite. An = Anorthite, Alb = Albite, Orth = Orthoclase. Representative core garnet analyses can be found in Table 4.6.2.

Appendix A.3: Monazite Trace Element Data

Table A.3.1: Monazite Trace Element Data. All values reported in wt%.

Sample	Spot	U	K	Th	Ca	S	P	Y	Sr	Si	Pb	La	Ce	Nd	Pr	Eu	Sm	Tb	Dy	Er	Gd	Tm	Yb	Ho	As	O	Total
2b	1	0.16	0.00	6.58	0.85	0.10	12.42	0.85	0.01	0.66	0.60	11.38	24.47	8.76	2.53	0.16	0.91	-0.04	0.29	-0.04	0.70	0.02	-0.04	-0.02	0.07	26.86	98.22
	2	0.23	0.00	7.14	0.89	0.02	12.84	0.85	0.00	0.43	0.69	11.36	25.00	8.83	2.54	0.21	0.90	-0.05	0.26	-0.03	0.62	0.00	0.01	0.06	0.16	27.29	100.22
	3	0.26	0.01	7.49	0.91	0.02	11.81	0.90	-0.01	0.45	0.72	11.87	25.93	9.30	2.71	0.24	1.04	-0.03	0.34	-0.02	0.74	0.05	0.05	0.11	0.33	26.60	101.83
19a	1	0.20	0.00	4.12	0.61	0.02	13.05	0.65	0.02	0.42	0.43	12.84	25.73	10.19	2.80	0.14	1.28	-0.07	0.25	-0.02	0.81	0.03	0.02	0.03	0.18	27.68	101.39
	2	0.16	0.00	4.51	0.64	0.02	12.57	0.49	0.01	1.24	0.46	12.49	24.81	9.56	2.58	0.11	1.08	-0.11	0.18	-0.06	0.64	0.03	-0.03	-0.02	0.00	27.47	98.81
	3	0.21	0.00	4.57	0.73	0.02	12.89	0.44	0.02	0.36	0.48	12.45	24.76	9.88	2.63	0.14	1.22	-0.10	0.17	-0.03	0.69	0.02	0.00	0.03	0.14	27.08	98.79
19b	4	0.14	0.01	3.80	0.64	0.04	11.96	0.55	0.02	2.62	0.37	11.58	23.49	9.27	2.45	0.09	1.10	-0.13	0.19	-0.09	0.64	-0.02	-0.09	-0.14	-0.03	27.68	96.13
	1	0.22	0.00	5.51	0.72	0.01	13.44	0.68	0.02	0.73	0.54	12.45	24.60	9.70	2.54	0.16	1.14	-0.09	0.27	-0.06	0.87	0.04	-0.01	0.03	0.10	28.33	101.89
	2	0.23	0.00	4.84	0.72	0.01	13.30	0.55	0.00	0.21	0.49	12.41	25.10	10.06	2.67	0.16	1.22	-0.09	0.20	-0.07	0.80	0.04	0.01	0.01	0.13	27.59	100.58
15-core	3	0.24	0.00	4.38	0.67	0.01	13.50	0.57	0.00	0.18	0.45	12.67	25.50	10.25	2.69	0.17	1.27	-0.08	0.20	-0.07	0.83	0.05	-0.01	0.02	0.09	27.89	101.44
	4	0.22	0.00	3.95	0.59	0.01	13.45	0.54	0.01	0.17	0.41	12.78	25.80	10.29	2.69	0.16	1.25	-0.09	0.20	-0.08	0.82	0.04	0.01	0.04	0.08	27.77	101.08
	5	0.18	0.00	4.67	0.65	0.01	13.17	0.47	0.02	0.41	0.46	13.53	26.37	9.52	2.63	0.14	0.95	-0.10	0.17	-0.06	0.57	0.03	-0.02	0.06	0.09	27.79	101.72
15-rim	1	0.41	0.01	4.41	0.73	0.01	13.28	0.68	0.01	0.13	0.52	13.08	25.11	9.57	2.57	0.16	1.39	0.04	0.30	0.02	0.90	0.00	-0.02	0.00	0.08	27.55	100.92
	2	0.39	0.01	5.23	0.82	0.01	13.34	0.80	0.01	0.17	0.58	12.54	24.52	9.60	2.58	0.16	1.45	0.04	0.35	0.04	0.94	0.02	-0.01	0.03	0.12	27.73	101.44
	3	0.41	0.01	5.49	0.85	0.01	13.25	0.80	0.01	0.18	0.61	12.81	25.26	9.91	2.70	0.18	1.52	0.05	0.37	0.04	0.98	0.02	-0.01	0.02	0.12	27.95	103.53
	4	0.27	0.01	3.76	0.60	0.01	13.41	0.72	0.02	0.13	0.40	13.02	25.80	9.93	2.63	0.16	1.43	0.03	0.30	0.01	0.92	0.01	-0.03	0.00	0.06	27.74	101.32
17-core	5	0.34	0.01	4.34	0.70	0.01	13.34	0.81	0.01	0.15	0.49	12.90	24.93	9.72	2.64	0.17	1.45	0.05	0.33	0.02	0.97	0.02	-0.03	0.01	0.12	27.69	101.19
	6	0.22	0.01	2.12	0.39	0.01	13.34	0.60	0.02	0.11	0.26	13.71	26.63	10.11	2.79	0.13	1.44	0.04	0.27	0.01	0.88	0.00	-0.05	-0.02	0.01	27.55	100.58
	1	0.35	0.03	4.41	0.77	0.01	13.21	0.62	0.01	0.14	0.49	12.47	24.64	9.74	2.58	0.14	1.42	0.02	0.30	0.02	0.99	0.04	0.02	0.04	0.13	27.37	99.93
	2	0.42	0.02	4.38	0.78	0.01	13.15	0.48	0.01	0.12	0.51	12.61	25.06	9.92	2.61	0.13	1.42	0.02	0.22	0.02	0.96	0.06	0.02	0.07	0.22	27.41	100.61
17-rim	3	0.43	0.03	4.34	0.78	0.01	13.19	0.43	0.01	0.14	0.50	12.73	24.79	9.73	2.64	0.13	1.45	0.02	0.24	0.04	0.95	0.02	0.02	0.02	0.05	27.31	99.97
	4	0.43	0.03	4.41	0.75	0.00	12.96	0.54	0.01	0.14	0.51	12.92	25.33	9.89	2.62	0.11	1.41	0.01	0.22	-0.01	0.90	0.01	0.00	0.00	-0.07	27.10	100.19
	1	0.27	0.00	3.78	0.62	0.01	13.28	0.24	-0.02	0.11	0.41	13.17	26.16	10.21	2.71	0.17	1.45	-0.01	0.16	0.01	0.80	-0.01	-0.03	-0.02	0.09	27.55	101.12
	2	0.29	0.00	6.18	0.88	0.01	13.15	0.23	0.02	0.23	0.63	12.44	24.74	9.72	2.60	0.15	1.38	0.00	0.15	0.04	0.78	0.01	0.00	0.05	0.15	27.54	101.36
17-core	3	0.24	0.00	3.19	0.52	0.01	13.29	0.21	0.00	0.11	0.35	13.50	26.74	10.29	2.77	0.16	1.44	-0.01	0.14	0.03	0.77	-0.01	-0.03	-0.01	0.04	27.56	101.29
	4	0.38	0.01	5.90	0.91	0.01	13.27	0.27	0.01	0.17	0.63	12.36	24.89	9.82	2.55	0.17	1.44	0.01	0.17	0.03	0.85	0.01	-0.02	0.01	0.14	27.65	101.63
	5	0.33	0.01	5.14	0.80	0.01	13.27	0.24	0.01	0.16	0.55	12.50	24.98	10.14	2.65	0.17	1.51	0.01	0.16	0.03	0.85	-0.01	-0.02	-0.02	0.08	27.57	101.13
	6	0.27	0.01	4.31	0.68	0.02	13.38	0.22	0.00	0.15	0.46	13.20	25.87	10.04	2.70	0.14	1.40	-0.01	0.15	0.02	0.77	-0.01	-0.03	-0.01	0.08	27.72	101.49
17-rim	1	0.32	0.01	4.86	0.83	0.00	13.23	0.59	0.01	0.65	0.53	12.44	24.81	9.86	2.57	0.16	1.42	0.01	0.19	-0.01	0.90	-0.01	-0.02	0.00	0.04	27.99	101.38
	2	0.35	0.01	4.82	0.81	0.01	13.22	0.48	0.01	0.16	0.53	12.55	24.98	9.89	2.64	0.14	1.43	0.00	0.18	-0.02	0.89	-0.01	-0.01	-0.03	0.10	27.48	100.63
	3	0.33	0.01	4.69	0.79	0.01	13.42	0.46	0.01	0.31	0.50	12.60	25.03	9.97	2.64	0.14	1.42	0.01	0.17	0.00	0.87	0.01	0.00	-0.01	0.11	27.90	101.39
	4	0.34	0.00	4.80	0.80	0.01	13.49	0.63	0.01	0.18	0.51	12.25	24.90	10.17	2.68	0.16	1.54	0.01	0.25	0.02	1.01	0.00	0.00	0.03	0.10	27.94	101.82
18-core	1	0.26	0.01	4.03	0.66	0.01	13.11	0.22	0.01	0.12	0.44	13.19	26.00	10.12	2.71	0.15	1.42	0.00	0.15	-0.01	0.80	0.01	-0.01	-0.01	0.06	27.33	100.75
	2	0.22	0.01	4.77	0.74	0.01	13.09	0.21	0.01	0.15	0.49	13.01	25.79	9.97	2.66	0.15	1.39	0.01	0.15	-0.01	0.74	0.02	0.00	-0.04	0.08	27.36	100.95
	3	0.22	0.01	4.86	0.75	0.01	13.08	0.22	0.00	0.15	0.49	12.98	25.73	9.92	2.71	0.14	1.36	0.00	0.15	0.01	0.76	0.00	-0.01	-0.02	0.10	27.37	101.00
	4	0.24	0.01	5.57	0.83	0.01	13.00	0.21	-0.01	0.18	0.56	12.69	25.42	9.82	2.66	0.14	1.40	0.01	0.15	0.02	0.77	0.03	-0.01	-0.01	0.15	27.35	101.19
22	5	0.32	0.01	4.95	0.79	0.01	13.08	0.24	0.00	0.13	0.53	12.72	25.35	9.95	2.72	0.15	1.45	0.01	0.16	0.00	0.83	0.01	0.00	-0.03	0.06	27.31	100.74
	6	0.30	0.01	4.51	0.75	0.01	13.01	0.25	0.00	0.13	0.49	12.74	25.72	10.09	2.69	0.15	1.46	0.01	0.18	0.01	0.79	0.02	0.01	-0.02	0.06	27.22	100.57
	1	0.44	0.02	5.09	0.94	0.01	13.42	0.46	0.02	0.12	0.59	12.47	24.99	9.89	2.66	0.14	1.45	0.00	0.21	0.01	0.86	0.02	-0.01	0.02	0.11	27.80	101.72
	2	0.30	0.02	5.71	0.91	0.01	13.32	0.27	0.02	0.17	0.59	12.38	24.84	9.96	2.61	0.16	1.45	0.01	0.15	0.01	0.86	0.01	-0.01	0.04	0.09	27.70	101.58
18-rim	3	0.52	0.03	4.89	0.91	0.01	13.24	0.76	0.02	0.10	0.59	12.46	24.89	9.94	2.65	0.13	1.42	0.02	0.29	0.04	0.92	0.04	0.00	0.08	0.09	27.62	101.64
	1	0.27	0.01	5.90	0.84	0.01	13.33	0.17	0.02	0.22	0.61	12.86	25.29	9.78	2.64	0.15	1.46	0.01	0.14	0.01	0.80	0.03	0.01	0.04	0.19	27.91	102.72
	2	0.28	0.02	5.31	0.80	0.01	13.42	0.17	0.03	0.18	0.55	12.95	25.49</														

Table A.3.2: Monazite Trace Element Data continued. All values reported in wt%.

Sample	Spot	U	K	Th	Ca	S	P	Y	Sr	Si	Pb	La	Ce	Nd	Pr	Eu	Sm	Tb	Dy	Er	Gd	Tm	Yb	Ho	As	O	Total
23b	1	0.31	0.01	0.93	0.21	0.01	13.29	0.23	0.02	0.05	0.18	14.30	28.15	10.67	2.89	0.17	1.42	0.01	0.13	0.01	0.73	0.03	-0.01	-0.05	0.01	27.50	101.15
	2	0.42	0.01	1.55	0.31	0.00	13.37	0.23	0.01	0.06	0.26	14.01	27.69	10.51	2.87	0.16	1.43	-0.01	0.13	0.00	0.75	0.02	-0.02	-0.04	0.01	27.61	101.34
	3	0.33	0.02	2.40	0.43	0.01	13.34	0.10	0.00	0.07	0.32	13.90	27.19	10.35	2.81	0.15	1.43	-0.01	0.08	0.00	0.60	0.01	-0.02	-0.01	0.03	27.55	101.06
	4	0.33	0.02	1.38	0.27	0.01	13.33	0.21	0.00	0.05	0.23	14.18	27.87	10.52	2.92	0.15	1.41	0.00	0.14	0.00	0.73	0.01	-0.01	-0.03	-0.01	27.55	101.26
	5	0.35	0.02	1.47	0.29	0.00	13.30	0.20	0.01	0.05	0.23	14.21	27.77	10.54	2.81	0.16	1.42	0.01	0.13	0.00	0.73	0.01	-0.03	-0.04	-0.01	27.50	101.13
23c	1	0.60	0.02	1.02	0.27	0.00	13.53	0.23	0.00	0.05	0.29	14.34	28.00	10.29	2.87	0.16	1.40	0.00	0.13	0.02	0.74	0.02	0.00	0.02	0.09	27.86	101.93
	2	0.77	0.02	1.31	0.32	0.01	13.50	0.23	-0.01	0.06	0.36	14.37	27.78	10.13	2.82	0.17	1.37	0.01	0.15	0.00	0.75	0.01	0.02	0.02	0.06	27.84	102.07
	3	0.85	0.02	1.06	0.30	0.01	13.55	0.24	0.01	0.05	0.37	14.54	28.15	10.21	2.82	0.17	1.39	0.00	0.16	0.02	0.74	0.02	0.01	0.03	0.06	27.98	102.73
	4	0.55	0.01	0.23	0.16	0.00	13.61	0.33	0.00	0.03	0.19	15.24	28.40	10.21	2.86	0.17	1.36	0.00	0.18	0.00	0.80	0.03	0.00	0.02	0.05	28.00	102.42
	5	0.22	0.01	1.20	0.23	0.01	13.64	0.20	0.00	0.04	0.17	14.36	28.48	10.55	2.93	0.16	1.38	0.00	0.12	0.00	0.70	0.03	0.00	0.03	0.09	28.06	102.58
f25a	6	0.22	0.04	1.03	0.21	0.01	13.64	0.19	-0.01	0.06	0.15	14.39	28.45	10.59	2.91	0.16	1.39	-0.01	0.13	-0.01	0.70	0.04	0.00	-0.02	0.05	28.03	102.33
	1	0.74	0.02	1.65	0.50	0.01	13.57	0.25	0.01	0.13	0.38	14.66	27.54	9.73	2.69	0.16	1.29	0.00	0.13	0.02	0.71	-0.02	-0.01	-0.04	0.04	28.01	102.16
	2	0.47	0.02	1.19	0.34	0.01	13.66	0.25	0.02	0.05	0.25	14.46	28.12	10.23	2.85	0.16	1.40	0.02	0.16	0.01	0.77	0.00	-0.01	-0.04	-0.02	28.04	102.39
	3	0.40	0.02	1.42	0.34	0.01	13.56	0.24	0.01	0.06	0.25	14.49	28.26	10.21	2.82	0.18	1.38	0.01	0.17	0.01	0.73	-0.02	-0.02	-0.03	0.00	27.96	102.45
	4	0.20	0.06	0.85	0.22	0.01	13.45	0.31	0.01	0.05	0.12	15.29	28.09	9.99	2.71	0.16	1.28	0.00	0.17	0.01	0.68	-0.02	-0.03	-0.03	-0.02	27.70	101.26
f25b	5	0.39	0.06	0.55	0.21	0.01	13.68	0.27	-0.01	0.05	0.16	15.36	28.45	9.91	2.81	0.13	1.25	0.01	0.16	0.01	0.69	-0.01	0.00	-0.05	-0.02	28.04	102.10
	6	0.44	0.03	0.84	0.29	0.03	13.60	0.30	0.02	0.06	0.21	14.99	28.07	10.10	2.77	0.20	1.37	0.01	0.18	-0.01	0.73	-0.01	-0.03	-0.04	-0.09	27.95	102.02
	1	0.78	0.03	1.26	0.37	0.01	13.55	0.32	0.01	0.06	0.36	14.49	27.67	9.98	2.78	0.17	1.33	0.01	0.19	0.01	0.72	0.02	0.01	0.02	0.08	27.92	102.13
	2	0.45	0.02	1.46	0.33	0.01	13.53	0.22	0.01	0.07	0.26	14.55	27.69	10.27	2.81	0.17	1.42	0.01	0.17	0.00	0.73	0.00	0.02	0.01	0.06	27.92	102.22
	3	0.40	0.04	1.90	0.37	0.01	13.57	0.23	0.02	0.06	0.29	14.40	27.59	10.32	2.85	0.14	1.40	-0.02	0.11	-0.01	0.68	0.01	0.00	0.06	0.09	28.00	102.48
f25c	4	0.23	0.03	1.15	0.23	0.01	13.49	0.21	0.00	0.05	0.17	14.63	28.13	10.40	2.87	0.16	1.39	0.01	0.14	0.00	0.73	0.01	0.02	0.03	0.01	27.81	101.90
	5	0.47	0.03	0.98	0.25	0.01	13.50	0.30	0.01	0.05	0.23	14.62	28.07	10.17	2.90	0.15	1.42	0.01	0.18	-0.01	0.75	-0.01	0.01	0.02	0.09	27.87	102.05
	6	0.50	0.03	0.71	0.23	0.01	13.61	0.43	0.01	0.04	0.21	14.64	28.19	10.33	2.87	0.17	1.42	0.02	0.23	0.00	0.76	-0.01	0.00	0.02	0.05	28.03	102.49
	1	0.19	0.05	1.43	0.27	0.01	13.66	0.15	0.00	0.08	0.18	14.86	28.27	10.32	2.84	0.17	1.40	-0.02	0.10	0.00	0.64	0.00	0.00	0.00	0.01	28.11	102.73
	2	0.62	0.05	1.95	0.41	0.01	13.72	0.28	-0.01	0.09	0.35	14.53	27.29	9.83	2.66	0.20	1.33	0.00	0.15	0.02	0.74	-0.01	0.00	0.00	0.05	28.15	102.42
f25d	3	0.81	0.05	2.12	0.51	0.01	13.65	0.29	0.00	0.10	0.43	14.58	27.03	9.75	2.72	0.18	1.33	0.02	0.17	0.03	0.70	0.00	0.00	-0.01	0.07	28.13	102.65
	4	0.59	0.06	1.75	0.41	0.01	13.65	0.23	0.00	0.07	0.32	14.53	27.49	10.08	2.73	0.19	1.36	-0.01	0.13	0.02	0.68	0.00	-0.01	0.01	0.06	28.06	102.37
	5	0.33	0.07	1.19	0.26	0.01	13.63	0.22	0.00	0.08	0.19	15.19	28.21	9.91	2.76	0.18	1.28	0.00	0.12	0.00	0.63	-0.02	-0.02	-0.04	0.00	28.01	102.16
	6	0.68	0.07	1.55	0.41	0.01	13.70	0.29	0.00	0.07	0.33	14.68	27.67	9.86	2.72	0.20	1.32	-0.01	0.15	0.02	0.73	-0.01	0.00	0.01	0.01	28.13	102.57

Appendix A.4: Energy-Dispersive (EDS) EPMA Garnet Elemental Distribution Maps for Additional Elements.

Figure A.4.1: EPMA element distribution maps for sample 12PBA-27A Garnet 1 (size class 1). (A) Al (B) K (C) Na (D) P (E) S (F) Ti (G) Zn (H) Zr.

Figure A.4.2: EPMA element distribution maps for sample 12PBA-27A Garnet 2 (size class 1). (A) Al (B) Cu (C) K (D) Na (E) P (F) S (G) Ti (H) Zn (I) Zr.

Figure A.4.3: EPMA element distribution maps for sample 12PBA-27A Garnet 4 (size class 7). (A) Al (B) Cu (C) K (D) Na (E) P (F) S (G) Ti (H) Zn (I) Zr.

Figure A.4.4: EPMA element distribution maps for sample 12PBA-27A Garnet 7 (size class 13). (A) Al (B) Cu (C) K (D) Na (E) P (F) S (G) Ti (H) Zn.

Figure A.4.5: EPMA element distribution maps for sample 14PBA-94A. (A) Al (B) Cu (C) K (D) Na (E) P (F) S (G) Ti (H) Zn (I) Zr.

Appendix A.5: THERIAK_DOMINO and THERIA_G Input Files

THERIN with observed chemistry

SI(60.85)AL(19.36)FE(8.63)MN(0.05)MG(3.49)CA(1.16)NA(1.54)K(4.50)TI(0.41)
H(60)O(?)

THERIN with modified K

SI(60.85)AL(19.36)FE(8.63)MN(0.05)MG(3.49)CA(1.16)NA(1.54)K(2.0)TI(0.41)
H(60)O(?)

THERIA_G DIF:

Kinetic parameters from Chakraborty and Ganguly (1992) at fO₂ defined by graphite buffer

5.1D-4	60569.0D0	6.0D0	MN: pre-exponential constant, activation energy, activation volume
6.4D-4	65824.0D0	5.6D0	FE: pre-exponential constant, activation energy, activation volume
1.1D-3	67997.0D0	5.3D0	MG: pre-exponential constant, activation energy, activation volume

THERIA_G CSD:

5	50.00	Thickness of successive garnet shells (Delta r_shell) [mue] and size of
0.1		radius class [mue]
0.11		no. of garnets in radius class 1 [grt/ccm] of the rock volume (add a line
0.15		for each radius class);
0.16		
0.17		
0.18		
0.20		
0.22		
0.25		
0.27		
0.29		
0.32		
0.40		
0.41		
0.39		
0.28		
0.2		
0.15		
0.1		

Solution Models:

AMPH1 – amphibole 1 – Dale *et al.* (2005)
ANAB – plagioclase - Newton *et al.* (1980)
ILM – Ilmenite - Holland and Powell (1998)
GARNET – garnet – Connolly (2005) see <http://perplex.ethz.ch>
CHTD – chloritoid – Holland and Powell (1998)
CHLR – chlorite – Gaidies *et al.* (2008A)
CLAMP – amphibole 2 - Holland and Powell (1998)
PHNG – <http://www.esc.cam.ac.uk/astaff/holland/ds5/muscovites/mu.html>
BIO - biotite – Holland and Powell (1998)
STAU – staurolite – Holland and Powell (1998)
CORD – cordierite – Holland and Powell (1998)

MELT – White *et al.* (2007)

Thermodynamic Database of Holland and Powell (1998):

****MINERAL DATA**** from Holland and Powell (1998+)

pyrope	SI(3)AL(2)MG(3)O(12)	py	3nh		
ST	0.0	-6284720.000	266.3000	11.3180	
C3	633.50000	0.0000000	-5196100.0	-4315.200	0.00
VHP	0.000043600	1737.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000260550		
almandine	SI(3)AL(2)FE(3)O(12)	alm	3nh		
ST	0.0	-5263520.000	340.0000	11.5110	
C3	677.30000	0.0000000	-3772700.0	-5044.000	0.00
VHP	0.000040300	1690.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000253500		
spessartine	SI(3)AL(2)MN(3)O(12)	spss	3nh		
ST	0.0	-5646400.000	367.0000	11.7920	
C3	584.60000	-0.0015930	-7516700.0	-2750.100	0.00
VHP	0.000046200	1790.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000268500		
grossular	SI(3)AL(2)CA(3)O(12)	gr	3nh		
ST	0.0	-6644150.000	255.0000	12.5350	
C3	626.00000	0.0000000	-5779200.0	-4002.900	0.00
VHP	0.000039300	1680.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000252000		
andalusite	SI(1)AL(2)O(5)	and	1nh		
ST	0.0	-2588800.000	92.7000	5.1530	
C3	277.30000	-0.0065880	-1914100.0	-2265.600	0.00
VHP	0.000041100	1334.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000200100		
kyanite	SI(1)AL(2)O(5)	ky	1nh		

ST	0.0	-2593110.000	83.5000	4.4140		
C3	279.40000	-0.0071240	-2055600.0	-2289.400	0.00	
VHP	0.000040400	1590.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000238500			
sillimanite	SI(1)AL(2)O(5)	sill	1nh			
ST	0.0	-2585680.000	95.5000	4.9860		
C3	280.20000	-0.0069000	-1375700.0	-2399.400	0.00	
VHP	0.000022100	1320.0	2200.0000	4.00	0.03500	
VH2	10.0000	4.0000	-0.000198000			
Mg-staurolite	SI(7.5)AL(18)MG(4)O(48)H(4)	mst	4nh			
ST	0.0	-25101490.000	910.0000	44.2600		
C3	2820.50000	-0.0593660	-13774000.0	-24126.000	0.00	
VHP	0.000012000	1200.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000180000			
Fe-staurolite	SI(7.5)AL(18)FE(4)O(48)H(4)	fst	4nh			
ST	0.0	-23753930.000	1010.0000	44.8800		
C3	2880.00000	-0.0565950	-10642000.0	-25373.000	0.00	
VHP	0.000012000	1200.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000180000			
Mn-staurolite	SI(7.5)AL(18)MN(4)O(48)H(4)	mnst	4nh			
ST	0.0	-24203880.000	1024.0000	45.4600		
C3	2873.30000	-0.0890640	-12688000.0	-24749.000	0.00	
VHP	0.000012000	1200.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000180000			
Mg-chloritoid	SI(1)AL(2)MG(1)O(7)H(2)	mctd	1nh			
ST	0.0	-3551420.000	140.0000	6.8750		
C3	464.40000	-0.0126540	-1147200.0	-4341.000	0.00	
VHP	0.000054200	1465.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000219750			
Fe-chloritoid	SI(1)AL(2)FE(1)O(7)H(2)	fectd	1nh			
ST	0.0	-3215380.000	155.0000	6.9800		
C3	484.60000	-0.0138080	-198900.0	-4762.200	0.00	
VHP	0.000054200	1465.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000219750			
Mn-chloritoid	SI(1)AL(2)MN(1)O(7)H(2)	mnctd	1nh			
ST	0.0	-3329280.000	166.0000	7.1750		
C3	464.40000	-0.0126540	-1147200.0	-4341.000	0.00	
VHP	0.000054200	1465.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000219750			
zoisite	SI(3)AL(3)CA(2)O(13)H(1)	zo	1nh			
ST	0.0	-6898610.000	297.0000	13.5750		
C3	595.70000	0.0622970	-5921300.0	-3394.700	0.00	
VHP	0.000067000	1120.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000168000			
clinozoisite	SI(3)AL(3)CA(2)O(13)H(1)	cz	1nh			
ST	0.0	-6898150.000	301.0000	13.6300		

C3	567.00000	0.0180630	-7034000.0	-2603.000	0.00
VHP	0.000046000	1120.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000168000		
epidote	SI(3)AL(2)FE(1)CA(2)O(13)H(1)			ep	2nh
ST	0.0	-6463210.000	328.0000	13.9100	
C3	544.60000	0.0247810	-11230000.0	-1192.100	0.00
VHP	0.000050500	1233.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000184950		
cordierite	SI(5)AL(4)MG(2)O(18)			crd	1nh
ST	0.0	-9163370.000	407.5000	23.3220	
C3	821.30000	0.0433390	-8211200.0	-5000.000	0.00
VHP	0.000007600	810.0	1800.0000	20.00	0.20000
VH2	10.0000	4.0000	-0.000121500		
Fe-cordierite	SI(5)AL(4)FE(2)O(18)			ferd	2nh
ST	0.0	-8436070.000	475.0000	23.7100	
C3	851.50000	0.0447240	-6645000.0	-5623.400	0.00
VHP	0.000007600	810.0	1800.0000	20.00	0.20000
VH2	10.0000	4.0000	-0.000121500		
Mn-cordierite	SI(5)AL(4)MN(2)O(18)			mncrd	1nh
ST	0.0	-8681180.000	475.0000	24.0270	
C3	847.70000	0.0284900	-7668200.0	-5311.400	0.00
VHP	0.000007600	810.0	1800.0000	20.00	0.20000
VH2	10.0000	4.0000	-0.000121500		
sphene	SI(1)TI(1)CA(1)O(5)			sph	1nh
ST	0.0	-2595550.000	131.2000	5.5650	
C3	233.70000	0.0040430	-2306500.0	-1207.600	0.00
VHP	0.000042000	1100.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000165000		
tremolite	SI(8)MG(5)CA(2)O(24)H(2)			tr	2nh
ST	0.0	-12310380.000	550.0000	27.2700	
C3	1260.20000	0.0038300	-11455000.0	-8237.600	0.00
VHP	0.000053400	762.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000114300		
ferroactinolite	SI(8)FE(5)CA(2)O(24)H(2)			fact	5nh
ST	0.0	-10511240.000	705.0000	28.2800	
C3	1290.00000	0.0299910	-8447500.0	-8947.000	0.00
VHP	0.000053400	760.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000114000		
tschermakite	SI(6)AL(4)MG(3)CA(2)O(24)H(2)			ts	2nh
ST	0.0	-12541200.000	545.0000	26.8000	
C3	1244.80000	0.0243480	-11965000.0	-8112.100	0.00
VHP	0.000053400	760.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000114000		
pargasite	SI(6)AL(3)MG(4)CA(2)NA(1)O(24)H(2)			parg	4nh
ST	0.0	-12720650.000	601.0000	27.1900	
C3	1280.20000	0.0229970	-12359500.0	-8065.800	0.00

VHP	0.000053400	912.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000136800		
glaucophane	SI(8)AL(2)MG(3)NA(2)O(24)H(2)	gl	2nh		
ST	0.0	-11969470.000	535.0000	26.0500	
C3	1717.50000	-0.1210700	7075000.0	-19272.000	0.00
VHP	0.000053000	883.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000132450		
riebeckite	SI(8)FE(5)NA(2)O(24)H(2)	rieb	2nh		
ST	0.0	-10035240.000	691.0000	27.4900	
C3	1746.90000	-0.1135720	9370300.0	-19468.700	0.00
VHP	0.000053000	890.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000133500		
anthophyllite	SI(8)MG(7)O(24)H(2)	anth	2nh		
ST	0.0	-12069200.000	536.0000	26.5400	
C3	1277.30000	0.0258250	-9704600.0	-9074.700	0.00
VHP	0.000050000	700.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000105000		
Fe-anthophyllite	SI(8)FE(7)O(24)H(2)	fanth	7nh		
ST	0.0	-9627230.000	725.0000	27.8700	
C3	1383.10000	0.0306690	-4224700.0	-11257.600	0.00
VHP	0.000050000	700.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000105000		
cummingtonite	SI(8)MG(7)O(24)H(2)	cumm	2nh		
ST	0.0	-12057480.000	540.0000	26.3300	
C3	1277.30000	0.0258250	-9704600.0	-9074.700	0.00
VHP	0.000050000	700.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000105000		
grunerite	SI(8)FE(7)O(24)H(2)	grun	7nh		
ST	0.0	-9613200.000	730.0000	27.8400	
C3	1383.10000	0.0306690	-4224700.0	-11257.600	0.00
VHP	0.000050000	648.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000097200		
gedrite	SI(6)AL(4)MG(5)O(24)H(2)	ged	5nh		
ST	0.0	-12319430.000	515.0000	25.8000	
C3	1307.70000	0.0236420	-9307400.0	-9799.000	0.00
VHP	0.000048000	770.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000115500		
muscovite	SI(3)AL(3)K(1)O(12)H(2)	mu	2nh		
ST	0.0	-5984180.000	292.0000	14.0830	
C3	756.40000	-0.0198400	-2170000.0	-6979.200	0.00
VHP	0.000059600	490.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000073500		
celadonite	SI(4)AL(1)MG(1)K(1)O(12)H(2)	cel	1nh		
ST	0.0	-5842420.000	290.0000	13.9570	
C3	741.20000	-0.0187480	-2368800.0	-6616.900	0.00
VHP	0.000059600	700.0	0.0000	0.00	0.00000

VH2	10.0000	4.0000	-0.000105000		
Fe-celadonite	SI(4)AL(1)FE(1)K(1)O(12)H(2)	fcel	1nh		
ST	0.0	-5477430.000	329.0000	14.0700	
C3	756.30000	-0.0191470	-1586100.0	-6928.700	0.00
VHP	0.000059600	700.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000105000		
paragonite	SI(3)AL(3)NA(1)O(12)H(2)	pa	+1nh		
ST	0.0	-5946340.000	276.0000	13.2110	
C3	803.00000	-0.0315800	217000.0	-8151.000	0.00
VHP	0.000077400	550.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000082500		
margarite	SI(2)AL(4)CA(1)O(12)H(2)	ma	1nh		
ST	0.0	-6241230.000	267.0000	12.9640	
C3	744.40000	-0.0168000	-2074400.0	-6783.200	0.00
VHP	0.000048700	1300.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000195000		
phlogopite	SI(3)AL(1)MG(3)K(1)O(12)H(2)	phl	2nh		
ST	0.0	-6219160.000	328.0000	14.9640	
C3	770.30000	-0.0369390	-2328900.0	-6531.600	0.00
VHP	0.000057900	513.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000076950		
annite	SI(3)AL(1)FE(3)K(1)O(12)H(2)	ann	3nh		
ST	0.0	-5151670.000	418.0000	15.4320	
C3	815.70000	-0.0348610	19800.0	-7466.700	0.00
VHP	0.000057900	513.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000076950		
Mn-biotite	SI(3)AL(1)MN(3)K(1)O(12)H(2)	mnbi	2nh		
ST	0.0	-5462840.000	433.0000	15.2640	
C3	809.90000	-0.0592130	-1514400.0	-6998.700	0.00
VHP	0.000057900	513.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000076950		
eastonite	SI(2)AL(3)MG(2)K(1)O(12)H(2)	east	2nh		
ST	0.0	-6338170.000	318.0000	14.7380	
C3	785.50000	-0.0380310	-2130300.0	-6893.700	0.00
VHP	0.000057900	513.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000076950		
Na-phlogopite	SI(3)AL(1)MG(3)NA(1)O(12)H(2)	naph	1nh		
ST	0.0	-6172820.000	318.0000	14.4500	
C3	773.50000	-0.0402290	-2597900.0	-6512.600	0.00
VHP	0.000057900	513.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000076950		
clinochlore	SI(3)AL(2)MG(5)O(18)H(8)	clin	2nh		
ST	0.0	-8912410.000	430.5000	21.0900	
C3	1161.80000	0.0101330	-7657300.0	-9690.900	0.00
VHP	0.000039800	870.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000130500		

amesite	SI(2)AL(4)MG(4)O(18)H(8)			ames	2nh	
ST	0.0	-9034440.000	410.0000	20.5200		
C3	1177.00000	0.0090410	-7458700.0	-10053.000	0.00	
VHP	0.000039800	870.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000130500			
daphnite	SI(3)AL(2)FE(5)O(18)H(8)			daph	3nh	
ST	0.0	-7134850.000	565.0000	21.3400		
C3	1237.40000	0.0135940	-3743000.0	-11250.000	0.00	
VHP	0.000039800	870.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000130500			
Mn-chlorite	SI(3)AL(2)MN(5)O(18)H(8)			mnchl	2nh	
ST	0.0	-7666530.000	595.0000	22.5900		
C3	1227.80000	-0.0269900	-6299800.0	-10469.400	0.00	
VHP	0.000039800	870.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000130500			
sudoite	SI(3)AL(4)MG(2)O(18)H(8)			sud	2nh	
ST	0.0	-8626160.000	404.0000	20.3000		
C3	1436.10000	-0.0487490	-2748500.0	-13764.000	0.00	
VHP	0.000039800	870.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000130500			
Fe-sudoite	SI(3)AL(4)FE(2)O(18)H(8)			fsud	2nh	
ST	0.0	-7903900.000	462.0000	20.4000		
C3	1466.30000	-0.0473650	-1182800.0	-14388.000	0.00	
VHP	0.000039800	870.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000130500			
pyrophyllite	SI(4)AL(2)O(12)H(2)			prl	2nh	
ST	0.0	-5640640.000	239.4000	12.8100		
C3	784.50000	-0.0429480	1251000.0	-8495.900	0.00	
VHP	0.000075000	525.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000078750			
talc	SI(4)MG(3)O(12)H(2)			ta	2nh	
ST	0.0	-5897100.000	260.0000	13.6250		
C3	622.20000	0.0000000	-6385500.0	-3916.300	0.00	
VHP	0.000037000	480.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000072000			
Fe-talc	SI(4)FE(3)O(12)H(2)			fta	2nh	
ST	0.0	-4802920.000	352.0000	14.2250		
C3	579.70000	0.0394940	-6459300.0	-3088.100	0.00	
VHP	0.000037000	480.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000072000			
tschermak-talc	SI(3)AL(2)MG(2)O(12)H(2)			tats	2nh	
ST	0.0	-5987990.000	259.0000	13.5100		
C3	549.50000	0.0363240	-8606600.0	-2515.300	0.00	
VHP	0.000037000	480.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000072000			
high-albite	SI(3)AL(1)NA(1)O(8)			abh	1nh	

ST	0.0	-3924800.000	223.4000	10.1090		
C3	452.00000	-0.0133640	-1275900.0	-3953.600	0.00	
VHP	0.000045600	593.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000088950			
microcline	SI(3)AL(1)K(1)O(8)	mic	1nh			
ST	0.0	-3975110.000	216.0000	10.8920		
C3	448.80000	-0.0100750	-1007300.0	-3973.100	0.00	
VHP	0.000033500	574.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000086100			
sanidine	SI(3)AL(1)K(1)O(8)	san	1nh			
ST	0.0	-3964960.000	230.0000	10.9000		
C3	448.80000	-0.0100750	-1007300.0	-3973.100	0.00	
VHP	0.000033500	574.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000086100			
anorthite	SI(2)AL(2)CA(1)O(8)	an	+1nh			
ST	0.0	-4233480.000	200.0000	10.0790		
C3	371.60000	0.0126150	-4110200.0	-2038.400	0.00	
VHP	0.000023800	919.0	2300.0000	11.00	0.05000	
VH2	10.0000	4.0000	-0.000137850			
quartz	SI(1)O(2)	q	1nh			
ST	0.0	-910830.000	41.5000	2.2688		
C3	110.70000	-0.0051890	0.0	-1128.300	0.00	
VHP	0.000006500	750.0	847.0000	4.95	0.11880	
VH2	10.0000	4.0000	-0.000112500			
tridymite	SI(1)O(2)	trd	1nh			
ST	0.0	-906690.000	46.1000	2.7000		
C3	97.90000	-0.0033500	-636200.0	-774.000	0.00	
VHP	0.000005000	750.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000112500			
cristobalite	SI(1)O(2)	crst	1nh			
ST	0.0	-905990.000	46.5000	2.6100		
C3	97.90000	-0.0033500	-636200.0	-774.000	0.00	
VHP	0.000008100	600.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000090000			
coesite	SI(1)O(2)	coe	1nh			
ST	0.0	-905470.000	40.8000	2.0640		
C3	96.50000	-0.0005770	-444800.0	-798.200	0.00	
VHP	0.000018000	1000.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000150000			
stishovite	SI(1)O(2)	stv	1nh			
ST	0.0	-875630.000	24.5000	1.4014		
C3	68.10000	0.0060100	-1978200.0	-82.100	0.00	
VHP	0.000025000	3160.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000474000			
rutile	Ti(1)O(2)	ru	1nh			
ST	0.0	-944180.000	50.6000	1.8820		

C3	90.40000	0.0029000	0.0	-623.800	0.00
VHP	0.000044300	2225.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000333750		
pyrophanite	Ti(1)MN(1)O(3)		pnt	1nh	
ST	0.0	-1359240.000	104.9000	3.2880	
C3	141.90000	0.0033730	-1940700.0	-407.600	0.00
VHP	0.000049500	1770.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000265500		
geikielite	Ti(1)MG(1)O(3)		geik	1nh	
ST	0.0	-1567490.000	74.6000	3.0860	
C3	151.00000	0.0000000	-1890400.0	-652.200	0.00
VHP	0.000049500	1770.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000265500		
ilmenite	Ti(1)FE(1)O(3)		ilm	1nh	
ST	0.0	-1231300.000	108.9000	3.1690	
C3	138.90000	0.0050810	-1288800.0	-463.700	0.00
VHP	0.000049500	1770.0	1900.0000	11.00	0.02000
VH2	10.0000	4.0000	-0.000265500		

***** GAS DATA *****

water.fluid	O(1)H(2)		H2O	1nh	
SPC	HHP98				
ST	0.0	-241810.000	188.8000	0.0000	
C3	40.10000	0.0086560	487500.0	-251.200	0.00
VHP	0.000000000	0.0	0.0000	0.00	0.00000
VH2	0.0000	0.0000	0.000000000		
carbon.dioxide	O(2)C(1)		CO2	1nh	
SPC	CHP98				
ST	0.0	-393510.000	213.7000	0.0000	
C3	87.80000	-0.0026440	706400.0	-998.900	0.00
VHP	0.000000000	0.0	0.0000	0.00	0.00000
VH2	0.0000	0.0000	0.000000000		

*****MINERAL DATA*****

sillimanite.liq	SI(1)AL(2)O(5)		sill	1nh	
ST	0.0	-2583100.000	39.0000	6.4190	
C3	237.60000	0.0000000	0.0	0.000	0.00
VHP	0.000010000	300.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000045000		
anorthite.liq	SI(2)AL(2)CA(1)O(8)		anL	1nh	
ST	0.0	-4257750.000	52.0000	10.2060	
C3	417.50000	0.0000000	0.0	0.000	0.00
VHP	0.000049000	200.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000030000		
H2O.liq	O(1)H(2)		h2oL	1nh	
ST	0.0	-295710.000	45.5000	1.4140	

C3	80.00000	0.0000000	0.0	0.000	0.00
VHP	0.001079000	40.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000006000		
K-feldspar.liq SI(3)AL(1)K(1)O(8) kspL 1nh					
ST	0.0	-3992670.000	129.5000	11.4680	
C3	367.30000	0.0000000	0.0	0.000	0.00
VHP	0.000060000	260.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000039000		
Silica.liq SI(1)O(2) qL 1nh					
ST	0.0	-920850.000	16.5000	2.6400	
C3	82.50000	0.0000000	0.0	0.000	0.00
VHP	-0.000005000	470.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000070500		
albite.liq SI(3)AL(1)NA(1)O(8) abL 1nh					
ST	0.0	-3934370.000	145.0000	10.7100	
C3	358.50000	0.0000000	0.0	0.000	0.00
VHP	0.000045000	390.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000058500		

****MINERAL DATA****

HM-BUFFER	H(2)	HM	*HM	
ST	0.000	000000.000	000.000000	0.000000
CP1	0.000000	0.00000	0.00	0.0
COM	magnetite[2] water.fluid[1] hematite[-3]			
-HM-BUFFER	H(-2)	-HM	*HM	
ST	0.000	000000.000	000.000000	0.000000
CP1	0.000000	0.00000	0.00	0.0
COM	HM-BUFFER[-1]			

***** SOLUTION DATA *****Newton et al. 1980
 ANAB (SITE,MARGULES) O(1):Na,Ca - T(2):Si,Al
 high-albite Na - Si,Al
 anorthite Ca - Al,Al

***** MARGULES PARAMETER *****

high-albite - anorthite
 122 28230.0 0 0
 112 8473.0 0 0

***** SOLUTION DATA ***** ilmenit ideal
 ILM (IDEAL)
 ilmenite
 geikielite
 pyrophanite

***** SOLUTION DATA ***** garnet, as in perplex
 GARNET (MARGULES,IDEAL)3 M(3):Ca,Mg,Fe,Mn
 grossular Ca,Ca,Ca - Al,Al
 pyrope Mg,Mg,Mg - Al,Al
 almandine Fe,Fe,Fe - Al,Al
 spessartine Mn,Mn,Mn - Al,Al

***** MARGULES PARAMETER *****

pyrope - grossular
 12 33000. 0.00 0.00
 pyrope - almandine
 12 2500. 0.00 0.00
 pyrope - spessartine
 12 4500. 0.00 0.00
 almandine - spessartine
 12 240. 0.00 0.00
 pyrope - andradite
 12 73000. 0.00 0.00
 almandine - andradite
 12 60000. 0.00 0.00
 spessartine - andradite
 12 60000. 0.00 0.00

***** SOLUTION DATA ***** chtd
 CHTD (IDEAL,MARGULES) M(1):Mn,Mg,Fe
 Mg-chloritoid Mg
 Fe-chloritoid Fe
 Mn-chloritoid Mn

***** MARGULES PARAMETER *****

Mg-chloritoid - Fe-chloritoid
 12 1000. 0.00 0.00

***** SOLUTION DATA ***** chlr, as in perplex
 CHLR (-SITE,MARGULES) M23(4):Mg,Fe,Mn - M1(1):Mg,Fe,Al,Mn -
 M4(1):Mg,Al,Fe,Mn - T1(2):Si,Al
 clinocllore Mg,Mg,Mg,Mg - Mg - Al - Al,Si
 daphnite Fe,Fe,Fe,Fe - Fe - Al - Al,Si
 amesite Mg,Mg,Mg,Mg - Al - Al - Al,Al
 Mn-chlorite Mn,Mn,Mn,Mn - Mn - Al - Al,Si

***** MARGULES PARAMETER ***** chlr

clinocllore - daphnite
 12 2500.0 0.0 0.0
 clinocllore - amesite
 12 18000.0 0.0 0.0

daphnite - amesite
12 13500.0 0.0 0.0

****MINERAL DATA**** phng
paragonite2 NA(1)AL(3)SI(3)O(12)H(2) pa2 nhm
ST 0.0 1420.000 0.0000 0.4000
COM paragonite[1]

***** SOLUTION DATA ***** phng
PHNG (-MARGULES,SITE) A(1):K,Na - M2A(1):Al,Mg,Fe - T1(2):Al,Si
muscovite K - Al - Al,Si
celadonite K - Mg - Si,Si
Fe-celadonite K - Fe - Si,Si
paragonite2 Na - Al - Al,Si

***** MARGULES PARAMETER ***** phng
muscovite - paragonite2
12 12000. 0.00 0.40
paragonite2 - celadonite
12 14000. 0.00 0.20
paragonite2 - Fe-celadonite
12 14000. 0.00 0.20

****MINERAL DATA**** biotite as in perplex
obiotite K(1)MG(2)FE(1)AL(1)SI(3)O(12)H(2) obi xnh
ST 0.0 -10730.000 0.0000 0.0000
COM phlogopite[2/3]annite[1/3]

***** SOLUTION DATA *****
BIO (-SITE,MARGULES) M2(2):Mg,Fe,Mn - M1(1):Mg,Fe,Al,Mn - T1(2):Si,Al
phlogopite Mg,Mg - Mg - Al,Si
annite Fe,Fe - Fe - Al,Si
eastonite Mg,Mg - Al - Al,Al
obiotite Mg,Mg - Fe - Al,Si
Mn-biotite Mn,Mn - Mn - Al,Si

***** MARGULES PARAMETER *****
phlogopite - annite
12 9000.0 0.0 0.0
phlogopite - eastonite
12 10000.0 0.0 0.0
phlogopite - obiotite
12 3000.0 0.0 0.0
annite - eastonite
12 -1000.0 0.0 0.0
annite - obiotite

12 6000.0 0.0 0.0
eastonite - obiotite
12 10000.0 0.0 0.0

***** SOLUTION DATA *****

STAU (IDEAL,MARGULES)4 M(4):Fe,Mg,Mn
Mg-staurolite Mg,Mg,Mg,Mg
Fe-staurolite Fe,Fe,Fe,Fe
Mn-staurolite Mn,Mn,Mn,Mn

***** MARGULES PARAMETER *****

Mg-staurolite - Fe-staurolite
12 -8000.0 0.0 0.0

***** SOLUTION DATA *****

CORD (SITE) M(2):Fe,Mg,Mn - B(1):n,h
cordierite Mg,Mg - n
Fe-cordierite Fe,Fe - n
Mn-cordierite Mn,Mn - n

****MINERAL DATA****

tschermakite2	CA(2)MG(3)AL(4)SI(6)O(24)H(2)	ts2	code
ST	0.0 10000.0 0.0000 0.0000		
COM	tschermakite[1]		
pargasite2	NA(1)CA(2)MG(4)AL(3)SI(6)O(24)H(2)	parg2	code
ST	0.0 15000.0 0.0000 0.0000		
COM	pargasite[1]		
glaucophane2	NA(2)MG(3)AL(2)SI(8)O(24)H(2)	gl2	code
ST	0.0 3000.0 0.0000 0.0000		
COM	glaucophane[1]		
cummingtonite2	MG(7)SI(8)O(24)H(2)	cumm2	code
ST	0.0 -6400.0 0.0000 0.0000		
COM	cummingtonite[1]		
grunerite2	FE(7)SI(8)O(24)H(2)	grun2	code
ST	0.0 -5000.0 0.0000 0.0000		
COM	grunerite[1]		
acam	MG(3)FE(4)SI(8)O(24)H(2)	acam	code
ST	0.0 -15100.0 0.0000 0.0000		
COM	cummingtonite[3/7]grunerite[4/7]		
bcam	MG(2)FE(5)SI(8)O(24)H(2)	bcam	code
ST	0.0 -17100.0 0.0000 0.0000		
COM	cummingtonite[2/7]grunerite[5/7]		
mgriebekite	NA(2)FE(2)MG(3)SI(8)O(24)H(2)	mrbr	code
ST	0.0 8000.0 0.0000 0.0000		
COM	glaucophane[1]jadeite[-2]acmite[2]		

***** SOLUTION DATA *****

CLAMP (-EXT,MARGULES) A(1):v,Na - M1(3):Mg,Fe - M2(2):Mg,Al,Fe,F3 -
M4(2):Ca,Na,Mg,Fe - T(4):Si,Al

tremolite	v - Mg,Mg,Mg - Mg,Mg - Ca,Ca - Si,Si,Si,Si	1.0	0	0
tschermakite2	v - Mg,Mg,Mg - Al,Al - Ca,Ca - Si,Si,Al,Al	1.5	0	0
pargasite2	Na - Mg,Mg,Mg - Mg,Al - Ca,Ca - Si,Si,Al,Al	1.7	0	0
glaucophane2	v - Mg,Mg,Mg - Al,Al - Na,Na - Si,Si,Si,Si	0.8	0	0
cummingtonite2	v - Mg,Mg,Mg - Mg,Mg - Mg,Mg - Si,Si,Si,Si	1.0	0	0
grunerite2	v - Fe,Fe,Fe - Fe,Fe - Fe,Fe - Si,Si,Si,Si	1.0	0	0
acam	v - Mg,Mg,Mg - Fe,Fe - Fe,Fe - Si,Si,Si,Si	1.0	0	0
bcam	v - Fe,Fe,Fe - Mg,Mg - Fe,Fe - Si,Si,Si,Si	1.0	0	0

***** MARGULES PARAMETER *****

tremolite - tschermakite2				
12	20000	0.0	0.0	
tremolite - pargasite2				
12	25000	0.0	0.0	
tremolite - glaucophane2				
12	65000	0.0	0.0	
tremolite - cummingtonite2				
12	45000	0.0	0.0	
tremolite - grunerite2				
12	75000	0.0	0.0	
tremolite - acam				
12	57000	0.0	0.0	
tremolite - bcam				
12	63000	0.0	0.0	
tremolite - mgriebekite				
12	65000	0.0	0.0	
tschermakite2 - pargasite2				
12	-40000	0.0	0.0	
tschermakite2 - glaucophane2				
12	25000	0.0	0.0	
tschermakite2 - cummingtonite2				
12	70000	0.0	0.0	
tschermakite2 - grunerite2				
12	80000	0.0	0.0	
tschermakite2 - acam				
12	70000	0.0	0.0	
tschermakite2 - bcam				
12	72500	0.0	0.0	
tschermakite2 - mgriebekite				
12	25000	0.0	0.0	
pargasite2 - glaucophane2				
12	50000	0.0	0.0	
pargasite2 - cummingtonite2				

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12      90000  0.0  0.0
pargasite2 - grunerite2
12      106700  0.0  0.0
pargasite2 - acam
12      94800  0.0  0.0
pargasite2 - bcam
12      94800  0.0  0.0
pargasite2 - mgriebekite
12      50000  0.0  0.0
glaucophane2 - cummingtonite2
12      100000  0.0  0.0
glaucophane2 - grunerite2
12      113500  0.0  0.0
glaucophane2 - acam
12      100000  0.0  0.0
glaucophane2 - bcam
12      111200  0.0  0.0
!glaucophane2 - mgriebekite
!12      0.0  0.0  0.0
cummingtonite2 - grunerite2
12      33000  0.0  0.0
cummingtonite2 - acam
12      18000  0.0  0.0
cummingtonite2 - bcam
12      23000  0.0  0.0
cummingtonite2 - mgriebekite
12      100000  0.0  0.0
grunerite2 - acam
12      12000  0.0  0.0
grunerite2 - bcam
12      8000  0.0  0.0
grunerite2 - mgriebekite
12      113500  0.0  0.0
acam - bcam
12      20000  0.0  0.0
acam - mgriebekite
12      100000  0.0  0.0
bcam - mgriebekite
12      111200  0.0  0.0

```

***** SOLUTION DATA ***** amphiboles Dale et al. 2005

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AMPH1  (-SITE,MARGULES)  A(1):v,Na - M4(2):Ca,Na - M13(3):Mg,F3 -
M2(2):Mg,Fe,Al - T1(1):AlSi,SiSi
  tremolite      v - Ca,Ca - Mg,Mg,Mg - Mg,Mg - SiSi      1.0
  tschermakite   v - Ca,Ca - Mg,Mg,Mg - Al,Al - AlSi      1.5
  pargasite      Na - Ca,Ca - Mg,Mg,Mg - Mg,Al - AlSi      1.7

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glaucophane	v - Na,Na - Mg,Mg,Mg - Al,Al - SiSi	0.8
ferroactinolite	v - Ca,Ca - F3,F3,F3 - Fe,Fe - SiSi	1.0
ferritschermak	v - Ca,Ca - Mg,Mg,Mg - Fe,Fe - AlSi	1.5

***** MARGULES PARAMETER *****

```

tremolite - tschermakite
12  20000.0  0.0  0.0
tremolite - pargasite
12  33000.0  0.0  0.0
tremolite - glaucophane
12  65000.0  0.0  0.0
tremolite - ferroactinolite
12  10000.0  0.0  0.0
tremolite - ferritschermak
12  20000.0  0.0  0.0
tschermakite - pargasite
12  -38000.0  0.0  0.0
tschermakite - glaucophane
12  25000.0  0.0  0.0
tschermakite - ferroactinolite
12  12500.0  0.0  0.0
!tschermakite - ferritschermak
!12  0000.0  0.0  0.0
pargasite - glaucophane
12  50000.0  0.0  0.0
pargasite - ferroactinolite
12  -1900.0  0.0  0.0
pargasite - ferritschermak
12  -38500.0  0.0  0.0
glaucophane - ferroactinolite
12  39300.0  0.0  0.0
glaucophane - ferritschermak
12  45900.0  0.0  0.0
ferroactinolite - ferritschermak
12  12500.0  0.0  0.0

```

*****MINERAL DATA*****

```

sillimanite8.liq  AL(3.2)SI(1.6)O(8)  silL8  nhl
ST      0.0  -10000.000  00.0000  0.0000
COM  sillimanite.liq[1.6]
Silica8.liq      SI(4)O(8)  qL8      nhl
ST      0.0  0000.000  00.0000  0.0000
COM  Silica.liq[4]

```

***** SOLUTION DATA *****

LIQtc (EXT,MARGULES)

Silica8.liq
albite.liq
K-feldspar.liq
anorthite.liq
sillimanite8.liq
H2O.liq

***** MARGULES PARAMETER *****

Silica8.liq - albite.liq
12 12000.0 0.0 -0.40
Silica8.liq - K-feldspar.liq
12 -2000.0 0.0 -0.50
Silica8.liq - anorthite.liq
12 -10000.0 0.0 0.00
Silica8.liq - sillimanite8.liq
12 12000.0 0.0 0.00
Silica8.liq - forsterite8.liq
12 12000.0 0.0 -0.40
Silica8.liq - fayalite8.liq
12 14000.0 0.0 0.00
Silica8.liq - H2O.liq
12 15000.0 0.0 0.00

albite.liq - K-feldspar.liq
12 -6000.0 0.0 3.00
albite.liq - sillimanite8.liq
12 12000.0 0.0 0.00
albite.liq - forsterite8.liq
12 10000.0 0.0 0.00
albite.liq - fayalite8.liq
12 2000.0 0.0 0.00
albite.liq - H2O.liq
12 1000.0 0.0 -0.20

K-feldspar.liq - anorthite.liq
12 0.0 0.0 -1.00
K-feldspar.liq - sillimanite8.liq
12 12000.0 0.0 0.00
K-feldspar.liq - forsterite8.liq
12 12000.0 0.0 0.00
K-feldspar.liq - fayalite8.liq
12 12000.0 0.0 0.00
K-feldspar.liq - H2O.liq
12 11000.0 0.0 -0.45

anorthite.liq - H2O.liq

12 9000.0 0.0 -0.85

sillimanite8.liq - forsterite8.liq

12 12000.0 0.0 0.00

sillimanite8.liq - fayalite8.liq

12 12000.0 0.0 0.00

sillimanite8.liq - H2O.liq

12 16000.0 0.0 0.00