Unravelling the P-T-t history of Grenvillian metamorphism in the Mazinaw Domain,
southeastern Ontario: Insights from phase equilibria modeling and geospeedometry

By

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Abstract

P-T-t conditions of Grenvillian metamorphism were derived from mineral assemblages, growth zoning in garnet and monazite geochronology from metapelites of the Flinton Group in southeastern Ontario. Initial conditions of garnet growth determined through isopleth thermobarometry yielded 3.7 kbar and 515°C and geothermal gradients of 40°C km⁻¹. Phase equilibria modeling revealed an increase from 615 to 715°C and 5.6 to 7.9 kbar across the study area. Forward modeling of growth zoning in a population of garnet porphyroblasts with the THERIA_G software revealed a clockwise path over the P-T interval 3.7 to 5.9 kbar and 513 to 615°C. Diffusional relaxation of growth zoning in relatively small porphyroblasts of the population provided an average heating rate of 2°C Ma⁻¹. In situ U-Pb monazite geochronology revealed a major age population at 977 ± 4 Ma, interpreted to represent monazite growth at the expense of allanite near the peak conditions of garnet growth and metamorphism.

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I would like to thank Peter Jones for all the help with the EPMA analyses, which I am sure, got boring after about the 1000th spot analysis on garnet. It was a pleasure to spend all that time up in the microprobe lab with you and your mineralogical knowledge was certainly an asset.

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Chris McFarlane at the University of New Brunswick is thanked for assistance with the in situ LA-ICP-MS U-Pb dating of monazite. Mike Easton at the Ontario Geological Survey is thanked for introducing me to the field area, providing access to the WDXRFA and EPMA labs at Geoscience Laboratories and thoughtful discussions concerning the regional context of the study. Dave Crabtree, Tara Kell and Yan Luo are thanked for assistance with the preparation of EPMA maps of garnet and monazite, whole rock chemistry and LA-ICP-MS analysis of monazite respectively. Willy Tschudin at Basel University is thanked for assistance with the preparation of centrally sectioned garnet porphyroblasts.

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Preface

This thesis represents research conducted by T. McCarron between September 2011 and September 2013 in the Department of Earth Sciences at Carleton University. It was prepared under the supervision of Dr. Fred Gaidies, and is divided into four chapters and an Appendix. Chapters 2 and 3 may be regarded as individual manuscripts.

Chapter 1 – Introduction

Chapter 2 – Conditions and timing of Grenvillian metamorphism in the Mazinaw Domain, southeastern Ontario

Chapter 3 – The analysis of chemical zoning in a garnet population: Determination of the P-T-t path of Grenvillian metamorphism in southeastern Ontario

Chapter 4 – Overall conclusions

Appendix

Contributions of the co-authors

The two individual manuscripts benefitted greatly from the contributions and insights of several co-authors. The contribution of each co-author is outlined below.

Chapter 2:

¹McCarron, T., ²Gaidies, F., ³McFarlane, C.R.M., ⁴Easton, R.M. & ⁵Jones, P. 2013. Conditions and timing of Grenvillian metamorphism in the Mazinaw Domain, southeastern Ontario.

The first author collected samples from the field, investigated the petrography of all samples, performed all the thermodynamic calculations, guided ablation pits for monazite geochronology using in situ laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) and took all back scattered electron images of accessory phases. The first author wrote the manuscript and drafted all tables and figures. The second author supervised the research, providing key insights into many aspects of the study. The third author assisted with the LA-ICP-MS U-Pb dating of monazite. In addition, the third author performed all offline data reductions and provided thoughtful discussions on the interpretation of the data. The fourth author introduced the first author to the field area and provided important discussions regarding the regional context of the outcomes of the study. The fifth author performed all electron probe micro-analyses on garnet under direction of the first author.

Chapter 3:

¹McCarron, T., ²Gaidies, F., ³Baumgartner, L.P., ⁴Putlitz, B. & ⁵Jones, P. 2013. The analysis of chemical zoning in a garnet population: Determination of the P-T-t path of Grenvillian metamorphism in southeastern Ontario

The first author collected the sample from the field, investigated the petrography, performed the high-resolution X-ray computed tomography (XR- μ CT) analyses, located each porphyroblast of different diameter and centrally sectioned them, and performed all thermodynamic calculations. In addition, the first author wrote the manuscript and drafted all tables and figures. The second author initiated the project, supervised the research and provided important insights along the way. The third and fourth authors provided access to the XR- μ CT facility at the University of Lausanne, trained the first author how to operate the instrument and provided thoughtful discussions regarding crystal size distributions of metamorphic minerals. The fifth author performed all electron probe micro-analyses under the direction of the first author on the centrally sectioned garnet porphyroblasts and provided important mineralogical insights along the way.

In addition, F. Gaidies revised all chapters providing important criticisms and suggestions, which significantly improved this thesis.

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CHAPTER 1:

Introduction

Although the rates of modern collisional events may be directly observed, as is the case for the Indo-Australian and Eurasian plate collision, estimates for the rate of tectonic processes in geological past are scarce. By understanding the rates and conditions of collisional events in the present day and geologic past, the evolution of plate tectonics may be better understood. In addition, it is important to understand the rates and conditions at which ancient orogenic belts form as they host the majority of Earth's resources. The study of rates and timescales of geological processes is known as geospeedometry (Lasaga, 1983). Specifically within metamorphic petrology geospeedometry aims to better understanding the rate with which temperature changes with time (i.e., heating/cooling rates) and the timescales of metamorphic processes. Geospeedometry often utilizes chemical zoning developed during the growth of minerals which is modified by intracrystalline diffusion as an indicator of metamorphic rate. Diffusion is a thermally activated process and if the boundary conditions are well constrained, then the degree to which minerals diffusionally relax chemical zoning is mainly a function of time. Recent geospeedometry studies have suggested that timescales of Barrovian style metamorphism may be much shorter than previously thought (Ague & Baxter, 2007; Spear et al., 2012).

Chemical zoning in minerals has long been recognized as a powerful recorder of petrological information (Spear, 1993). Metamorphic garnet in particular has been extensively used as a petrological indicator of pressure, temperature and time (P-T-t)

(e.g., Selverstone et al., 1984; Spear et al., 1984; Evans, 2004; Gaidies et al., 2006; Gaidies et al., 2008A; Gaidies et al., 2008B; Gaidies et al., 2008C; Moynihan & Pattison, 2013). The ability of garnet to retain chemical zoning is in part controlled by slow intracrystalline cation diffusion (e.g., Loomis et al., 1985; Chakraborty & Ganguly, 1992). In addition, the thermodynamic properties of garnet have been well described (e.g., Berman, 1988; Holland & Powell, 1998; Holland & Powell, 2011) allowing for accurate reconstructions of observed chemical zoning via thermodynamic calculations along specific P-T-t paths (Gaidies et al., 2008A). It was hypothesized by Gaidies et al. (2008A) that due to steeper initial chemical gradients developed during growth, relatively small garnet porphyroblasts of a garnet population may be more sensitive to diffusional relaxation and therefore heating/cooling rates than larger porphyroblasts. Diffusional relaxation in small porphyroblasts of a population can be used to infer rates of metamorphic processes while larger porphyroblasts, which may record growth zoning to a larger extent, can be used to infer the P-T path experienced by a rock. Thus far, diffusional relaxation in a population of garnet porphyroblasts has not been used for geospeedometry.

Although geospeedometry may provide important constraints on the relative timescales of metamorphism and tectonic episodes, it cannot provide absolute time constraints. Monazite, $\text{LREE}(\text{PO}_4)$, is an ideal geochronometer in igneous and metamorphic rocks. Monazite incorporates negligible common Pb and is resistant to diffusive Pb loss at high temperatures (Cherniak et al., 2004; McFarlane & Harrison, 2006) and has been used in many U-Pb geochronology and petrological studies (e.g.,

Williams & Jercinovic, 2002; Kohn & Malloy, 2004; McFarlane et al., 2005; McFarlane & McCulloch, 2007; Gaidies et al., 2008C). Because monazite-forming reactions have been well documented (e.g., Pyle et al., 2001; Kohn & Malloy, 2004; Yang & Pattison, 2006; Thomkins & Pattison, 2007) it is possible to constrain the P-T conditions at which monazite crystallizes along the prograde path. More importantly because monazite incorporates yttrium and because yttrium strongly partitions into garnet, garnet may record accessory phase reactions or periods of garnet resorption and regrowth, both of which may be important mechanisms of monazite formation.

This study seeks to better understand the P-T-t conditions associated with the Grenville Orogeny in southeastern Ontario, a large scale orogenic event responsible for the formation of supercontinent Rodinia (Easton, 1992). As it stands, estimates for the rates of tectonic processes and the P-T paths experienced by continental crust during Grenville Orogeny are lacking in southeastern Ontario. P-T-t estimates will be derived from garnet-bearing metapelites of the Flinton Group using modern thermobarometry techniques such as phase equilibria modeling with the THERIAK-DOMINO software, garnet isopleth thermobarometry, in situ laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) U-Pb monazite geochronology and for the first time, forward modeling of growth zoning in a population of garnet porphyroblasts.

More specifically, growth zoning in a population of garnet porphyroblasts characterized by high-resolution X-ray micro-computed tomography from a single sample will be coupled with thermodynamic and diffusion modeling to determine the P-T evolution and relative rates and timescales of metamorphic processes associated with

the Grenville Orogeny. In situ U-Pb monazite geochronology will be coupled with detailed accessory phase petrography, trace element zoning in garnet and results from garnet growth simulations, to provide an absolute calibration for the relative timescales predicted through diffusion modeling in a population of garnet porphyroblasts.

Chapter 2:

Conditions and timing of Grenvillian metamorphism in the Mazinaw Domain, southeastern Ontario

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2.0 Abstract

Metapelites of the Flinton Group in southeastern Ontario were metamorphosed at upper greenschist to amphibolite facies during the Grenville Orogeny (ca. 1080-980 Ma). Phase equilibria modeling suggests an increase in pressure and temperature from 5.6 to 7.9 kbar and 615 to 715°C across the study area from the southwest to northeast. Isopleth thermobarometry applied to the cores of garnet porphyroblasts revealed similar conditions of initial garnet growth. Initial garnet growth was calculated in several samples across the field area at approximately 3.7 kbar and 515°C with a corresponding geothermal gradient of 40°C km⁻¹. The high geothermal gradient may represent elevated geotherms in response to crustal delamination and upwelling of hot asthenosphere following the Shawinigan Orogeny or effects from the Midcontinent rift system. In situ laser ablation - inductively coupled plasma - mass spectrometry U-Pb monazite geochronology revealed a major age population at 977 ± 4 Ma. Based on trace element zoning in garnet and the distribution of accessory phases, the age was interpreted to represent monazite growth at the expense of allanite and apatite late in garnet's growth

history. The conditions of monazite growth were constrained to 4.5 to 6.8 kbar and 540 to 620°C based on results from phase equilibria modeling. This age is significantly younger than other metamorphic ages currently available. The results of this study suggest that the Grenville Orogeny was long, hot and still well in effect at 977 ± 4 Ma in southeastern Ontario.

Keywords: garnet, monazite, allanite, metapelite, THERIAK-DOMINO, garnet isopleth thermobarometry, LA-ICP-MS, Flinton Group, Mazinaw Domain, Grenville

2.1 Introduction

Garnet has been utilized in many petrologic studies to determine the pressure-temperature-time (P-T-t) evolution of metamorphic terranes (e.g., Spear et al., 1984; Carlson, 1989; Evans, 2004; Gaidies et al., 2006; Gaidies et al., 2008A; Gaidies et al., 2008B; Gaidies et al., 2008C; Caddick et al., 2010) due to its stability over a range of P-T conditions in rocks of different composition (Spear, 1993), its ability to record chemical zoning sensitive to the P-T-t evolution of the rock (Spear, 1993) and its well-characterized thermodynamic properties (e.g., Berman, 1988; Holland & Powell, 1998).

Monazite, a light rare earth phosphate ((LREE)PO₄), is a common accessory phase in garnet-bearing rocks that is routinely used in U-Pb geochronology and petrologic studies (e.g., Williams & Jercinovic, 2002; Kohn & Malloy, 2004; McFarlane et al., 2005; McFarlane & McCulloch, 2007; Gaidies et al., 2008C). Monazite is an ideal geochronometer as it incorporates negligible common lead and is resistant to radiogenic lead loss even at high temperatures (Cherniak et al., 2004; McFarlane & Harrison, 2006). Metapelite monazite has been documented forming through a variety of reactions

involving accessory phases (e.g., Yang & Pattison, 2006; Tomkins & Pattison, 2007) and major silicates such as garnet (e.g., Pyle & Spear, 1999; Kohn & Malloy, 2004).

It is well established that yttrium partitions orders of magnitude stronger into garnet than into any other major silicate in metapelitic rocks (Jaffe, 1951; Lanzirotti, 1995). Accessory phases such as allanite, monazite, xenotime, apatite, and zircon, may incorporate significant quantities of yttrium and other trace elements (Wark & Miller, 1993). Hence, yttrium zoning in garnet may record reactions involving Y-rich accessory phases as well as periods of garnet resorption and regrowth, important events that may influence the formation of monazite and interpretation of U-Pb ages (e.g., Pyle & Spear, 1999; Pyle & Spear, 2000; Pyle et al., 2001; Yang & Rivers, 2002; Yang & Pattison, 2006).

In this communication P-T estimates and the timing of Grenvillian metamorphism in southeastern Ontario are derived by the interpretation of phase equilibria modeling, garnet isopleth thermobarometry (e.g., Evans, 2004; Gaidies et al., 2006) and in situ laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) U-Pb monazite geochronology. Using this approach the conditions and timing of orogenic processes associated with the Grenville Orogeny may be resolved and better understood.

2.2 Regional Geology

The Grenville Orogeny was a major continent-continent scale collisional event between Laurentia and an outboard continent, thought to be Amazonia, to form the supercontinent Rodinia between 1080 and 980 Ma (Easton, 1992; Carr et al., 2000; Tollo, 2010). In Canada the Grenville Province is approximately 400 km wide and stretches

from southeastern Ontario through Quebec and into Labrador (Easton, 1992) (Fig. 2.1a). The Grenville Province is composed of complexly deformed and polymetamorphosed rocks of volcanic, sedimentary and plutonic origin. In southeastern Ontario the Grenville Province can be subdivided into two main divisions, the Central Gneiss Belt (CGB) and the Central Metasedimentary Belt (CMB). The CMB is characterized by 1290-1240 Ma metavolcanic and metasedimentary rocks, which were intruded by plutonic rocks between 1250-1230 Ma and 1180-1070 Ma (Easton, 1992; Easton, 2006). The CMB is divided into several terranes and domains, separated from one another by large shear zones (Fig. 2.1b). The domains and terranes of the Central Metasedimentary Belt amalgamated and accreted to eastern margin of Laurentia during the Elzevirian Orogeny between 1250 and 1190 Ma (Easton, 1992; Tollo, 2010).

The Mazinaw Domain, the focus of this study, is part of the CMB and is separated from the Grimsthorpe Domain in the west by the Mooroton shear zone and from the Sharbot Lake Domain in the east by the Robertson Lake Shear zone. Both the Mooroton and Robertson Lake shear zones have kinematic indicators suggesting early northwest directed thrusting in response to continental collision which is overprinted by late southeast-directed post-orogenic extension (Busch et al., 1996). The Mazinaw Domain is characterized by northeast trending structures, relatively high metamorphic grade in comparison to the surrounding domains, and the presence of the Flinton Group, a northeast-southwest trending succession of metasediments (Moore & Thompson, 1980; Easton, 2006). The Mazinaw Domain was subjected to two phases of regional metamorphism, one prior to and one following the deposition of the Flinton Group

Figure 2.1. (A) The Grenville Province within Canada. The Central Metasedimentary Belt is outlined in the stippled box. Modified after Hynes & Rivers (2010). (B) The Central Metasedimentary Belt (CMB) in southeastern Ontario. The domains and terranes, which compose the CMB are illustrated on the map and are separated from one another by large-scale shear zones. For reference, the city of Ottawa (Ontario) is approximately 80 km northeast of Perth. Modified after Easton (2006).

(Easton, 1992). The first phase of metamorphism predates deposition of the Flinton Group and affected rocks of the Grenville basement, 1290 to 1240 Ma metavolcanics and metasediments, locally reaching granulite facies (Easton, 1992). This first phase of metamorphism was associated with the Shawinigan Orogeny between ca. 1190 and 1140 Ma when Adirondis was accreted to eastern margin of Laurentia (Tollo, 2010). The Flinton Group provides a unique look into Grenvillian metamorphism as its deposition post-dates metamorphism experienced by the Grenville basement (Moore & Thompson, 1980; Easton & Ford, 1991) making the Flinton Group a monometamorphic window into a polymetamorphic geological terrane.

The Flinton Group

The Flinton Group has been the focus of several regional mapping and petrological studies (Hounslow & Moore, 1966; Hutcheon & Moore, 1973; Moore & Thompson, 1980; Thompson & Leclair, 1987; Easton & Ford, 1991; Sager-Kinsmen & Parrish, 1993; Corfu & Easton, 1995; Ford, 2002; Easton 2006). It lies unconformably on top of supracrustal and plutonic rocks of the Grenville Supergroup and Elsevier and Methuen plutonic suites (Fig. 2.2) (Moore & Thompson, 1980; Easton, 2006). Sager-Kinsman & Parrish (1993) identified a detrital zircon population in a quartzite from the Bishops Corner Formation of the Flinton Group ranging in age from 1280 to 1150 Ma putting deposition of the Flinton Group sometime after 1150 Ma. The Bishops Corner Formation is the basal unit of the Flinton Group and is characterized by graphite-poor metapelitic schists rich in magnetite, quartzite, micaceous quartzo-feldspathic metapsammites and quartzite pebble metaconglomerates (Moore & Thompson, 1980). The Myers Cave

Figure 2.2. Simplified geologic map of the Flinton Group and the location of samples discussed in this study. Modified after Moore & Thompson (1980) and Easton (2006).

Formation, which overlies the Bishops Corner Formation, is characterized by graphite-rich metapelitic schists, dolomite marbles and carbonate clast metaconglomerates and metabreccias (Moore & Thompson, 1980). Moore & Thompson (1980) suggested deposition of the Flinton Group in an extensional tectonic regime in a fluvial to shallow marine environment. Alternatively, Easton & Ford (1991) suggested deposition of the Flinton Group in a fluvial-lacustrine environment where sedimentation was partly controlled by rift valleys. Moore & Thompson (1980) noted that upward from the base there is a trend from oxidized to increasingly reduced sediments. They attributed this oxidation trend to restricted circulation in the depositional environment or the generation of sediment from a less-weathered source.

The Flinton Group developed metamorphic mineral assemblages characteristic of the upper amphibolite facies in the northeast and greenschist facies in the southwest during the Ottawa or “Grenville” Orogeny between 1080 and 980 Ma (Easton, 1992).

Temperature estimates in the Marble Lake and Ompah areas (Fig. 2.2) derived using garnet-biotite thermometry yielded 500-580°C and 670-700°C respectively (Hodges & Spear, 1982; Ferry & Spear, 1978; Indares & Martingole, 1985; Easton, 2006). In an U-Pb geochronology study of the Mazinaw Domain, Corfu & Easton (1995) identified a major period of metamorphism and deformation between 1100 and 980 Ma.

Metamorphic zircon and monazite from Flinton Group metapelites northeast of Ompah (Fig. 2.2) yielded overlapping ages of 1020 ± 3 Ma (Corfu & Easton, 1995). However, details on the timing of metamorphic zircon and monazite growth along the prograde path of Grenvillian metamorphism are unknown.

Three phases of deformation are preserved in the Flinton Group. D₁ produced northeast trending isoclinal folds with variable plunge (Fig. 2.2). The pervasive foliation observed in the Flinton Group is parallel to the axial plane of D₁ (Moore & Thompson, 1980). D₂ was coaxial to D₁, refolding and tightening D₁ structures. D₁ and D₂ structures were then subsequently folded by D₃ producing open folds about a northwest trending axial plane (Moore & Thompson, 1980) (Fig. 2.2).

Busch et al. (1996) reported ⁴⁰Ar/³⁹Ar hornblende cooling ages in the Mazinaw Domain between 950 and 930 Ma. This suggests that the Flinton Group and Mazinaw Domain remained above the hornblende closing temperature late in the history of the Grenville Orogen. Wolczanski et al. (2013) reported ⁴⁰Ar/³⁹Ar muscovite cooling ages of 902 Ma further constraining the low temperature cooling history of the Flinton Group. Cooling rates of 1-4°C Ma⁻¹ across the Grenville Orogen were determined by Cosca et al. (1991). Uniformity in cooling rates across the entire Grenville Orogen was interpreted to represent a thermally relaxed crust, which may have existed during late Grenvillian metamorphism (Cosca et al., 1991). Although uniform cooling rates were determined across the Grenville orogen, large differences in cooling ages across domain boundaries are thought to represent differential uplift along major shear zones during post orogenic extension.

Representative metapelitic samples were collected from the Bishops Corner Formation and Myers Cave Formation between the Marble Lake and Ompah areas (Fig. 2.2; Table 2.1). P-T-t estimates from these samples will be discussed in this

communication and will be used to constrain the evolution of southeastern Ontario during the Grenville Orogeny.

2.3 Methods

2.3.1 WDXRFA

Wavelength-dispersive X-ray fluorescence analysis (WDXRFA) was used to determine the major element chemistry of the samples of this study. Samples approximately 10 x 10 x 10 cm in size, macroscopically devoid of chemical heterogeneities and alteration were crushed and fused for analysis. A Philips PW1400 X-ray fluorescence spectrometer was used to determine major element chemistry at Geoscience Laboratories, Sudbury (Ontario). Several samples were analyzed at the University of Ottawa (Ontario) on a Philips PW2400 X-ray fluorescence spectrometer. Major element chemistry for the studied samples is also provided in Table 2.1.

2.3.2 EPMA

Quantitative electron probe microprobe analyses (EPMA) were performed on garnet from samples 12TM16, 11TM14, 11TM18, 12TM5E, 11TM6D, 12TM10B and 12TM12 using a Cameca Camebax MBX electron microprobe at Carleton University, Ottawa (Ontario). EPMA traverses were performed at 20 μm resolution. Operating conditions included a 20 kV accelerating potential and a beam current of 20 nA. Peak counting time was 40s or 62500 counts for Ca, Fe, Mn, Mg, Si, Al and Ti whereas a 100s was used for Y. The Cameca PAP matrix correction was applied to convert counts into elemental weight %. Both natural and synthetic standards were used for internal calibration.

Table 2.1. GPS locations in NAD 83 and zone 18, and whole rock chemistry as determined by WDXRFA for the studied samples from the Bishops Corner Formation (B.C.) and Myers Cave Formation (M.C.). The average low-grade metapelite of Symmes & Ferry (1991) is provided for reference.

Sample	Formation	Easting	Northing	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	MnO	Na ₂ O	K ₂ O	L.O.I	Total
11TM14	B.C.	331098	4966674	62.72	17.26	1.16	9.38	0.06	0.12	1.04	0.69	4.34	2.66	98.43
11TM6A	B.C.	343240	4974702	55.82	22.81	1.39	15.59	0.44	0.06	0.03	0.48	1.19	0.94	98.77
11TM23	B.C.	347642	4976773	59.32	18.42	1.40	12.09	0.89	0.24	0.02	2.32	2.87	1.58	99.13
12TM16	M.C.	349762	4985022	57.28	18.16	1.11	12.56	2.01	1.12	0.16	0.34	4.27	2.37	100.77
11TM18	M.C.	331098	4966674	62.72	17.26	1.16	8.44	0.06	0.12	1.04	0.69	4.34	2.66	98.41
12TM5E	M.C.	332610	4967734	61.96	16.28	1.17	10.90	1.85	0.24	0.11	0.37	3.12	1.18	100.00
11TM6D	M.C.	334435	4968894	58.95	20.53	1.49	8.12	1.47	0.42	0.06	0.73	4.68	2.66	98.63
12TM10B	M.C.	349760	4985027	58.02	19.05	1.17	12.93	1.35	0.36	0.03	0.51	3.56	1.75	100.16
12TM12	M.C.	357110	4985828	59.15	19.72	0.90	6.98	1.99	2.67	0.10	4.38	2.12	1.86	100.64
Average*				59.77	16.57	--	5.88**	2.62	2.17	0.07	1.73	3.53	2.49	100.00

*Symmes & Ferry (1991)

** Reported as FeO

Qualitative element distribution maps for garnet and monazite from 12TM5E were prepared using a Cameca SX 100 electron microprobe at Geoscience Laboratories, Sudbury. Element distribution maps for garnet were prepared using an accelerating potential of 20 kV and a beam current of 200 nA. The $K\alpha$ line was measured for Mg, Mn, Fe and Ca and the $L\alpha$ was measured for Y. Counting time was 10ms/pixel over a pixel grid of 512 x 512. Element distribution maps for monazite were prepared using an accelerating potential of 20 kV and beam current of 200 nA. Wavelength dispersive spectroscopy was used to prepare element distribution maps for Ca, Th, Y, U and P while energy dispersive spectroscopy was used to prepare maps for La and Ce. $K\alpha$, $L\alpha$, $M\beta$, $K\alpha$ and $M\alpha$ were measured for Ca, Y, U, P and Th respectively. Ca and P were measured on PET, U and Th on LPET, and Y on LTAP crystals. Counting times of 40-50ms/pixel over a pixel grid of 256 x 192 were used to map monazite.

2.3.3 Trace element imaging of garnet and U-Pb monazite geochronology

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) trace element imaging of garnet and in situ LA-ICP-MS U-Pb monazite geochronology was performed at the University of New Brunswick using a Resonetics M-50-LR 193 nm laser ablation system coupled to an Agilent 770x quadrupole ICP-MS. Trace element distribution maps were prepared by a series of raster scans using a 60 μm crater and 10 Hz pulse rate, which were then integrated offline into concentration maps using the Iolite software (Paton et al., 2011). Light rare earth element (LREE) maps could not be

prepared due to the presence of allanite and monazite inclusions in garnet, which flooded the ICP-MS detector.

EPMA element distribution maps of 41 monazites were used to guide ablation pits. Both standards and unknowns were ablated using 6 μm diameter craters, a repetition rate of 4.5 Hz, a laser output of 90 mJ, and ablation time of 25s. Ablation sequences consisting of standards and unknowns were prepared. Three to five standards were analyzed for every one unknown. The following monazite standards were used: Trebilcock (Tomascak et al., 1996) that has a U-Pb ID-TIMS age of 272 ± 2 Ma and 44069 (Aleinikoff et al., 2006) that has an ID-TIMS age of 424 ± 0.4 Ma. VisualAge (Petrus & Kamber, 2012) was used to determine the most concordant portion of the analyses, which were identified by time slices with constant $^{207}\text{Pb}/^{235}\text{U}$, ^{206}Pb , ^{238}U and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Exported data were analyzed using Isoplot v.3.71 (Ludwig, 2003). Concordant ages for the monazite standards were reproduced using the same operating conditions as the unknowns, validating the accuracy of the calculated unknown ages.

2.3.4 Phase equilibria modeling and garnet isopleth thermobarometry

The THERIAK-DOMINO software package (de Capitani & Brown, 1987; de Capitani & Petrakakis, 2010) was used to calculate rock specific phase diagrams in the model system $\text{MnO}-\text{Na}_2\text{O}-\text{CaO}-\text{K}_2\text{O}-\text{FeO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2-\text{TiO}_2$. Calculations were made using the internally consistent thermodynamic database of Holland and Powell (1998) (THERMOCALC version 3.21) (see Appendix). The reader is directed to the Appendix for a description of the specific solution models used. It has been well documented that the presence of graphite during metamorphism may influence

the activity of water and stability of major silicates (e.g., Pattison, 2006). To account for such a phenomenon in graphite-bearing metapelites of the Myers Cave Formation, a graphite-buffered C-O-H fluid (Evans & Powell, 2006) was considered (D. Tinkham, personal communication). SiO_2 and H_2O were considered in excess for all calculations. To estimate the initial conditions of garnet growth and to calculate geothermal gradients, garnet isopleth thermobarometry (Evans, 2004; Gaidies et al., 2006) was applied to the cores of the largest garnet porphyroblasts identified in thin section for the garnet-bearing samples of this study.

2.4 Results

2.4.1 Petrography

Five samples from the Myers Cave Formation and three samples of the Bishops Corner Formation are described below in order of increasing metamorphic grade. Mineral abbreviations where used are after Whitney and Evans (2010) and are listed in the Appendix.

Three fabrics are present in the Flinton Group. The earliest fabric, S_0 , is now observed as linear inclusion trails of quartz and ilmenite in porphyroblastic phases such as garnet and biotite. S_1 is the pervasive foliation observed within the Flinton Group and is observed wrapping all porphyroblastic phases. S_0 inclusion trails lie at an angle to the S_1 foliation. A weak crenulation, S_2 , is also developed in all studied samples, refolding the S_1 foliation. Although not all fabrics are observed in the photomicrographs presented in Figures 2.3 and 2.4, they have been observed in all the studied samples. In particular the

orientation of some thin sections prevents direct observation of the crenulation S_2 . An example of the S_2 crenulation is shown in Figure. 2.3c.

Myers Cave Formation

12TM16

The rock matrix is composed of fine-grained Ph, Ilm, Qtz, Tur and Gph and together these phases form the foliation of the rock. The external foliation, S_1 , wraps Grt porphyroblasts. Grt porphyroblasts range up to 6 mm in diameter and are, to varying degrees, resorbed. Although found as an inclusion in Grt, Chl is not found in the matrix. Inclusions of Ilm, Rt, Chl and Qtz densely populate core regions of Grt and define linear inclusion trails which record an earlier fabric, S_0 . Inclusion trails are at a slight angle to the external foliation, S_1 . Alteration of Grt to Chl occurs along fractures. A weak crenulation, S_2 , is also observed. Bt porphyroblasts occur throughout the matrix and within large patches of randomly orientated coarse-grained Ph (Fig. 2.3a). In both the matrix and Ph patches, Ph can be found replacing Bt. Bt, in addition to Grt, deflects the pervasive foliation, S_1 . Diamond-shaped patches of coarse-grained Ph and Bt show sharp boundaries against the rock matrix and range in size up to 2 mm (Fig. 2.3a). Ph has no preferred orientation within the coarse-grained patches. Where in contact with the coarse-grained Ph patches, Grt porphyroblasts are resorbed. The diamond shape of the coarse-grained Ph patches is consistent with the cross sectional shape of St porphyroblasts. Evidence for the pseudomorphing of St by coarse-grained, randomly orientated Ph is provided in Figure 2.3b.

11TM18

Figure 2.3. Photomicrographs (plane polarized light) of Myers Cave Formation samples (A) 12TM16, (B) 11TM18 (C) 12TM5E, (D) 11TM6D, (E) 12TM10B and (F) 12TM12. Mineral abbreviations after Whitney & Evans (2010).

Ilm, Bt, Ph, Qtz, Tur and Gph define the S_1 foliation of the rock. Ilm has to varying degrees been replaced by Rt. Trace amounts of Chl are present in the matrix. Unlike 12TM16, a lower grade rock that has developed large Bt porphyroblasts, Bt in 11TM18 is considerably smaller, occurring as a foliated phase in the matrix. St porphyroblasts are up to 1 mm in size, are idioblastic, contain abundant Qtz inclusions and are commonly twinned (Fig. 2.3b). St porphyroblasts are generally aligned with the S_1 foliation and the foliation is observed wrapping St. Grt porphyroblasts are up to 2 mm in diameter and are slightly resorbed. The S_1 foliation wraps the Grt porphyroblasts (Fig. 2.3b). Inclusions of Qtz, Ilm, St and possible Chd have been observed in Grt. Inclusion trails lie at an angle to external foliation. St, Bt and Grt when in contact share straight grain boundaries. Small amounts of Py were also observed.

12TM5E

The rock has a well-developed foliation, S_1 , defined by the preferential alignment of Ph, Ilm, Qtz, Tur, Rt and Gph. A weak crenulation, S_2 , has also been observed. Common accessory phases include Zrn, Xtm, Aln and Mnz. Grt porphyroblasts are idioblastic and range in size up to 4 mm (Fig. 2.3c). The Grt porphyroblasts have inclusion rich cores with linear inclusion trails, S_0 , at a slight angle to the external foliation, S_1 . Ilm and Qtz are dominant as inclusions in Grt and rare Ph and St inclusions have been observed as well. The S_1 foliation is observed wrapping Grt porphyroblasts. Grt and Bt when in contact share straight grain boundaries. Bt form large, idioblastic porphyroblasts that range in size up to 2.5 mm. In a similar fashion to Grt, Bt contain inclusion trails that lie at a high angle to the S_1 foliation. The S_1 foliation wraps Bt porphyroblasts. An

interesting texture that Bt from this locality exhibits is the presence of hourglass inclusion zoning. Large diamond-shaped patches of randomly orientated Ph are common. Resorbed St is often found in the core of the Ph. Highly resorbed remnants of Bt occur throughout with St within coarse-grained Ph patches. The S_1 foliation wraps the Ph patches. Grt porphyroblasts show resorbed grain boundaries when in contact with Ph patches. Retrograde Chd is observed overgrowing the S_1 foliation.

11TM6D

The sample contains porphyroblasts of Grt, Bt and St set in a fine-grained matrix, which is dominated by Qtz with only small amounts of Pl, Ph and Ilm (Fig. 2.3d). The rock has a weakly developed foliation, S_1 , due to the lack of Ph. Trace Tur is also observed in the matrix. Grt porphyroblasts make up 15% of the rock, range up to 2 mm in diameter, range from weakly to moderately resorbed and have inclusion rich cores. The foliation where it can be observed is deflected by Grt. Inclusion trails in Grt are linear in the core but begin to curve near the rim. When in contact with St and Bt, Grt porphyroblasts are moderately resorbed (Fig. 2.3d). St and Bt when in contact share straight grain boundaries. St porphyroblasts make up 40% of the rock, range in size up to 5 mm in diameter and are commonly twinned. Inclusions of Qtz are common while rare Bt inclusions have also been observed. Bt porphyroblasts make up 30% of the rock, range in size up to 4 mm, are idioblastic and are generally inclusion free. Rare inclusions of Qtz and Ph have been observed. Ph has been observed replacing Bt in a few instances.

12TM10B

Bt, Pl and Qtz are abundant in the rock matrix along with lesser amounts of Ph, St, Rt, Tur, Mnz, Zrn and Ilm (Fig. 2.3e). Preferential alignment of Bt and prismatic Sil define the S_1 foliation. Grt porphyroblasts range up to 6 mm in diameter and are moderately resorbed and fractured (Fig. 2.3e). Along fractures Grt has been weakly chloritized. The S_1 foliation wraps around Grt porphyroblasts. Both Grt and Bt, and Grt and Sil share straight grain boundaries. Inclusions of Bt, Ilm, Rt and Qtz are common in Grt. Both matted patches and prismatic Sil are common (Fig. 2.3e). The slender prismatic Sil is aligned with the S_1 foliation of the rock while the matted aggregates appear to have no preferred orientation. Prismatic Sil has also been observed grading into more fibrolitic matted aggregates of Sil. St crystals are oval/circular in shape, generally less than 0.1 mm in diameter and although not common, are generally surrounded by Pl (Fig. 2.3e). Coarse-grained Ph overgrows the S_1 foliation and is observed replacing Bt.

12TM12

Porphyroblasts of Grt and Sil are set in a matrix of Ph, Bt, Tur and Pl (Fig. 2.3f). Ph and Bt define the S_1 foliation. Coarse grained, randomly orientated Ph can also be found partially replacing Bt. Grt porphyroblasts are large, ranging up to 6 mm in diameter, have resorbed grain boundaries and are wrapped by the S_1 foliation. Inclusions of Ilm, Rt and Bt are common in Grt. Grt can often be found semi surrounded by Bt, Qtz and Pl to form a corona. This corona often separates Grt from Sil. Large patches of prismatic Sil are common. In addition to Sil, Ky is also present as small blebs ranging up to 300 μm in diameter at the core of Sil patches. These aluminosilicate patches often form diamond shapes in thin section consistent with the cross sectional shape of St (Fig. 2.3f).

Bishops Corner Formation

11TM14

The rock contains porphyroblasts of Grt, Bt and Ky set in a fine-grained matrix of Ph, Afs, Chl, Mag, Tur and other accessory phases (Fig. 2.4a). The rock has a well-developed foliation, S_1 , defined by the preferential alignment of Ph, and Mag. The foliation wraps Bt, Grt and Ky. Grt porphyroblasts are 400-600 μm in diameter, idioblastic, have inclusion-rich cores and constitute less than 5% of the rock. Inclusion trails in Grt lie at a high angle to S_1 foliation. Inclusions of Qtz, Mag and Ph are common. Bt porphyroblasts range from 300 to 1000 μm in size. Inclusions of Qtz, Mag and Ph are common. Bt has irregular grain boundaries and to varying degrees has been chloritized. Some Bt crystals show anomalous green pleochroism. Ky porphyroblasts range up to 1000 μm in size and have ragged grain boundaries. The porphyroblastic phases constitute less than 20% of the rock.

11TM6A

The rock contains porphyroblasts of Ky, Bt and Pl set in a fine-grained matrix of Ph, Qtz, Mag and Tur (Fig. 2.4b). The rock has a well-developed foliation, S_1 , defined by the preferential alignment of Ph. Ky porphyroblasts range up to 12 mm in length and 2 mm in width, are commonly twinned, are idioblastic and are foliated but not lineated. Inclusion rich cores and inclusion free rims are observed. Rare Chl has been observed in contact with Ky. The S_1 foliation is observed wrapping Ky. Bt porphyroblasts range up to 2 mm in width, exhibit irregular grain boundaries and deflect the external foliation. Ph has also been observed replacing Bt and in some cases it appears that Pl replaces Bt.

Figure 2.4. Photomicrographs of Bishops Corner Formation (plane polarized light) (A) 11TM14, (B) 11TM6A and (C) 11TM23. Mineral abbreviations after Whitney & Evans (2010).

When Bt is in contact with Ky straight grain boundaries are observed. Mag ranges in size up to 1 mm in diameter. Pl ranges up to 2 mm in size, deflects the S_1 foliation and can easily be recognized by the high inclusion density. Pl is often found in close association with Ky and in some cases appears to be replacing Ky.

11TM23

The rock contains porphyroblasts of Ky, Bt and Ab set in a fine-grained matrix of Ph, Qtz, Mag and Tur (Fig. 2.4c). The rock has a pervasive foliation, S_1 , and well developed crenulation, S_2 , which are defined by the preferential alignment of Ph (Fig. 2.4c). Ky porphyroblasts are idioblastic and range up to 2 mm in width and 10 mm in length and are foliated but not lineated. The foliation is observed wrapping around Ky, and Qtz pressure shadows have been developed. Inclusions of Qtz and Mag are common. Rare Bt inclusions have also been observed. Bt and Ky share smooth grain boundaries. Ky porphyroblasts also occur as inclusions in Ab. Ab porphyroblasts range in diameter up to 3 cm. The S_1 foliation is observed wrapping Ab. Both simple and polysynthetic twins are observed and strained. The Ab grains are very inclusion rich with inclusions of Ky, Bt, Qtz, Ph, St, Mag and Tur. It is important to note that St is not observed in the rock matrix. An interesting texture that is commonly observed in the Ab is that Bt inclusions are preferentially resorbed at the contact with polysynthetic twins of Ab to form a “sawtooth” texture. The grain boundaries of Ab are inundated producing an irregular contact with the matrix. Bt porphyroblasts range up to 1 mm in diameter and have to varying degrees been chloritized. The S_1 foliation is observed wrapping the larger Bt porphyroblasts. Inclusions of Qtz and Mag are common. Kinked Bt has been observed which have the same

orientation as the S₂ crenulation. Mag in the matrix ranges up to 1.5 mm in diameter and is aligned with the S₁ foliation.

2.4.2 Garnet chemistry

EPMA traverses were performed on the largest Grt porphyroblasts identified in thin section in 11TM14, 12TM16, 11TM18, 12TM5E, 11TM6D, 12TM10B and 12TM12.

From hereafter Ca, Mn, Fe and Mg in Grt will be referred to as X_{grs} , X_{sps} , X_{alm} and X_{pyp} , where $X_{\text{grs}} = (\text{Ca}/(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg}))$, $X_{\text{sps}} = (\text{Mn}/(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg}))$, $X_{\text{alm}} = (\text{Fe}/(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg}))$ and $X_{\text{pyp}} = (\text{Mg}/(\text{Ca}+\text{Mn}+\text{Fe}+\text{Mg}))$.

Myers Cave Formation

12TM16

The compositional profile for the largest Grt identified in 12TM16 is presented in Figure 2.5a. X_{sps} decreases and X_{alm} and X_{pyp} increase from core to rim while X_{grs} remains approximately constant. X_{sps} is 0.073 in the core and smoothly decreases to 0.003 at the rim. X_{grs} is approximately 0.12 in the core and outward with a slight decrease observed at the rim. X_{pyp} increases gradually from 0.05 in the core to 0.08 at the rim. X_{alm} increases from core to rim from 0.75 to 0.81. No trends are observed in yttrium.

11TM18

The profile for the largest Grt identified in thin section from sample 11TM18 is shown in Figure 2.5b. X_{sps} and X_{grs} decrease while X_{alm} and X_{pyp} increase from core to rim. X_{sps} is homogenous in the core at 0.06 before decreasing gently toward the rim to 0.02. X_{grs} is homogenous in the core but shows slightly more scatter than X_{sps} . X_{grs} decreases toward the rim at 240 and 760 μm respectively. A slight shoulder in X_{grs} is

Figure 2.5. EPMA compositional profiles across the largest garnet porphyroblasts identified in thin section for (A) 12TM16, (B) 11TM18, (C) 12TM5E, (D) 11TM6D, (E) 12TM10B, (F) 12TM12 and (G) 11TM14. EPMA traverses were performed across the grains at 20 μm resolution.

observed at 850 μm and corresponds to a plateau in X_{alm} . X_{alm} is homogenous in the core before gently increasing toward the rim from 0.80 to 0.84 at 240 and 760 μm . Diffusional zoning is developed at the rim on the right hand side of the profile where X_{alm} increases and X_{pyr} decreases. X_{pyr} is homogeneous in the core before gently increasing toward the rim from 0.08 to 0.10. The core of the garnet has a broad Y enriched domain before decreasing toward the rim.

12TM5E

Due to the abundance of Mnz in 12TM5E as inclusions in Grt, EPMA element distribution maps were prepared for Grt porphyroblasts in 12TM5E to help better understand the origin of Y zoning. EPMA maps for the largest porphyroblast are shown in Figure 2.6 while Y maps for other analyzed porphyroblasts from 12TM5E are shown in Figure 2.7. X_{grs} decreases from core to rim. However, a steep decrease in X_{grs} occurs in a “half moon” fashion around the core (Fig. 2.6a). This region of Grt chemical zoning is not symmetrical (i.e., the X_{grs} in the NW portion of the crystal is unaffected) and is inclusion rich. X_{sps} , like X_{grs} , shows a decrease while X_{alm} behaves antithetically to both X_{grs} and X_{sps} in the “half moon” region, showing an abrupt increase (Fig. 2.6d). The inclusion rich half moon region is enriched in Y (Fig. 2.6e). Another interesting feature in the Y map is the presence of an yttrium annulus located just inward from the rim of garnet (Figs. 2.6e, 2.7). The annulus is approximately parallel to the crystal faces and is present in all analyzed porphyroblasts from 12TM5E (Figs 2.6e, 2.7).

The position of the EPMA traverse is shown in Figure 2.6b and the corresponding compositional profile is shown in Figure 2.5c. As seen in the element distribution maps,

Figure 2.6. EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for the porphyroblast identified in sample 12TM5E. The Y rich domain in (E) is outlined in (A) and (D). Bright white spots within the Y-rich core are xenotime inclusions. The compositional profile for 12TM5E was generated along the stippled line labelled A - B in (B).

Figure 2.7. EPMA distribution maps for Y in all analyzed garnet porphyroblasts from 12TM5E.

the EPMA traverse reveals a decrease in X_{sps} and X_{grs} from core to rim and an increase in X_{alm} and X_{pyp} . X_{sps} decreases from core to rim from 0.08 to 0. A slight shoulder in X_{sps} is observed at 1160 μm with no corresponding changes in the other elements analyzed. The most striking feature in X_{grs} from core to rim is the sharp decrease from 0.09 to 0.07 at 1990 μm . This decrease in X_{grs} is accompanied by a sharp increase in both Y from 300 to 3000 ppm and X_{alm} from 0.78 to 0.82. This observation suggests a petrological relationship between Ca, Fe and Y in garnet. Moving rim ward from the disruption at 1990 μm , X_{grs} plateaus until 2720 μm where it drops off toward the rim. A slight shoulder in X_{grs} is observed at 2900 μm and can be correlated to a small peak in Y. From this shoulder, X_{grs} drops off sharply toward the rim. On the left hand side of the profile away from the Y rich domain, decreases in X_{grs} are observed at 870 and 600 μm respectively. X_{alm} , like X_{grs} , is strongly affected by the Y rich domain of garnet. Moving away from the Y domain toward the rim, X_{alm} increases at 2680 μm from 0.84 to 0.86. At 2900 μm a slight trough in X_{alm} occurs before X_{alm} increases continuously toward the rim. This trough is correlated to a shoulder in X_{grs} and a peak in Y. On the left hand side of the profile moving toward the rim X_{alm} increases from 0.79 to 0.81 at 890 μm . Moving rim ward of this feature, X_{alm} plateaus from 800 to 600 μm . At 600 μm X_{alm} continuously increases toward the rim from 0.81 to 0.88. The increase in X_{alm} from 0.86 to 0.88 in the outermost 20 μm on either side of the profile is mirrored by a decrease in X_{pyp} . X_{pyp} is homogenous in the core of the crystal, increasing gently toward the rim from the core from 0.04 to 0.09. The Y domain does not affect X_{pyp} .

11TM6D

The profile for the largest Grt identified in thin section in sample 11TM6D is shown in Figure 2.5d. In comparison to other Myers Cave Formation Grts that were analyzed, Grt in this sample shows much flatter compositional gradients from core to rim. X_{sps} , X_{grs} and X_{pyp} from core to rim are 0.08, 0.06 and 0.13 respectively. A peak in X_{grs} is observed at 2000 μm and is mirrored by a trough in X_{alm} . X_{alm} is homogenous in the core at 0.71 before gently increasing to 0.75 at the rim. The increase in X_{alm} at the rim is mirrored by a decrease in X_{pyp} . The Grt has a broad Y enriched core from which the Y content decreases gently toward the rim from 1500 to 100 ppm.

12TM10B

The EPMA profile for the largest Grt identified in thin section from sample 12TM10B is shown in Figure 2.5e. X_{sps} , X_{grs} , X_{pyp} and X_{alm} are 0.03, 0.04, 0.14 and 0.80 from core to rim respectively. A slight increase in X_{alm} is observed at the rim and is mirrored by a decrease in X_{pyp} . No discernible trends in Y are observed.

12TM12

The EPMA profile for the largest Grt identified in thin section from sample 12TM12 is shown in Figure 2.5f. X_{sps} is homogeneous from core to rim at 0.002. Slight zoning is observed for X_{grs} , where X_{grs} decreases from 0.013 to 0.009 from core to rim. A peak in X_{grs} is observed at 2580 μm and correlates to trough in X_{alm} . X_{alm} is approximately 0.90 in the core before gently increasing toward the rim at 1740 and 5640 μm respectively to 0.91. X_{pyp} is homogeneous from core to rim at 0.08 until the rim where a slight decrease is observed from 0.082 to 0.077. This decrease in X_{pyp} is mirrored by an increase in X_{alm} . No discernible trends in Y are observed.

Bishops Corner Formation

11TM14

The profile for the largest Grt identified in 11TM14 is shown in Figure 2.5g. The analyzed Grt is 600 μm in diameter, idioblastic and contains abundant inclusions in its core. The distinctly high X_{sps} of 0.30 and low X_{alm} of 0.50 distinguish this garnet from other analyzed Grts from the Flinton Group. X_{grs} , X_{pyr} , and X_{sps} are homogeneous throughout the crystal whereas some scatter is observed for X_{alm} . The concentrations of X_{sps} , X_{alm} , X_{grs} and X_{pyr} are 0.3, 0.5, 0.07 and 0.13 respectively. Diffusional profiles have developed in the outer 20 μm where X_{alm} and X_{sps} increase and X_{grs} and X_{pyr} decrease. The Y concentration of the garnet is 4000 ppm in its core and decreases sharply toward the rim at 60 and 560 μm respectively to 500 ppm.

2.4.3 Phase equilibria modeling and P-T constraints

Equilibrium phase diagrams and isopleths for Grt (if present) were calculated using the whole rock chemistry provided in Table 2.1 for each of the samples.

Myers Cave Formation

12TM16

The observed mineral assemblage of this rock is composed of Pl, Ilm, Grt, Ph, Bt, St, Gph and Qtz. The stability field for this assemblage is highlighted in dark grey in Figure 2.8a. The assemblage is predicted to be stable over 3.5 to 5.6 kbar and 540 to 615°C. An area of isopleth intersection was generated using the core composition of the largest Grt (Table 2.2) slightly away from the Grt in curve spanning less than ca. 10°C and 0.4 kbar (Fig. 2.8f). The intersection occurs in the stability field of (2)Pl, Ilm, Grt, Ph, Chl, Bt,

Table 2.2. Core chemistry of the largest garnet porphyroblasts identified in select Flinton Group samples as determined by EPMA analysis. All Fe is assumed to be Fe²⁺. These spot analyses were used for garnet isopleth thermobarometry (Figs. 2.8f, 2.9f, 2.10f).

Sample	12TM16	11TM18	12TM5E	11TM6D	12TM10B	12TM12	11TM14
SiO ₂	36.25	37.14	37.00	37.40	37.92	36.49	36.84
Al ₂ O ₃	20.38	20.98	20.73	21.92	21.26	20.72	20.32
TiO ₂	0.21	0.01	0.08	0.09	0.00	0.00	0.08
FeO	34.26	35.34	34.48	31.88	35.34	39.24	22.30
MgO	1.27	2.03	0.93	3.40	3.45	1.98	3.31
CaO	4.25	1.84	3.23	1.98	1.27	0.44	2.31
MnO	3.25	2.57	3.76	3.67	0.02	0.10	12.84
Total	99.96	99.59	100.21	99.53	100.62	99.01	99.59
Oxygen	24	24	24	24	24	24	24
Si	5.92	6.01	6.01	6.02	6.04	6.00	6.02
Al	3.88	3.96	3.93	3.94	3.95	3.97	3.87
Ti	0.02	0.00	0.00	0.01	0.00	0.00	0.01
Fe ²⁺	4.68	4.78	4.68	4.29	4.70	5.39	3.05
Mg	0.31	0.49	0.22	0.81	0.82	0.48	0.80
Ca	0.74	0.32	0.56	0.34	0.21	0.07	1.77
Mn	0.45	0.35	0.51	0.50	0.18	0.01	12.96
X _{alm}	0.756	0.804	0.782	0.721	0.794	0.902	0.501
X _{pyp}	0.050	0.083	0.037	0.137	0.014	0.081	0.134
X _{grs}	0.012	0.054	0.094	0.057	0.037	0.013	0.067
X _{sps}	0.073	0.059	0.086	0.084	0.030	0.002	0.294

Qtz, Gph and H₂O. (2)Pl refers to the unmixing of plagioclase into an albite-rich and anorthite-rich phase. Taking the middle point of the intersection, initial Grt growth is estimated at 4.0 kbar and 512°C (Fig. 2.8f)

11TM18

The observed mineral assemblage of this rock is Pl, Ilm, Grt, Ph, Bt, St, Qtz and Gph. The predicted stability field for this mineral assemblage is highlighted in dark grey in Figure 2.9a. The mineral assemblage has a large stability field in P-T space from 2.6 to 7.5 kbar and 520 to 650°C. Using the X_{alm}, X_{grs} and X_{sps} isopleths, an area of isopleth intersection was generated slightly away from the Grt in curve spanning 20°C and 0.8 kbar within the stability field of Pl, Ilm, Grt, Chd, Chl, Ph and Bt (Fig. 2.9f). Taking the middle point of the area of isopleth intersection, the initial conditions of garnet growth are estimated to be 3.7 kbar and 520°C.

12TM5E

12TM5E contains Pl, Ilm, Grt, Ph, Bt, St, Qtz and Gph. The stability field for this predicted assemblage occurs over the P-T interval 3.7-7.5 kbar and 530 to 640°C (Fig. 2.10a). In addition to 12TM5E, 5 other samples were collected at the same locality. All samples contain the same mineral assemblage and exhibit identical textures to that of 12TM5E. Whole rock chemistry and equilibrium phase diagrams for the 5 additional samples can be found in the Appendix. Figure 2.10f illustrates the positions of the mineral assemblage stability fields for the 5 samples. The mineral assemblage stability field is constrained to 4.5 to 6.8 kbar and 540 to 620°C by overlapping the different samples. A tight area of isopleth intersection within 2°C of the Grt in curve was obtained

Figure

2.9. (A) Equilibrium phase diagram, (B-E) garnet isopleths and (F) isopleth intersection calculated for sample 11TM18. The stability field of garnet-bearing assemblages in (A) and (F) is highlighted in light grey. The observed mineral assemblage in this rock and isopleth intersection are highlighted in dark grey in (A) and (F) respectively

Figure 2.10. (A) Equilibrium phase diagram, (B-E) garnet isopleths and (F) isopleth intersection calculated for sample 12TM5E. The stability field of garnet-bearing assemblages in (A) and (F) is highlighted in light grey. The observed mineral assemblage in this rock and isopleth intersection are highlighted in dark grey in (A) and (F) respectively. In addition to 12TM5E, 5 additional samples were collected. The observed mineral assemblage fields for the different samples are overlapped in (F). The dark grey area represents the P-T area common to all the samples at this locality.

using the garnet core X_{alm} , X_{grs} and X_{sps} (Fig. 2.10f). The isopleth intersection occurs within the phase assemblage Pl, Ilm, Grt, Chl, Ph, Qtz and Gph. Taking the middle point of the isopleth intersection area the initial P-T conditions of garnet growth are estimated at 3.7 kbar and 515°C.

11TM6D

The rock sample contains Pl, Ilm, Grt, Bt, St, Ph, Qtz and Gph. The stability field for this predicted assemblage occurs over the P-T interval 4.1 to 7.5 kbar and 580 to 670°C (Fig. 2.11a). A tight area of isopleth intersection could not be generated using the core chemistry of the largest Grt (Table 2.2).

12TM10B

The mineral assemblage of 12TM10B contains Pl, Ilm, Grt, Bt, Sil, Qtz and Gph and is predicted to occur between 2.5 to 5.0 kbar and 590 to 690°C as highlighted in Figure 2.12a. A tight area isopleth intersection could not be generated for 12TM10B using the core chemistry of the largest garnet.

12TM12

12TM12 contains Pl, Ilm, Grt, Ph, Bt, Ky, Sil, Qtz and Gph. The mineral assemblage, excluding Ky, is predicted between 5.5 and 7.9 kbar and 620 and 715°C (Fig. 2.13a). A Ky-bearing assemblage is predicted over a small P-T window from 6.4 to 7.9 kbar and 640 and 700°C. The Ky-Sil transition is predicted between 6.4 and 7.9 kbar and 640 and 700°C. Evidence for partial melting was not observed.

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11TM14

Figure 2.11. (A) Equilibrium phase diagram and (B-E) garnet isopleths calculated for sample 11TM6D. The stability field of garnet-bearing assemblages in (A) is highlighted in light grey while the observed mineral assemblage in this rock is highlighted in dark grey.

Figure 2.12. (A) Equilibrium phase diagram and (B-E) garnet isopleths calculated for sample 12TM10B. The stability field of garnet-bearing assemblages in (A) is highlighted in light grey while the observed mineral assemblage in this rock is highlighted in dark grey. The dotted line in (A) represents the solidus.

Figure 2.13. (A) Equilibrium phase diagram and (B-E) garnet isopleths calculated for sample 12TM12. The stability field of garnet-bearing assemblages in (A) is highlighted in light grey while the observed mineral assemblage in this rock is highlighted in dark grey. The dotted line in (A) represents the solidus.

11TM14 contains the mineral assemblage Pl, Mag, Grt, Ph, Bt, Ky and Qtz. This mineral assemblage is not predicted over the modeled P-T interval 2.5 to 7.5 kbar and 450 to 650°C (Fig. 2.14a). In addition to the observed mineral assemblage it is interesting to note that Ky is not predicted to be part of the stable mineral assemblage anywhere over the modeled P-T range. Grt isopleths corresponding to the measured core X_{alm} , X_{sps} , and X_{pyr} are also not predicted over the modeled P-T interval (Fig. 2.14b-e). The predicted Grt compositions over the P-T range modeled have higher X_{alm} and lower X_{sps} and X_{pyr} than the observed (Figs. 2.5g).

11TM6A

11TM6A contains the mineral assemblage Pl, Mag, Grt, Ph, Bt and Qtz. This mineral assemblage is not predicted over the modeled P-T range of 2.5 to 7.5 kbar and 450-650°C (Fig. 2.15a). Moreover, Ky is not predicted to occur anywhere over the modeled P-T interval. Because the sample does not contain Grt, Grt isopleths were not calculated.

11TM23

Sample 11TM23 contains Ab, Mag, Ky, Ph, Bt and Qtz. The observed mineral assemblage is not predicted over the modeled P-T interval (Fig. 2.15b). Ky was not predicted to be stable over the modeled P-T interval. Because the sample does not contain Grt, Grt isopleths were not calculated.

2.4.4 Accessory phase distribution

Figure 2.14. (A) Equilibrium phase diagram and (B-E) garnet isopleths for sample 11TM14. The stability field of garnet-bearing assemblages in (A) is highlighted in light grey. The observed mineral assemblage was not predicted over the modeled P-T range. An isopleth intersection could not be generated due to major differences between predicted and observed garnet chemistry.

Figure 2.15. Equilibrium phase diagram calculated for samples (A) 11TM6A and (B) 11TM23. The stability field of garnet-bearing assemblages in both diagrams is highlighted in light grey. The observed mineral assemblages were not predicted over the modeled P-T range.

Due to the abundance of monazite as inclusions in garnet of 12TM5E this sample was chosen to carefully characterize accessory phases, their distribution and their relationship to trace element zoning in garnet to understand the formation of monazite.

In addition to monazite, xenotime, allanite, zircon and apatite are common accessory phases in 12TM5E. Apatite and zircon occur ubiquitously throughout the sample in both the matrix and as inclusions in porphyroblastic phases. Xenotime and allanite are found as inclusions in garnet and are absent from the matrix or as inclusions in other phases (Fig. 2.16). Monazite is common in the matrix and is found as inclusions in the outer 250 μm of garnet porphyroblasts (Fig. 2.16b). Monazite was not observed included in any other phase.

The distribution of xenotime, allanite and monazite in garnet is systematic. Xenotime occurs as inclusions less than 10 μm in diameter in Y enriched core domains in garnet (Fig. 2.16a). The Y rich domains, which range between 3500 and 5000 ppm, do not coincide with the geometric core of the crystal but as distinct domains surrounding the core (Fig. 2.6e). Traversing toward the rim away from the Y rich domains, the Y concentration drops sharply and xenotime can no longer be found in garnet. Approximately 250 μm inwards of the rim a Y annulus is observed (Figs. 2.5c, 2.6e, 2.7).

Allanite is observed as inclusions in garnet ranging up to 80 μm in diameter (Fig. 2.16c). In general the allanite inclusions have ragged grain boundaries and are often surrounded by radial cracks. Allanite inclusions are observed from the core outward to the Y annulus near the rim, although allanite was never observed within the Y-rich core domains. It is important to note that allanite inclusions are only observed on the core-

Figure 2.16. Backscattered electron (BSE) images showing accessory phase distribution in 12TM5E. (A) Xenotime inclusions in garnet are restricted to Y-rich domains near the core. Xenotime inclusions can also be observed in Figure 2.6e. (B) Allanite occurs commonly in the core regions of garnet outward rim-ward to the Y annulus. An allanite inclusion in garnet can also be observed in Figure 2.6e. (C) Monazite inclusions are common in the outer 200 µm of garnet, rim-ward of the Y annulus, and in the matrix. (D) Allanite inclusion in garnet with radial cracks emanating away which are filled with monazites.

ward side of the Y annulus. On the rim-ward side of the Y annulus inclusions of monazite are common. Monazite has been observed in radial cracks emanating away from allanite inclusions in garnet (Fig. 2.16d). Monazite also occurs as a foliated phase within the rock matrix.

2.4.5 Trace element zoning in garnet

In addition to Y zoning determined through EPMA analysis, trace element distribution maps were prepared using LA-ICP-MS for one representative Y-zoned garnet to help interpret the origin of Y zoning and the formation of monazite.

The Y rich domain semi-surrounding the core of garnet (Fig. 2.17e) is enriched in the heavy rare earth elements (HREE) Lu, Dy, Er, and Yb (Fig. 2.17a-d). Traversing away from the Y-HREE enriched domain toward the rim, the Y-HREE concentration drops sharply. Approximately 150-250 μm inwards from the rim an Y annulus is observed (Figs. 2.6e, 2.7, 2.17e). The annulus is also enriched in the HREEs Lu, Dy, Er and Yb, and the MREE Gd (Figs. 2.17a-f). Sc is enriched in the core of the garnet but is depleted in the Y-HREE rich “half moon” regions. Sc gradually decreases toward the rim until the Y-HREE annulus where it drops sharply (Fig. 2.17g).

2.4.6 Monazite U-Pb geochronology

On average the monazites are 25 x 35 μm in size and have a slightly elongated shape. Representative EPMA X-ray maps are shown in Figure 2.18. It is important to note that the zoning patterns of monazites included in garnet and the matrix are identical. The cores of monazite are enriched in Ca and Th and depleted in LREE and Y. Surrounding the monazite core is a ring of Y enrichment from which Y gradually decreases toward the

Figure 2.17. Trace element distribution maps for (A) Er, (B) Dy, (C) Yb, (D) Lu, (E) Y, (F) Gd and (G) Sc in one representative rare earth element (REE)-zoned garnet from 12TM5E as determined by LA-ICP-MS.

Figure 2.18. Representative EPMA element distribution maps for monazites from 12TM5E. Brighter colors represent higher concentrations. (A) and (B) are monazites in the matrix while (C) and (D) are included in garnet. The chemical zoning in either type of monazite is identical. An apatite inclusion in monazite is present in (D).

rim. The monazites commonly have small inclusions of apatite (Fig. 2.18c). Seventy-five spot analyses were performed on monazites included in the rim of garnet and in the matrix (see Appendix). Data greater than $\pm 2\%$ discordant were discarded, leaving 41 concordant data points. Poor placement of 6 μm ablation pits on small monazite grains was a major source of error (i.e., partially missing grains). Three age populations were identified (Fig. 2.19a-c). A small population defined by three analyses is present at 1015 ± 15 Ma with a MSWD value of 0.17 and probability of concordance of 0.68 (Fig. 2.19a). A large population containing 30 analyses is present at 977 ± 4 Ma with a MSWD value of 0.04 and a probability of concordance of 0.95 (Fig. 2.19b). A third monazite age population, defined by three analyses, is present at 956 ± 10 Ma with an MSWD value of 0.04 and a probability of concordance of 0.83 (Fig. 2.19c).

2.5 Discussion

2.5.1 P-T estimates of metamorphism

Assuming an average crustal density ranging from that of a granite to a basalt (2.7 to 3.0 g cm^{-3}) (Spear, 1993) geothermal gradients may be estimated using the initial P-T conditions of garnet crystallization obtained in this study. Geothermal gradients of $34\text{-}38^\circ\text{C km}^{-1}$, $37\text{-}41^\circ\text{C km}^{-1}$ and $37\text{-}41^\circ\text{C km}^{-1}$ were calculated for samples 12TM16, 11TM18 and 12TM5E respectively. Several thermo-mechanical processes may explain the high geothermal gradient recorded by Flinton Group metapelites. Crustal delamination and upwelling of hot asthenosphere during eastward migration of the subduction zone following the Shawinigan Orogeny (ca. 1190-1140 Ma) may have provided additional heat flow. Such an event could raise geotherms within the continental

Figure 2.19. Concordia diagrams for three age populations, (A) 1015 ± 15 Ma (B) 977 ± 4 Ma and (C) 956 ± 10 Ma, in monazite as determined by in situ LA-ICP-MS using 6 μm ablation pits on 41 monazites from 12TM5E

crust leading to elevated geothermal gradients. The Midcontinent rift system, active between 1100-995 Ma (White, 1997), was suggested by Carr et al. (2000) to have potentially played an important role at elevating the crustal geotherm underneath the Grenville Orogen. It is interesting to note that the cessation of the Midcontinent rift system coincides with the initial stages of the Grenville Orogeny (Carr et al. 2000). The extensional basin in which the Flinton Group was deposited (Easton & Ford, 1991) may have also played an important role at elevating crustal geotherms. The similarity in the initial conditions of garnet crystallization along the field area may be a result of the crust's ability to thermally relax following tectonic perturbation (Spear, 1993). It is well understood that tectonic processes operate on timescales orders of magnitude faster than the ability of thermal gradients to be relaxed. During a long, slow orogenic event such as the Grenville Orogeny, it may have been possible for the crust to maintain or approach thermal equilibration. Cosca et al. (1991) suggested that late in the history of the Grenville Orogeny, stable isotherms existed across the Grenville Orogen. Stable isotherms may have existed earlier in the history of Grenville Orogeny at the time of initial garnet growth, giving rise to similar P-T conditions of incipient garnet crystallization at different points along the study area.

Based on the assumption that the phase assemblage stability fields may not shift significantly during chemical fractionation associated with garnet growth in the calculated equilibrium phase diagrams, the peak metamorphic P-T conditions, in addition to the initial conditions of garnet growth, may be estimated.

For samples 12TM16, 11TM18, 12TM5E and 11TM6D the mineral assemblages observed in thin section are interpreted to represent peak metamorphic conditions. Although staurolite in both 12TM16 and 12TM5E is replaced by coarse-grained, randomly orientated white mica, staurolite is considered part of the peak mineral assemblage. The mineral assemblage in 12TM16 occurs over a limited P-T window, constraining the peak P-T conditions to 3.5 to 5.6 kbar and 540 to 615°C (Fig. 2.8a). In contrast the mineral assemblage in 11TM18 is predicted over a wider range of P-T space, 2.6 to 7.5 kbar and 520 to 650°C (Fig. 2.9a). As previously mentioned, 5 samples were collected at the sample locality of 12TM5E. Because no structural discontinuities were documented within the outcrop, it is assumed that all samples experienced the same P-T history. By overlapping the phase assemblage fields the peak P-T conditions are constrained to 4.5 to 6.8 kbar and 540 to 620°C (Fig. 2.10f). Because 11TM18 is from a location between 12TM16 and 12TM5E and no structural breaks are documented, the maximum pressure and temperature experienced by 11TM18 may be constrained to below 6.5 kbar and 620°C. The mineral assemblage in 11TM6D is predicted over a narrow P-T range, constraining the peak metamorphic conditions to 4.1 to 7.5 kbar and 580 to 670°C. It is also suggested that the samples evolved along P-T paths emanating away from their area of isopleth intersection into the stability fields of the mineral assemblages they now preserve. In doing so several important reactions must have been crossed in order to account for the differences between the observed peak mineral assemblages and the mineral assemblages in which garnet was initially predicted to grow.

Due to the homogeneous nature of garnet's from Fernleigh (Fig. 2.2) and to the northeast including samples 11TM6D, 12TM10B and 12TM12, it is interpreted that due to high temperatures, growth zoning in the garnet porphyroblasts has been relaxed due to efficient intracrystalline diffusion. Due to the equilibrated nature of these garnet's, robust isopleths intersections could not be generated. However, by coupling careful petrographic observations and phase equilibria modeling, some important P-T constraints may be inferred for these samples.

Although staurolite and white mica were observed in thin section, neither is interpreted to be part of the peak mineral assemblage in 12TM10B (Figs. 2.3e, 2.12a). Staurolite was observed as small (<0.1 mm) oval shaped crystals and appears to have been consumed during prograde metamorphism (Fig. 2.3e). White mica is coarse grained and lies at high angle to the foliation and like staurolite constitutes a very small portion of the rock. White mica is interpreted to have grown under static conditions during cooling. To help understand observed textures and to better constrain the P-T evolution of the sample, two P-T paths labeled in Figure 2.12a were modeled across important reactions (Fig. 2.20). Model P-T path A starts in the stability field of Pl, Ilm, Grt, Ph, Bt, St, Qtz and Gph and moves across the staurolite-out reaction into the stability field of Pl, Ilm, Grt, Ph, Sil, Qtz and Gph. Sillimanite is predicted to enter the stable mineral assemblage at the expense of staurolite and white mica (Fig. 2.20a). Staurolite and sillimanite coexist over a temperature interval of 1-2°C before staurolite is completely consumed. The presence of small isolated staurolite blebs in sample 12TM10B is consistent with numerical modeling results where staurolite is consumed during prograde heating.

Staurolite breakdown is also accompanied by growth of garnet. The following reaction is inferred, $St = Sil + Grt + H_2O$.

Model P-T path B for 12TM10B starts in the stability field of the assemblage Pl, Ilm, Grt, Ph, Bt, Sil, Qtz and Gph and crosses the white mica-out reaction into the stability field of the assemblage Pl, Ilm, Grt, Bt, Sil, Qtz and Gph (Fig. 2.12a, 2.20b). White mica and garnet are predicted to be consumed at the expense of sillimanite and biotite (Fig. 2.20b). The following reaction, $Ph + Grt = Bt + Sil$, is inferred. Garnet porphyroblasts are resorbed in 12TM10B, consistent with model results along PT path B.

The absolute P-T conditions at which the rock experienced these reactions are not known but from petrographic observations and P-T modeling it is inferred that they took place during prograde metamorphism. The absence of sanidine constrains the metamorphic peak conditions to temperatures below 690°C (Fig. 2.12a). It is also inferred that the rock did not experience pressures exceeding 7.0 kbar based on the previous presence of a staurolite-bearing assemblage.

The mineral assemblage in 12TM12 consists of Pl, Ilm, Grt, Ph, Bt, Ky, Sil, Gph and Qtz. In contrast to 12TM10B where white mica is inferred to have been consumed during prograde growth of sillimanite and staurolite, white mica is widespread and forms part of the foliation in 12TM12, which is why it is interpreted to be part of the prograde assemblage. Although kyanite was observed in thin section it is not interpreted to be part of the peak metamorphic assemblage as it forms <400 µm blebs at the heart of sillimanite clots (Fig. 2.3f). These clots are often diamond in shape, which is consistent with the cross-sectional shape of staurolite. It is interpreted that sillimanite grew at the expense of

Figure 2.20. Model results along P-T paths across the (A) Sil-in and (B) Ph-out reactions for 12TM10B (see P-T path A and B in Fig. 2.12a). Modal abundance the major silicate phases is plotted against temperature.

kyanite and that kyanite initially grew at the expense of staurolite to form a pseudomorph texture. The Ky-Sil transition is predicted over a limited P-T window, 6.4 to 7.9 kbar and 640 to 700°C (Fig. 2.13a). Segments of a P-T path corresponding to the inferred mineral reactions are sketched in Figure 2.13a. The initial reaction involves kyanite growth at the expense of staurolite and the second reaction is the Ky-Sil transition. No evidence of partial melting was observed constraining the peak conditions experienced by 12TM12 to temperatures below 715°C and pressures below 7.9 kbar based on the stability fields of staurolite and kyanite-bearing assemblages.

Based on these findings, peak metamorphic P-T conditions in the Flinton Group are estimated to increase from Marble Lake to Ompah from 615 to 715°C and 5.6 to 7.9 kbar over a distance of 40 km (Fig. 2.20). The increase in peak conditions across the field area probably represents differential uplift of the Mazinaw Domain.

2.5.2 Origin of trace element zoning in garnet

Xenotime and allanite's absence from the matrix of 12TM5E suggests prograde consumption of the phases and preferential preservation in garnet. The presence of xenotime inclusions and high concentrations of HREE in the Y-rich domain of garnet (Figs. 2.6e, 2.16a) is consistent with prograde consumption of xenotime (Pyle & Spear, 1999). The initial increase in Y away from the core from 250 to 3000 ppm (Fig. 2.5c) is interpreted to represent the breakdown of xenotime. Consumption of xenotime would release both Y and HREEs for garnet. The following drop in Y is interpreted to represent the removal of xenotime, a Y-buffering phase, from the stable mineral assemblage. Any remaining Y in the rock would partition between garnet and other Y-bearing phases.

Xenotime's breakdown may be accompanied by growth of allanite, as signified by the associated changes in X_{grs} and X_{alm} across the Y-rich "half moon" regions near the core. These observations are consistent with those of others. For example Pyle and Spear (1999), in an investigation of major and accessory phase reactions in mica schists of the Appalachians, found that initial garnet growth was contemporaneous with xenotime breakdown, leading to the development of garnet porphyroblasts with Y rich cores sprinkled with xenotime inclusions. It is suggested here that xenotime breakdown was not contemporaneous with initial garnet growth giving rise to a Y-HREE poor garnet core. Instead it is suggested that xenotime breakdown initiated soon after initial garnet growth producing the observed region of Y-HREE enrichment sprinkled with xenotime inclusions around the garnet core (Figs. 2.5c, 2.6e, 2.7, 2.17).

The presence of Y annuli is a common phenomenon in medium grade metapelitic garnet and several interpretations have been offered (e.g., Pyle & Spear, 1999; Kohn & Malloy, 2004; Yang & Pattison, 2006). Several mechanisms of Y annulus formation were originally discussed by Lanzirotti (1995) including open system-fluid infiltration, continuous growth zoning by a single reaction, resorption and regrowth of garnet, changes in the growth rate of garnet and breakdown of Y-enriched phases.

Open system-fluid infiltration and introduction of a Y-rich fluid is unlikely in the case of the Flinton Group. Other than rare late pegmatites that crosscut the Flinton Group a fluid source to enrich the Flinton Group in Y is unknown. The tight area of isopleth intersection for 12TM5E argues against metasomatism. If the thermodynamically relevant bulk rock composition from which garnet grew was significantly altered through

Figure 2.21. Geologic map of the Flinton Group and P-T estimates derived from the samples of this study. Initial conditions of garnet growth determined in 12TM16, 11TM18 and 12TM5E are bolded. Peak P-T estimates are not bolded.

metasomatism during or after garnet growth than the bulk composition used to calculate equilibrium phase diagrams and isopleths for garnet would fail to yield such a robust isopleth intersection. However to rule out this possibility completely, detailed fluid-rock and isotope studies would be required.

If Y diffusion across the rock is slow than the availability of Y at the surface of the growing garnet crystal will be strongly controlled by the growth rate of garnet and the diffusion rate of Y. Gaidies et al. (2008A) predicted that the radial growth rate of garnet may decrease during crystallization. This finding is consistent with the observation that the cores of garnet crystals are generally inclusion rich and that the inclusion density decreases from core to rim. If the radial growth rate of garnet decreases with time and if Y diffusion across the rock volume is slow than an asymmetric annuli may be expected. This is not consistent with the observation of a sharp Y annulus, which occurs over a very narrow radial range in garnet. A very sudden reduction in the radial growth rate of garnet may produce such a steep Y annulus. Concentric Y zoning would not be expected if Y diffusion was slow relative to the moving garnet-matrix interface. Instead, Y zoning in garnet would be strongly controlled by the local supply of Y leading to asymmetric zoning. A highly symmetric Y annulus is observed in every analyzed garnet from 12TM5E (Fig. 2.7).

Resorption and regrowth of garnet may be a potential explanation for the presence of the Y annulus in garnet. The Y annulus is enriched in HREEs (Figs. 2.17a-d). In metapelitic rocks the major sinks for HREEs are garnet, xenotime and zircon. Assuming xenotime has been previously consumed during earlier garnet growth it is unlikely that

xenotime played a role in the formation of the Y-HREE-Gd annulus. Zircon is ubiquitous in sample 12TM5E, occurring as inclusions in garnet and as a phase in the matrix. There is no obvious textural relationship between zircon and the annulus. Garnet is known to be a large repository for HREEs (Jaffe, 1951). It is expected that resorption of garnet may release both Y and HREEs. If garnet were to resume growth such an annulus may form. Major silicate reactions, in particular reactions involving staurolite, have been identified in several studies (e.g., Pyle & Spear, 1999; Kohn & Malloy, 2004) as a mechanism for garnet resorption and Y annuli formation. Based on resorbed grain boundaries between white mica pseudomorphs after staurolite and garnet, staurolite is interpreted to have grown at some point at the expense of garnet. The presence of staurolite inclusions well inside the Y annulus suggests that staurolite formed at an earlier point in growth history of garnet and not the point of Y-annulus formation. However, it is possible that a second generation of staurolite or another major silicate may have also formed at the expense of but textural evidence for such an event is lacking.

Another potential annuli forming mechanism is the breakdown of an Y-rich accessory phase. The presence of allanite core-ward and monazite rim-ward of the Y annuli suggests they are related to the observed Y zoning in garnet. Hickmott and Spear (1992), in an investigation of trace element zoning in garnet found that the breakdown of clinozoisite causes increases in Y, Zr and HREE in garnet, in particular if clinozoisite had an allanitic core. In their study Y, Zr and MREE/HREE increased in garnet during clinozoisite breakdown while Sc and X_{grs} decreased. It is important to note that the Y annulus, in addition to HREE, is enriched in Gd and that Sc sharply decreases at the

annulus (Fig. 2.17f-g). In Figure 2.5c, a slight shoulder in X_{grs} and drop in X_{alm} is developed at the yttrium annulus before X_{grs} decreases and X_{alm} increases sharply toward the rim. Both of these features are consistent with clinozoisite/allanite consumption (Hickmott & Spear, 1992; Menard & Spear, 1993). Although clinozoisite was never identified in any thin section from 12TM5E, allanite is relatively common only as an inclusion in garnet. It is suggested that allanite breakdown is responsible for the development of Y zoning and formation of monazite late in garnet's growth history.

It is interesting to note that the Y zoning produced by the breakdown of xenotime in the core region of garnet is asymmetric while the Y zoning produced by the breakdown of allanite near the rim is symmetric. These observations may represent a shift from diffusion controlled to interface controlled crystallization of garnet with respect to trace elements. The production of a symmetrical Y annulus from allanite breakdown may have been assisted by the release of H_2O from allanite and apatite.

2.5.3 Monazite geochronology and interpretation

The major monazite age population at 977 ± 4 Ma (Fig. 2.19b) is interpreted based on textural evidence to represent monazite growth at the expense of allanite late in garnet's growth history. The 977 ± 4 Ma population provides a P-T path time anchor. Monazite growth is constrained to post D_1 as garnet growth post dates D_1 and pre D_2 as the external foliation wraps garnet porphyroblasts and matrix monazite is foliated. Allanite has been identified as a precursor to monazite in many studies of metapelitic rocks (e.g., Wing et al., 2003; Yang & Pattison, 2006; Tomkins & Pattison, 2007; Gaidies et al., 2008C; Janots et al., 2009). The enrichment of Ca^{2+} and Th^{4+} in the core of monazite may represent

growth at the expense of allanite, a phase enriched in Ca^{2+} and Th^{4+} . The coupled substitution mechanism $\text{Ca}^{2+} + \text{Th}^{4+} = 2\text{LREE}^{3+}$ (brabantite substitution) is dominant in metamorphic monazites (Spear & Pyle, 2003). Apatite, which commonly occurs as inclusions in monazite (Fig. 2.18d), may have also been a reactant and a source of P and LREE for monazite. Rim ward from the Y annulus in garnet where monazite inclusions are common there is a sharp decrease in X_{grs} and increase in X_{alm} , probably related to allanite breakdown (Hickmott & Spear, 1992; Menard & Spear, 1993). The following reaction is envisioned as the major monazite forming reaction in 12TM5E, $\text{Aln} + \text{Apa} = \text{Mnz} + \text{Grt (Fe \& Ca components)} + \text{H}_2\text{O}$.

The peak P-T conditions of 12TM5E were constrained to 540-640°C and 4.5-6.8 kbar (Fig. 2.10f). The monazite forming reaction is likely to have occurred over this P-T interval as monazite formed late in garnet's growth history, implied by its presence in only the outer portion of garnet. The 956 ± 10 Ma monazite population probably represents monazite growth along the retrograde path. $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende cooling studies in the Finton Group provide cooling ages of 950-930 Ma (Busch et al., 1996), which are within error of the 956 ± 10 Ma monazite age population. The 1015 ± 15 Ma monazite population represents an earlier generation of metamorphic monazite, the origin of which is not known but may have been related to garnet resorption during initial staurolite growth. Using the two age populations 1015 ± 15 Ma and 977 ± 4 Ma, metamorphism in at this locality is constrained to a minimum timescale of at 19-57 Ma.

2.5.4 Influence of oxidation state of the rock on metamorphic mineral assemblages

Magnetite and hematite bearing mineral assemblages are common in the Flinton Group, particularly in the Bishops Corner Formation from which samples 11TM14, 11TM6A and 11TM23 (Figs. 2.4a-c) were collected. The mineral assemblage Pl, Mag, Ky, Bt, Ph $\pm$ St is commonly developed in the Bishops Corner Formation metapelites. In samples 11TM14, 11TM6A and 11TM23 the mineral assemblage and garnet chemistry could not be predicted (Figs. 2.14, 2.15) indicating that variables other than pressure and temperature exerted controls on the formation of mineral assemblages and chemistry during metamorphism.

Hounslow and Moore (1967) in a study of metapelitic schists from the Flinton Group found that rocks with Ky-Mag bearing assemblages were richer in Al_2O_3 and Fe_2O_3 compared to rocks whose dominant iron oxide was Ilm. They also noted that FeO:MgO ratios in silicate minerals showed extreme variations that correlates well with oxidation state of the rock. As a result they deemed the effect of pressure and temperature insignificant in comparison to the role of oxidation state of the rock on the mineral assemblages that formed during metamorphism. Samples 11TM14, 11TM6A and 11TM23 are correlative to those studied by Hounslow & Moore (1967) in the vicinity of Fernleigh (Fig. 2.2).

Chinner (1960) also noted the influence of oxidation state of the rock on mineral assemblages developed in metapelitic gneisses in Glen Cova, Scotland. Chinner (1960) observed that the amount of Ph and Mag increases with increasing ferric/ferrous ratio while the amount of Grt and Bt decreases. In particular, with increasing oxidation state the FeO content of Grt systemically decreases while MnO increases producing Mn-rich

Grt, similar to that of 11TM14 (Fig. 2.5g). Chinner (1960) found that in Mag-free assemblages Gph is present and that the dominant iron oxide is Ilm with only minor amounts of Mag. In our study, the Myers Cave Formation metapelites are distinguished from the Bishops Corner Formation by the presence of Gph and Ilm as the primary iron oxide (Moore & Thompson 1980; Easton 2006). The observed mineral assemblages and Grt core chemistries of the Myers Cave Formation could be predicted in this study as a function of P-T for the rocks' chemistry assuming low $f(\text{O}_2)$.

The presence of oxidized and reduced mineral assemblages in metapelites of the Flinton Group provides a natural setting to understand how Fe^{3+} partitions among major silicate phases during metamorphism. The presence of Ky porphyroblasts in Mag-bearing assemblages of the Bishops Corner Formation has led to erratic Ky isograds (see Easton, 2006) and assumed fault contacts to account for the apparent change in pressure. Adopting similar interpretations to those of Chinner (1960) and Hounslow & Moore (1967), it is suggested that the presence of Fe^{3+} in the Flinton Group destabilizes Grt and Bt and stabilizes Ky in metapelites of the Bishops Corner Formation. It is suggested that the distribution of Fe^{3+} and not geological structure is responsible for the erratic distribution of Ky bearing assemblages. In order to accurately predict phase equilibria in metapelitic samples of the Bishops Corner Formation, detailed thermodynamic data is required for Fe^{3+} end members of major silicate phases.

2.6 Conclusions

New P-T-t estimates were provided for the Flinton Group in this communication, further constraining the tectonic evolution of southeastern Ontario during the Grenville

Orogeny. An initial deformation event formed a pervasive foliation in the Flinton Group over which all porphyroblastic phases grew. Porphyroblast growth is interpreted to be syn-post deformation producing rotated porphyroblasts with linear inclusions at a high angle to a external foliation which wraps all porphyroblastic phases. The Flinton Group was metamorphosed under a high geothermal gradient of approximately $40^{\circ}\text{C km}^{-1}$, which may have developed in response to crustal delamination or elevated isotherms associated with the Midcontinent rift system. The initial P-T conditions of garnet growth are remarkably similar along the study area at 3.7 kbar and 515°C . Results from phase equilibria modeling suggest an increase in pressure and temperature across the study area from the southwest to the northeast from 5.6 to 7.9 kbar and 615 to 715°C over a distance of 40 km. Metamorphic monazite, dated in situ using LA-ICP-MS U-Pb geochronology, provided time constraints for Grenvillian metamorphism in southeastern Ontario. A major monazite population was identified at 977 ± 4 Ma and is interpreted to reflect monazite growth at the expense of allanite and apatite late in garnet's growth history as recorded by Y zoning in porphyroblastic garnet. The P-T conditions of monazite formation were constrained to $540\text{-}640^{\circ}\text{C}$ and 4.5-6.8 kbar providing a time anchor for peak metamorphism. A small monazite population was identified at 1015 ± 15 Ma and although its origin is unknown, it is interpreted to represent growth of monazite during prograde metamorphism. Coupling the two age populations, the timescale over which Grenvillian metamorphism may have occurred in the Flinton Group is constrained to at least 19-57 Ma.

Chapter 3:

The analysis of chemical zoning in a garnet population: Determination of the P-T-t path of Grenvillian metamorphism in southeastern Ontario

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3.0 Abstract

Growth zoning in a population of garnet porphyroblasts has been successfully used to infer the metamorphic P-T-t history of a sample. The studied sample is a garnet-biotite-staurolite bearing metapelite of the Flinton Group, a package of metasediments in southeastern Ontario metamorphosed during the Grenville Orogeny (ca. 1089-980 Ma). Characterization of the garnet population with high-resolution X-ray micro-computed tomography revealed a unimodal, slightly positively skewed crystal size distribution (CSD). Garnet porphyroblasts ranging from 4000 to 200 μm in diameter from the different size classes of the CSD were centrally sectioned. EPMA analysis of the centrally sectioned porphyroblasts revealed decreasing X_{sps} and X_{grs} and increasing X_{alm} and X_{pyr} from core to rim consistent with a prograde zoning. Garnet growth simulations with the THERIA_G software were used to reproduce the observed growth zoning along a specific P-T-t path. Large porphyroblasts of the population were used to determine a clockwise P-T path over the interval 3.7 to 5.9 kbar and 513 to 615°C while modification of growth zoning via intracrystalline diffusion in relatively small porphyroblasts was used to infer an average heating rate of 2°C Ma⁻¹.

Keywords: garnet, growth zoning, metapelite, intracrystalline diffusion, crystal size distribution (CSD), X-ray tomography, THERIA_G, THERIAK, Flinton Group, Grenville

3.1 Introduction

Chemical zoning that develops in metamorphic garnet during growth is highly sensitive to the pressure-temperature-time-composition (P-T-t-X) evolution of the garnet-bearing rock (Spear, 1993). Garnet growth zoning has been used in many petrologic studies to infer the P-T-t evolution of metamorphic terranes (e.g., Selverstone et al., 1984; Spear et al., 1984; Kohn et al., 1992; Evans, 2004; Gaidies et al., 2006; Gaidies et al., 2008B; Gaidies et al., 2008C). It is important to understand the conditions and rates at which ancient and modern orogenic belts formed as they can provide important clues to the evolution of the continental crust and plate tectonics through time. From an economic standpoint it is also important to understand orogenic processes as ancient orogenic belts host the majority of Earth's resources.

The THERIA_G software program (Gaidies et al., 2008A) can be used to predict along any specified P-T-t path growth zoning that develops in a population of garnet porphyroblasts during prograde metamorphism. THERIA_G has been used to successfully predict growth zoning of garnet in several studies (Gaidies et al., 2008B; Gaidies et al., 2008C; Moynihan & Pattison, 2013). However, characterization of the entire garnet populations with high resolution X-ray micro-computed tomography (XR- μ CT) was impractical due to the coarse-grained nature of the samples. This is why the

predicted metamorphic P-T-t paths were based on chemical zoning of a single garnet porphyroblast and not an entire population.

In this study chemical zoning of an entire garnet population as obtained from XR- μ CT and electron probe micro-analysis (EPMA) is integrated with forward modeling of garnet growth using THERIA_G. It will be shown that this approach can be used to infer details of the rock's metamorphic P-T-t evolution that cannot be obtained from the study of growth zoning in a single garnet crystal. Gaidies et al. (2008A) showed that the largest grains of a garnet population may be used to infer the P-T path of a garnet-bearing sample due to relatively sluggish intracrystalline diffusion and minimal modification of their growth zoning. The presumed steeper chemical gradients in smaller crystals of a population are more sensitive to diffusional relaxation and may be good indicators of metamorphic rate (Gaidies et al., 2008A). In this communication differently sized crystals within a population of garnet porphyroblasts are used to infer the P-T-t path experienced by a metapelitic rock sample during the Grenville Orogeny in southeastern Ontario.

3.2 Geological Background

The rock sample discussed in this communication (12TM5E of McCarron et al. (2013)) is part of the Flinton Group, a sequence of metasediments within the Grenville Province in southeastern Ontario (Moore & Thompson, 1980). The Grenville Province is a complexly deformed and polymetamorphosed geological province that stretches from southeastern Ontario, through Quebec and into Labrador (Easton, 1992) (Fig. 3.1a). The Grenville formed through several orogenic episodes that led to the eventual formation of supercontinent Rodinia between 1080 and 980 Ma (Easton, 1992). In southeastern

Ontario, the Flinton Group outcrops within the Mazinaw Domain of the Central Metasedimentary Belt (CMB) (Fig. 3.1b). The CMB is a complex mosaic of geological domains and terranes composed of metavolcanic, metaplutonic and metasedimentary rocks, which have been deformed and metamorphosed to varying degrees (Easton, 1992). The domains and terranes of the CMB are separated by large scale shear zones which record early northwest directed thrusting during continental collision which is overprinted by late southeast directed post-orogenic extension (Davidson, 1986; Busch et al., 1996).

The Flinton Group is a northeast-southwest trending succession of metasediments that were deposited after 1150 Ma (Moore & Thompson, 1980; Sager-Kinsman & Parrish, 1993) on top of supracrustal and plutonic rocks of the Grenville basement (Moore & Thompson, 1980) (Fig. 3.2). Whereas the Grenville basement was metamorphosed and deformed during earlier orogenic events (Moore & Thompson, 1980; Easton, 1992; Easton, 2006), the Flinton Group was metamorphosed during the Ottawa or “Grenville” Orogeny, which was the last major phase of orogenesis that led to the formation of supercontinent Rodinia (Easton, 1992). The Ottawa Orogeny is thought to have been a collisional event between the eastern margin of Laurentia and Amazonia (Tollo, 2010). Corfu and Easton (1995) obtained bulk metamorphic monazite and zircon ages of 1020 ± 3 Ma from the Flinton Group. McCarron et al. (2013) provided additional monazite ages of 1015 ± 15 Ma and 977 ± 4 Ma, which were interpreted to represent monazite crystallization during prograde metamorphism. Rates of cooling experienced by the Flinton Group have been constrained by Cosca et al. (1991) to $1\text{--}4^\circ\text{C Ma}^{-1}$ with $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende cooling ages of 950 and 930 Ma (Cosca et al., 1991). Details concerning the

Figure 3.1. (A) The Grenville Province within Canada. The Central Metasedimentary Belt is outlined in the stippled box. Modified after Hynes & Rivers (2010). (B) The Central Metasedimentary Belt (CMB) in southeastern Ontario. The domains and terranes, which compose the CMB are illustrated on the map and are separated from one another by large-scale shear zones. For reference, the city of Ottawa (Ontario) is approximately 80 km northeast of Perth. Modified after Easton (2006).

Figure 3.2. Simplified geologic map of the Flinton Group and the location of the sample discussed in this study. Modified after Moore & Thompson (1980) and Easton (2006).

rates of tectonic processes during the Ottawa Orogeny and the P-T path experienced by the Flinton Group are still scarce.

3.3 Methods

3.3.1 WDXRFA

Major element chemistry of one metapelitic sample, 12TM5E, was determined through wavelength dispersive x-ray fluorescence analysis (WDXRFA) using a Philips PW2400 X-ray fluorescence spectrometer at the University of Ottawa, Ontario. Approximately 1 kg of sample devoid of chemical alteration, weathering or visible chemical inhomogeneities was crushed and fused for analysis. Major element chemistry is provided in Table 3.1.

3.3.2 XR- μ CT

High-resolution X-ray micro-computed tomography (XR- μ CT) was used to characterize the size, spatial distribution and abundance of garnet in the sample of this study. Five cylindrical cores 19 mm in diameter and 19 mm in length (Fig. 3.3a) were cone-scanned using an X-ray source of 80kV/124nA and a 1 mm Al filter on a Skyscan 1072 microtomograph at the University of Lausanne. The samples were rotated 360° through the incoming X-rays at 0.225° rotation steps. 15 frames were acquired at each rotation step using an exposure time of 1.3s/frame. One additional cylindrical core 27 mm in diameter and 51 mm in length (Fig. 3.3a) was cone-scanned using a Skyscan 1173 microtomograph with an X-ray source of 130kV/61nA at the University of Lausanne. This cylindrical core was rotated 360° at rotation steps of 0.225° through the incoming X-rays and 20 frames were acquired at each rotation step with an exposure time of 800ms/

Table 3.1. Major element chemistry in wt% for sample 12TM5E.

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	MnO	Na ₂ O	K ₂ O	L.O.I.	Total
12TM5E	58.95	20.53	1.49	9.02	1.47	0.42	0.06	0.73	4.68	2.66	100.45

Figure 3.3. (A) The hand sample from which the cylindrical cores for XR- μ CT were drilled. The third dimension is 6 cm long. (B) Crystal size distribution (CSD) of garnet in 12TM5E determined through XR- μ CT. The CSD is unimodal and slightly positively skewed. Garnet porphyroblasts from size classes 1, 2, 4, 5, 6, 8 and 10 were centrally sectioned and analyzed by EMPA.

frame. Tomography projection images were converted into cross-sectional images using the Skyscan NRecon software package. The BLOB3D image processing software (Ketcham, 2005) was used to quantify the size, distribution and abundance of garnet. The three-dimensional dataset was used to locate garnet porphyroblasts of different radius, which were then centrally sectioned to ensure that the geometric core of the crystal lied within the plane of the thin section. The garnet crystal size frequency distribution (CSD) of the studied sample is given in Figure 3.3b. Garnet from size classes 1, 2, 4, 5, 6, 8, and 10 were centrally sectioned (Fig. 3.4). The radial width of each respective size class is 150 μm .

3.3.3 EPMA

A Cameca Camebax MBX electron probe micro-analyzer (EPMA) at Carleton University was used to quantitatively analyze the chemistry of centrally sectioned garnet porphyroblasts using wavelength dispersive spectrometry. EPMA traverses were performed at 20 μm resolution across each centrally sectioned garnet porphyroblast. Operating conditions included a 20 kV accelerating potential and a beam current of 20 nA. Peak counting time was 40s or 62500 counts for Ca, Fe, Mn, Mg, Si, Al and Ti whereas a 100s was used for Y. The Cameca PAP matrix correction was applied to convert counts into elemental weight %. Both natural and synthetic standards were used for internal calibration. Qualitative element distribution maps for Ca, Mn, Fe, Mg and Y were prepared for each centrally sectioned garnet on a Cameca SX 100 microprobe at Geoscience Laboratories, Sudbury. Operating conditions included a counting time of 10

Figure 3.4. Backscattered electron images of the centrally sectioned garnet porphyroblasts from size classes (A) 1, (B) 2, (C) 4, (D) 5, (E) 6, (F) 8 and (G) 10.

ms/pixel over a 512 x 512 pixel grid using an accelerating potential of 20 kV and a beam current of 200 nA.

3.3.4 Phase equilibria and garnet crystallization modeling

Rock specific phase equilibria diagrams were calculated using the DOMINO software (de Capitani & Petrakakis, 2010) and the whole rock chemistry of 12TM5E (Table 3.1). Garnet crystallization was simulated using the THERIA_G software program (Gaidies et al., 2008A) for various P-T-t scenarios to determine the best match between the observed and predicted chemistry of the garnet population. Calculations with DOMINO and THERIA_G were made in the model system $\text{MnO-Na}_2\text{O-CaO-K}_2\text{O-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2\text{-TiO}_2$ using the thermodynamic database of Holland & Powell (1998). To account for the influence of graphite on the stability of major silicate minerals during metamorphism, a graphite-buffered C-O-H fluid (Evans & Powell, 2006) was considered (D. Tinkham, personal communication). For a complete description of the solution models used the reader is directed to the Appendix. For modeling of cation diffusion in garnet with the THERIA_G software the diffusion parameters of Chakraborty & Ganguly (1992) were used. All input files used for THERIA_G modeling are provided in the Appendix. For a rigorous explanation of THERIA_G the reader is directed to Gaidies et al. (2008A). A brief overview of the software program is provided below.

THERIA_G uses the THERIAK algorithm of de Capitani & Brown (1987) and an internally consistent thermodynamic database (i.e., Holland & Powell, 1998) to predict equilibrium phase relations in a rock along a specified P-T-t path. THERIA_G simulates garnet growth as the successive addition of shells. It iteratively searches along the

specified path for the P-T step required to form the volume of all new shells, which have the same thickness independent of crystal size and are added to all co-crystallizing garnets. The shell thickness used for this study was 5 μm . The number of crystals in each size class of the garnet crystal size distribution, the garnet radius and the shell thickness determine the volume required to form each successive shell. THERIA_G generates each size class as a series of discrete nucleation events. Once an earlier generation of growing crystals exceeds the radial range that defines the size of a size class, the number of garnets in the next size class is nucleated and begins to co-crystallize with previously nucleated and crystallizing porphyroblasts. Because garnet crystallization may lead to chemical fractionation of the whole rock, THERIA_G subtracts the amount of chemical components required to form each additional shell from the whole rock. Chemical fractionation becomes increasingly efficient with increases in the number and sizes of co-crystallizing garnet porphyroblasts. Chemical equilibrium is assumed between the garnet rim and the matrix during garnet growth. As THERIA_G simulates garnet growth along the specified P-T-t path, changes to the equilibrium phase assemblage are monitored and their impact on garnet chemistry is considered. In addition to nucleation, crystal growth and chemical fractionation, THERIA_G simulates multi-component diffusion between successive shells and diffusional fluxes between garnet and the rock matrix.

It has been shown that intracrystalline diffusion in garnet may become efficient at high temperatures or over long timescales (e.g., Loomis et al., 1985; Chakraborty & Ganguly, 1992; Gaidies et al., 2008), both of which are characteristic of the Grenville Orogeny (Easton, 1992; Rivers, 2009; Hynes & Rivers, 2010). In addition, Ca^{2+} has been

shown to be the slowest diffusing major cation in almandine garnet (Loomis et al., 1985; Chakraborty & Ganguly, 1992). For this reason, Ca^{2+} zoning in garnet was used to fit the predicted and observed zoning along a specific P-T path, as Ca^{2+} best records the original compositional zoning.

3.4 Results

3.4.1 Sample description

Sample 12TM5E belongs to the Myers Cave Formation of the Flinton Group. The rock contains porphyroblasts of garnet, staurolite and biotite set in a graphite-rich fine-grained matrix of white mica, ilmenite, tourmaline and other accessory phases (Fig. 3.5). The rock has a pervasive foliation, S_1 , and weak crenulation, S_2 , which is defined by the preferential alignment of white mica and ilmenite. S_1 is observed wrapping garnet, biotite and staurolite (Figs. 3.5a-c) and is part of a second generation of structures. Garnet porphyroblasts range in size between 0.2 to 3 mm in diameter. Garnet porphyroblasts are idioblastic and have inclusion rich cores and relatively inclusion free rims. Linear inclusion trails in garnet lie at a slight angle to the external foliation and record an earlier fabric S_0 (Fig. 3.5a). Inclusions of quartz, ilmenite and rutile are common with lesser amounts of xenotime, allanite and monazite. Rare staurolite inclusions have also been observed. Biotite porphyroblasts are idioblastic and range in size up to 3 mm in diameter. Biotite and garnet share smooth grain boundaries. Coarse-grained, randomly orientated

Figure 3.5. Photomicrographs of 12TM5E in both plane polarized light (PPL) and crossed polarized light (XPL). (A) Garnet porphyroblast with inclusions trails (S_0) at an angle to the external foliation (S_1). S_1 wraps the garnet. (B) Hourglass inclusion zoning in biotite. (C) The external foliation can be seen wrapping both biotite and garnet. Inclusion trails in biotite are at a high angle to the external foliation (S_0). The top biotite in the photomicrograph shows hourglass inclusion zoning. (D) Large patch of coarse-grained randomly orientated white mica replacing staurolite. S_1 wraps the randomly orientated white mica. (E) Pseudomorphic replacement of staurolite and biotite by coarse-grained randomly orientated white mica. The contact with the matrix is sharp and is highlighted by the dotted black line. (F) Contact between garnet and the white mica pseudomorphs after staurolite. Garnet is resorbed when in contact with the pseudomorphs.

white mica is observed, to varying degrees, replacing biotite porphyroblasts (Figs. 3.5e, f). Biotite porphyroblasts commonly show hourglass inclusion zoning (Fig. 3.5b).

Inclusion trails in biotite lie at a greater angle to the external foliation than inclusion trails in garnet and like inclusions trails in garnet record an earlier fabric, S_0 (Figs. 3.5b,c). The orientations of inclusion trails are similar between different biotite porphyroblasts.

Staurolite occurs as resorbed vestiges at the heart of large patches of randomly orientated coarse-grained white mica (Fig. 3.5e). The large patches of white mica are diamond shaped in cross section and are consistent with cross sectional shape of staurolite (Figs. 3.5d,e). The contact with the fine-grained matrix white mica is sharp. The patches range in size up to 5 mm in diameter and may be up to 10 mm in length. The replacement of staurolite by white mica ranges from slight to complete. Garnet porphyroblasts have resorbed grain boundaries when observed in contact with the coarse-grained white mica pseudomorphs after staurolite (Fig. 3.5f).

Three-dimensional analysis with XR- μ CT yielded 2084 garnet porphyroblasts from 56.22 cm³ of sample. The garnet CSD is unimodal and has a slight positive skew of 0.2938 (Fig. 3.3b).

3.4.2 Garnet chemistry

Ca, Mn, Fe and Mg in garnet will hereafter be referred to as X_{grs} , X_{sps} , X_{alm} and X_{pyr} , where $X_{\text{grs}} = (\text{Ca}/(\text{Ca}+\text{Mn}+\text{Fe}^{2+}+\text{Mg}))$, $X_{\text{sps}} = (\text{Mn}/(\text{Ca}+\text{Mn}+\text{Fe}^{2+}+\text{Mg}))$, $X_{\text{alm}} = (\text{Fe}^{2+}/(\text{Ca}+\text{Mn}+\text{Fe}^{2+}+\text{Mg}))$ and $X_{\text{pyr}} = (\text{Mg}/(\text{Ca}+\text{Mn}+\text{Fe}^{2+}+\text{Mg}))$. EPMA element distribution maps were prepared for each centrally sectioned garnet porphyroblast. Representative element distribution maps for size classes 1 and 4 are shown in Figures 3.6 and 3.8. Element

distribution maps for the remaining size classes are provided in the Appendix. EPMA traverses for size classes 1, 2, 4, 5, 6, 8 and 10 are shown in Figure 3.7a-g respectively.

Several chemical trends are present within the garnet population. X_{sps} and X_{grs} decrease and X_{alm} and X_{pyp} increase from core to rim in every garnet porphyroblast. In addition, there is a strong positive correlation between the X_{sps} content of the core and the size of the respective garnet. In general the observed chemical gradients become less steep in progressively smaller crystals. This is particularly evident for X_{sps} . Yttrium zoning near the core of the crystals correlates to areas of decreased X_{grs} and increased X_{alm} . Yttrium zoning near the rim correlates to a shoulder in X_{grs} from which X_{grs} steeply decreases toward the rim and a trough in X_{alm} from which X_{alm} steeply increases toward the rim. More detailed descriptions specific to each size class are given below.

Size class 1

X_{sps} and X_{grs} decrease and X_{alm} and X_{pyp} increase from core to rim in garnet from size class 1 (Figs. 3.6a-e, 3.7a). The garnet has an inclusion rich core and relatively inclusion free rim. Around the geometric core of the porphyroblast is a “half moon” region of decreased X_{grs} and increased X_{alm} content (Figs. 3.6a,d, 3.7a). This “half moon” region corresponds to an area of yttrium enrichment. The bright white spots within the yttrium-rich “half moon” region are small xenotime inclusions (Fig. 3.6e). An important feature to note in addition to the yttrium “half moon” is the presence of an yttrium annulus approximately 200 μm inwards of the rim (Fig. 3.6e).

X_{sps} gradually decreases from core to rim from 0.08 to 0.002. X_{grs} is slightly scattered in the core (Fig. 3.7a). The most striking feature in X_{grs} from core to rim is the sharp

Figure 3.6. EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 1. EPMA results along the dotted line in (B) are shown in Fig. 3.7a. Yttrium zoning is highlighted in (E) and superimposed on (A) and (D).

decrease from 0.09 to 0.07 at a distance of ca. 2000 μm from A. This decrease in X_{grs} is accompanied by a sharp increase in yttrium from 300 to 3000 ppm and X_{alm} from 0.78 to 0.82. Traversing toward B, X_{grs} plateaus until 2720 μm where it then steeply decreases toward the rim. A slight shoulder in X_{grs} is observed at 2900 μm and can be correlated to a small peak in yttrium and a trough in X_{alm} . From the shoulder X_{grs} drops off sharply toward the rim. On the left hand side of the profile decreases in X_{grs} are observed at 870 and ~600 respectively. X_{alm} , like X_{grs} , is strongly affected by the yttrium rich domain of garnet near the core. Traversing away from the yttrium domain toward the rim, X_{alm} increases at 2680 μm from 0.84 to 0.86. At 2900 μm a slight trough in X_{alm} occurs before X_{alm} increases continuously toward the rim. This trough is correlated with a slight shoulder in X_{grs} and a small peak in yttrium. On the left hand side of the profile traversing toward the rim an increase from 0.79 to 0.81 is observed at 890 μm . Traversing rim-ward of this feature, X_{alm} plateaus at 0.81 from 800 to 600 μm . At 600 μm X_{alm} continuously increases toward the rim from 0.81 to 0.88. The increase in X_{alm} from 0.86 to 0.88 in the outermost 20 μm on either side of the profile is mimicked by a decrease in X_{pyp} . X_{pyp} is homogenous in the core before gently increasing toward the rim from 0.04 to 0.09.

Size class 2

X_{sps} and X_{grs} decrease and X_{alm} and X_{pyp} increase from core to rim in garnet from size class 2 (Fig. 3.7b). X_{sps} is homogeneous in the core before it gradually decreases toward the rim from 0.07 to 0.002. X_{grs} decreases from 0.10 in the core to 0.04 at the rim. Sharp decreases in X_{grs} are observed at 1200 and 1980 μm and correlate to increases in X_{alm} and yttrium. Yttrium zoning forms a double peak about the core at 1080 and 2100 μm . On the

Figure 3.7. EPMA traverses across the centrally sectioned garnet porphyroblasts from the different size classes of the CSD (Fig. 3.3b). Results for size classes 1, 2, 4, 5, 6, 8 and 10 are presented in (A), (B), (C), (D), (E), (F) and (G) respectively.

right side of the profile X_{grs} plateaus from 2000 to 2500 μm at 0.08 before decreasing gradually toward the rim to 0.04. X_{alm} increases steeply away from the core from 0.79 to 0.87 at 800 and 2300 μm . X_{alm} plateaus at 0.87 at 300 and 2800 μm respectively until the rim with no further changes. X_{pyr} is homogeneous in the core and increases gently toward to rim from 0.04 to 0.09.

Size class 4

X_{sps} and X_{grs} decrease and X_{alm} and X_{pyr} increase from core to rim in garnet of size class 4 (Figs. 3.7c, 3.8). Like size class 1, the porphyroblast from size class 4 has a yttrium rich core that corresponds to depletion in X_{grs} and enrichment in X_{alm} . A yttrium annulus is also observed inwards of the rim (Fig. 3.8e). In Figure 3.8e, the yttrium-rich core forms the shape of a trapezoid off center of the crystal as outlined on the Y, Fe and Ca element distribution maps. Small white spots within the yttrium rich core are small xenotime inclusions (Fig. 3.8e). The yttrium annulus can also be observed in the neighboring garnet crystal. Yttrium zoning near the core in garnet from both size classes 1 and 4 causes a small degree of asymmetric zoning.

X_{sps} decreases smoothly from 0.06 in the core to 0.002 at the rim (Fig. 3.7c). A shoulder in X_{sps} is developed between 1450 and 1690 μm , which corresponds to a decrease in X_{grs} and increase in X_{alm} and yttrium. X_{grs} decreases from 0.09 to 0.03 from core to rim. A sharp decrease in X_{grs} is observed at 1400 μm . From this drop X_{grs} plateaus at 0.07 until 2460 μm where X_{grs} decreases sharply toward the rim to 0.03. A small shoulder is developed in X_{grs} at 2400 μm , which corresponds to a trough in X_{alm} and a peak in yttrium. On the left side of the profile X_{grs} decreases smoothly toward the rim

Figure 3.8. EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 4. EPMA results along the dotted line in (B) are shown in Fig. 3.7c. Yttrium zoning is highlighted in (E) and superimposed on (A) and (D).

until 300 μm where X_{grs} begins to decrease much steeper toward the rim from 0.06 to 0.03. X_{alm} is homogenous in the core at 0.80 and begins to increase toward the rim at 950 and 1400 μm respectively. The initial increase in X_{alm} broadens into a plateau before increasing toward the rim on the left side of the profile from 0.85 to 0.88. X_{pyr} gently increases from core to rim from 0.04 to 0.09.

Size class 5

X_{sps} and X_{grs} decrease and X_{alm} and X_{pyr} increase from core to rim in garnet of size class 5 (Fig. 3.7d). X_{sps} decreases gently from 0.04 to 0.002 from core to rim. X_{grs} decreases from 0.11 to 0.02 from core to rim with abrupt changes in slope at 450 and 1400 μm traversing away from the core. At these two points X_{grs} decreases steeply from 0.08 to 0.06. From these points X_{grs} gradually decreases toward the rim until sharply decreasing toward the rim at 150 and 2050 μm from 0.04 to 0.02. The sharp drop in X_{grs} near the rim is mimicked by a sharp increase in X_{alm} from 0.86 to 0.88. X_{alm} is homogeneous in the core before increasing from 0.82 to 0.86 at 800 and 1800 μm . Traversing rim-ward of these two points X_{alm} plateaus at 0.86 until 150 and 2050 μm respectively where it steeply increases to the rim. X_{pyr} increases gradually from 0.05 to 0.10 from core to rim. Minimal zoning is observed for yttrium.

Size class 6

X_{sps} and X_{grs} decrease and X_{alm} and X_{pyr} increase from core to rim in garnet of size class 6 (Fig. 3.7e). X_{sps} decreases from 0.02 to 0.002 from core to rim however X_{grs} initially increases away from the core from 0.06 to 0.08 at 540 and 1090 μm respectively. This initial increase away from the core in X_{grs} is antithetic to X_{alm} . X_{alm} initially

decreases away from the core from 0.85 to 0.83 at 540 and 1090 μm respectively. The core region from which X_{grs} increases and X_{alm} decreases is enriched in yttrium. The increase in X_{grs} and decrease in X_{alm} occurs traversing away from the yttrium-enriched core. From the prominent peaks at 540 and 1090 μm , X_{grs} decreases toward the rim. Small shoulders are developed in X_{grs} at 100 and 1520 μm , which correspond to a peak in yttrium and a slight trough in X_{alm} . From the shoulder X_{grs} decreases steeply toward the rim from 0.05 to 0.03. X_{alm} increases steeply from the troughs developed around the yttrium-enriched core from 0.83 to 0.86 at 300 and 1250 μm respectively. From these two points X_{alm} increases gradually toward the rim until 90 and 1600 μm where X_{alm} increases steeply from 0.86 to 0.88 at the rim. The sharp increase in X_{alm} is antithetic to a sharp decrease in X_{grs} . X_{pyp} gradually increases from core to rim from 0.07 to 0.09. A slight decrease in X_{pyp} occurs at the left hand side of the profile and is mimicked by a slight increase in X_{alm} .

Size class 8

X_{sps} and X_{grs} decrease and X_{alm} and X_{pyp} increase from core to rim in garnet of size class 8 (Fig. 3.7f). X_{sps} shows minimal zoning, decreasing from 0.008 in the core to 0.002 at the rim. X_{grs} is homogenous in the core at 0.06 before decreasing at 320 and 580 μm from 0.06 to 0.05 respectively. From these points X_{grs} gradually decreases toward the rim until 80 and 800 μm where X_{grs} decreases sharply toward the rim from 0.04 to 0.02. X_{alm} is antithetic to X_{grs} in these two regions near the rim, increasing from 0.86 to 0.87. X_{alm} is homogeneous in the core at 0.84 and then increases at 320 and 580 μm from 0.84 to 0.85. X_{alm} increases gradually until 80 and 800 μm where it increases steeply toward the rim,

behaving antithetically to X_{grs} . X_{pyr} shows minimal zoning from core to rim, increasing from 0.08 to 0.09. Slight decreases in X_{pyr} and increases in X_{alm} are observed at the rim on both sides of the profile. Minimal yttrium zoning is developed. Two points of elevated yttrium concentration are observed at 100 and 760 μm . These two points roughly correspond to the sharp decreases in X_{grs} and increases in X_{alm} at the rim.

Size class 10

Size class 10 contains the smallest grains of 12TM5E. X_{sps} and X_{pyr} are homogeneous from core to rim at 0.002 and 0.09 respectively (Fig. 3.7g). Only slight zoning is developed in X_{pyr} in the outer 20 μm , where a small decrease is observed. In contrast, steep gradients are observed for X_{alm} and X_{grs} across the crystal. X_{alm} increases gradually from 0.84 in the core to 0.87 in the rim. The small decrease in X_{pyr} at the rim is mimicked by a small increase in X_{alm} . X_{grs} decreases gradually from 0.06 in the core to 0.04 at the rim. Minimal zoning is observed for yttrium.

3.4.3 Garnet growth simulations

Metamorphic crystallization along various P-T-t paths was modeled with THERIA_G to predict the observed zoning. The P-T path that yielded the best results is shown in Figure 3.9 and is provided in Table 3.2. Garnet growth is predicted to start at 512°C and 3.7 kbar and finish at 615°C and 5.9 kbar. Phase relations prior to and subsequent to garnet growth are illustrated in Figures 3.9 and 3.10.

For each size class the predicted zoning is plotted against the observed zoning in Figure 3.11. All of the results represent simulations along the P-T path illustrated in

Table 3.2. P-T-t points used for THERIA_G modeling. Variable heating rates are provided.

T (°C)	P (bar)	t (Ma) for heating/cooling rate of				
		20°C Ma ⁻¹	10°C Ma ⁻¹	5°C Ma ⁻¹	2°C Ma ⁻¹	1°C Ma ⁻¹
509.04	3687.47	0.0000	0.0000	0.0000	0.0000	0.0000
527.53	3933.01	0.9234	1.8485	3.6971	9.2427	18.4854
542.87	4406.21	1.6914	3.3829	6.7658	16.9144	33.8288
560.94	5093.78	2.5948	5.1896	10.3791	25.9478	51.8956
582.73	5710.45	3.6844	7.3688	14.7375	36.8438	73.6877
597.50	5900.95	4.4229	8.8457	17.6914	44.2286	88.4572
615.34	5914.12	5.3149	10.6298	21.2596	53.1491	106.2982
615.48	5921.29	5.3222	10.6444	21.2888	53.2220	106.4440
618.95	5834.63	5.4953	10.9906	21.9812	53.9530	109.9059
618.99	5669.99	5.4976	10.9953	21.9906	54.9530	109.9530
611.19	5411.29	5.8881	11.7761	23.5522	54.9765	117.7611
580.06	4648.33	7.4445	14.8890	29.7780	74.4450	148.8899
515.76	3448.52	10.6592	21.3184	42.6369	106.5922	213.1844

Figures 3.9 and 3.10 but differ in terms of the rates with which P-T change (see Table 3.2).

THERIA_G modeling was to a large extent successful in reproducing the observed chemical zoning in the different size classes along the specified P-T path. Good matches are observed for X_{grs} , X_{sps} and X_{alm} . Metamorphic rates of $1\text{-}2^{\circ}\text{C Ma}^{-1}$ provide the best results. For the different heating rates, a good match was considered when there was less than a 0.02 difference between the predicted and observed X_{sps} core. THERIA_G has issues to predict the observed X_{pyp} zoning. The predicted X_{pyp} is significantly lower in the core of garnet and the compositional gradients across the grains are steeper than the observed, which is particularly evident in the smaller size classes. A detailed discussion of each size class is given below.

Size class 1

Results produced by THERIA_G for size class 1 are shown in Figure 3.11a. Generally there is a good fit between the predicted and observed chemical zoning from core to rim. However, the predicted X_{sps} core is approximately 0.01 higher than the observed for all rates considered. The predicted X_{alm} fits the observed X_{alm} core and compositional gradients well however the increase in X_{alm} from 1400 to 1600 μm at the rim could not be predicted. Similarly, the predicted X_{grs} fits the observed core chemistry and compositional gradients well however the rim is 0.01 higher than the observed. In general the predicted X_{pyp} matches the observed X_{pyp} . Several changes in the predicted compositional gradient are not observed in the measured chemical zoning, which is much smoother. With slower rates the initial X_{pyp} compositional gradients begin to smoothen to

Figure 3.9. (A) Equilibrium phase diagram and (B-E) garnet composition predicted for the whole rock chemistry of 12TM5E (Table 3.1). (F) shows the modal amount of garnet as a function of P-T. Quartz, graphite and H₂O are considered in excess. The P-T path that yielded the best results is illustrated with a dashed line. Mineral abbreviations after Whitney & Evans (2010).

Figure 3.10. (A) Equilibrium phase diagram and (B-E) garnet composition following garnet growth. These diagrams take into account chemical fractionation of the whole rock chemistry due to garnet crystallization. (F) shows the modal amount of garnet as a function of P-T. The P-T path that yielded the best results is illustrated with a dashed line.

better match the observed zoning. With rates of $1\text{-}2^{\circ}\text{C Ma}^{-1}$ an overall better fit is observed for X_{sps} and X_{alm} than for faster rates. X_{grs} and X_{pyr} are the least sensitive to heating rate in garnet of this size and little difference is observed for the different heating rates in comparison to X_{alm} and X_{grs} . It is important to note that THERIA_G predicted garnet $200\text{ }\mu\text{m}$ smaller in diameter than the observed.

Size class 2

There is a general good fit from core to rim between the observed and predicted chemical zoning (Fig. 3.11b). Like size class 1, the predicted X_{sps} core is 0.01 higher than the observed for all rates considered. There is a good match between the predicted and observed core chemistries for X_{pyr} , X_{alm} and X_{grs} . Some mismatch between the predicted and observed compositional gradients is observed for X_{pyr} . Predicted compositional gradients for X_{pyr} are much steeper than those observed. With slower rates of $1\text{-}2^{\circ}\text{C Ma}^{-1}$ the steep compositional gradients for X_{pyr} begin to smoothen and there is also a better fit for X_{sps} and X_{alm} compared to results along faster rates. There is an overall good match for X_{alm} , however the observed plateau at $1125\text{ }\mu\text{m}$ is 0.02 higher than that predicted. An initial drop in X_{grs} at $375\text{ }\mu\text{m}$ could not be matched by THERIA_G modeling. This portion of garnet corresponds to a yttrium rich domain (Fig. 3.7b). Beyond this area of mismatch there is a good fit for X_{grs} between the predicted and observed compositional gradients, however THERIA_G is unable to predict the proper rim composition. The predicted X_{grs} rim composition is 0.02 higher than that observed. THERIA_G is unable to grow the correct radius of garnet.

Size class 4

Figure 3.11. Results from THERIA_G modeling along the P-T path provided in Table 3.2 for different heating rates. The predicted core to rim growth zoning is plotted against the observed for each size class, (A) 1, (B) 2, (C) 4, (D) 5, (E) 6 and (F) 8. In addition to different heating rates where diffusion is considered, a scenario where diffusion is not considered is also plotted against the observed zoning and is depicted in the legend as “ ∞ fast”. The observed zoning is plotted as white squares, while results for different heating rates are plotted as stippled lines.

There is a good fit between the predicted and observed X_{alm} , X_{grs} and X_{sps} (Fig. 3.11c). THERIA_G is unable to predict the increase in X_{alm} and decrease in X_{grs} in the outer 200 μm . Similarly, THERIA_G failed to accurately predict X_{pyp} . The predicted X_{pyp} core is 0.01 lower than the observed and the predicted chemical gradients are steeper than those observed. However, with slower rates of $1-2^{\circ}C Ma^{-1}$ the initially steep X_{pyp} gradients begin to shallow and become closer to the observed. With heating rates of $1-2^{\circ}C Ma^{-1}$ there is a good match for both X_{alm} and X_{sps} . For X_{sps} a heating rate of $1^{\circ}C Ma^{-1}$ results in an almost perfect match between the predicted and observed whereas a heating rate of $2^{\circ}C Ma^{-1}$ results in a difference of 0.02 between the predicted and observed core. For X_{alm} a $1^{\circ}C$ and $2^{\circ}C Ma^{-1}$ heating rate straddle the observed core chemistry. The predicted X_{alm} profile matches the observed profile well. A good match is observed for X_{grs} from core to rim. It is important to note that heating rate has little effect on the X_{grs} .

Size class 5

There are general good fits for X_{alm} , X_{grs} and X_{sps} and some mismatch for X_{pyp} (Fig. 3.11d). Rates of $1-2^{\circ}C Ma^{-1}$ provide the best results. Results along the $1^{\circ}C$ and $2^{\circ}C Ma^{-1}$ heating rates straddle the observed X_{sps} zoning. A $2^{\circ}C Ma^{-1}$ results in an almost perfect match for X_{alm} . The observed X_{alm} rim is 0.03 higher than that predicted. All rates provide a good match for X_{grs} from core to rim. The predicted X_{grs} rim is 0.02 higher than that observed. For the core X_{sps} , a difference of 0.07 is observed between the scenario where no diffusion is considered and the $1^{\circ}C Ma^{-1}$ rate indicating that smaller porphyroblasts are increasingly more sensitive to heating rate. In comparison, for size class 4 the

difference in the core X_{sps} between the no diffusion scenario and $1^{\circ}\text{C Ma}^{-1}$ rates was 0.03. The predicted X_{pyr} core is 0.02 lower than that observed. The predicted gradients for X_{pyr} are steeper than those observed. Slower rates begin to relax the initially steep compositional gradients in the X_{pyr} profile. As was the case for larger size classes, the increase in X_{alm} and decrease in X_{grs} near the rim and the correct radius of garnet could not be predicted.

Size class 6

Good fits for X_{alm} , X_{grs} and X_{sps} are observed for size class 6 (Fig. 3.11e). A $2^{\circ}\text{C Ma}^{-1}$ heating rate matches the observed X_{sps} zoning well. For X_{sps} a $1^{\circ}\text{C Ma}^{-1}$ heating rate results in a flatter profile than that observed. X_{alm} is predicted to decrease from core to rim for rates slower than $2^{\circ}\text{C Ma}^{-1}$. A $2^{\circ}\text{C Ma}^{-1}$ rate produces a good match between the predicted and observed core X_{alm} composition. A good match is observed for X_{grs} . The initial increase in X_{grs} away from the core corresponds to a yttrium rich domain (Fig. 3.7e). The largest discrepancy between the predicted and observed X_{pyr} is observed in size class 6. A difference of 0.04 is observed between the predicted and observed core X_{pyr} , however a good match for the latter half of the profile is observed.

Size class 8

In general good fits are observed for X_{sps} , X_{grs} , X_{pyr} and X_{alm} (Fig. 3.11f). For rates less than $10^{\circ}\text{C Ma}^{-1}$ there is little difference between the predicted X_{sps} . The best match between the predicted and the observed X_{pyr} is observed in size class 8. The different rates have little affect on the predicted X_{pyr} zoning. However, for the scenario where diffusion is not considered there is a large difference between the observed and predicted

X_{pyr} and X_{sps} cores. The observed compositional gradient for X_{alm} is slightly steeper than that predicted by THERIA_G for all rates. There is a good match between the predicted and observed X_{alm} core composition. Rates of $1\text{-}2^{\circ}\text{C Ma}^{-1}$ provide the best results for the different end members. Like larger size classes, THERIA_G was unable to predict the proper X_{alm} and X_{grs} rim compositions and radius of garnet.

Size class 10

THERIA_G did not nucleate size class 10 during growth simulations along the specified P-T-t path.

3.5 Interpretation and Discussion

3.5.1 Diffusion vs. interface controlled crystallization of garnet

Interface controlled garnet crystallization assumes that diffusion of reactive chemical components throughout the matrix is fast relative to attachment and detachment processes at the traversing garnet-matrix interface (Kretz, 1966; Gaidies et al., 2008A). In contrast, diffusion controlled crystallization implies relatively slow diffusion of chemical components throughout the rock matrix (Carlson, 1989; Denison & Carlson, 1997). A consequence of interface-controlled crystallization is that co-crystallizing garnet porphyroblasts independent of their size grow with the same radial rate (Kretz 1966; Spear & Daniel, 1998; Gaidies et al., 2008A). It also implies that the core chemistries reflect the P-T-X conditions at which the crystals began to crystallize if not modified by subsequent processes such as intracrystalline diffusion and that all garnet porphyroblasts stop crystallizing at the same time and have the same rim composition. Under an interface-controlled crystallization mechanism initial compositional gradients will be

steeper in smaller crystals than in larger crystals making them more vulnerable to modification via intracrystalline diffusion (Gaidies et al., 2008A). Under a diffusion-controlled crystallization mechanism the chemistry of a garnet population will not reflect the P-T-X conditions of crystallization but the availability of reactive chemical components to the moving garnet-rock matrix interface, which may be different for each individual grain.

Results from THERIA_G modeling suggest slow heating rates for 12TM5E on the order of $1\text{-}2^{\circ}\text{C Ma}^{-1}$. Over such a timescale, diffusional modification of garnet growth zoning may be efficient. Because Ca^{2+} is the slowest diffusing major cation in almandine garnet (e.g., Chakraborty & Ganguly, 1992), X_{grs} may be considered the best recorder of growth zoning. A core-rim plot of X_{grs} was prepared for all analyzed size classes to compare core compositions, compositional gradients and rim compositions (Fig. 3.12). Although a small amount of scatter is observed, the compositional gradients from core to rim for the different size classes are remarkably similar. In addition, all garnet porphyroblasts have the same rim composition. The X_{grs} core composition systematically decreases in larger to smaller porphyroblasts, reflecting the relative timing and the change in P-T-X conditions of garnet nucleation. Size class 6 is an exception with a noticeably lower X_{grs} core composition. In this size class, X_{grs} initially increases away from the core. The area of low X_{grs} in the core is correlated to enrichment in yttrium and X_{alm} (Fig 3.7e). This chemical trend is common in the core regions of the analyzed garnet population and may represent xenotime breakdown and growth of allanite.

Figure 3.12. Core to rim profiles for X_{grs} for the different size classes analyzed in this study indicating similar compositional gradients and rim compositions. The major differences between the size classes are the core chemistries, which reflect the change in P-T-X conditions at which the different sizes classes nucleated during prograde metamorphism. The anomalously low core chemistry of size class 6 reflects local reactions involving xenotime (see text).

Because all porphyroblasts exhibit similar compositional gradients and similar rim compositions, it is suggested that an interface-controlled crystallization mechanism may be a good approximation for the formation of garnet in the studied sample. Furthermore we assume that reactions at the surface of garnet were significantly faster than the rate with which the rock was exposed to changes in P-T-X.

Because the garnet porphyroblasts were located in several cylindrical cores drilled from a hand specimen, the minimum size of the equilibrium domain may be estimated. Figure 3.3a shows the hand specimen from which the cylindrical cores were drilled constraining the size of the equilibrium domain to a minimum of 12 x 5 x 6 cm. In addition to similar garnet chemistries, the mineral assemblages and textures observed in the different cylindrical cores were the same, which suggests that chemical equilibrium was at least attained across the volume of rock analyzed.

3.5.2 P-T-t path of metamorphism

Incipient garnet growth is predicted at 512°C and 3.7 kbar in equilibrium with Pl, Ilm, Chl, Ph, Qtz, Gph and COH fluid (Fig. 3.13). Garnet is predicted to grow in equilibrium with this assemblage over a 3°C interval until 515°C, when biotite enters the equilibrium assemblage. At 519°C and 3.8 kbar chloritoid enters the assemblage. At 533°C and 4.1 kbar staurolite enters the equilibrium assemblage for a <1°C temperature interval after which garnet leaves the stable assemblage for a temperature interval of 22°C (Fig. 3.13). It is important to note that garnet porphyroblasts in 12TM5E are idioblastic except when in contact with coarse-grained patches of white mica which replace staurolite forming a pseudomorphing texture. This observation is interpreted to represent garnet resorption

Garnet bearing assemblages:

- 1 Pl Ilm Grt Ph Chl Qtz Gph H₂O
- 2 Pl Ilm Grt Ph Chl Bt Qtz Gph H₂O
- 3 Pl Ilm Grt Ph Chl Chd Bt Qtz Gph H₂O
- 4 Pl Ilm Grt Ph Chl Chd Bt St Qtz Gph H₂O
- 5 Pl Ilm Grt Ph Bt St Qtz Gph H₂O

Figure 3.13. Core to rim plots of the observed zoning plotted against the 2°C Ma⁻¹ heating rate which produced the best results for the garnet porphyroblast from size class 1. The mineral assemblages which garnet is predicted to grow in equilibrium with are labeled 1 through 5 and dashed lines indicate where from core to rim the mineral assemblages change. In addition, the temperatures at which the mineral assemblages change are provided at the top of the figure. It should be noted that when staurolite enters the stable mineral assemblage, garnet is predicted to leave the assemblage for a 22°C interval before it begins to grow again.

during prograde staurolite growth. In Figures 3.9 and 3.10, the model amount of garnet in the rock is predicted to decrease at the staurolite-in reaction. However, THERIA_G does not account for resorption and the corresponding changes to the whole rock chemistry, which may explain some of the discrepancies between the observed and predicted garnet chemistry. The model P-T path intercepts the garnet-in curve again at 555°C and 4.8 kbar causing garnet to resume crystallization. Over the 22°C temperature interval in which garnet did not grow both chlorite and chloritoid are consumed and leave the equilibrium assemblage. When garnet crystallization begins again at 555°C it is in equilibrium with the phase assemblage Pl, Ilm, Ph, Bt, St, Gph and COH fluid. Garnet grows with this assemblage along the P-T-t path until 615°C and 5.9 kbar. The P-T path is interpreted to turn around following this point, as sillimanite is not observed in the rock. This constrains the P-T path post garnet grow to below the sillimanite-in reaction. The peak assemblage inferred from petrographic observations is in line with that predicted by THERIA_G. It is likely that pseudomorphic replacement of staurolite by white mica occurred during cooling, as the coarse-grained white mica is randomly orientated suggesting growth under static conditions.

It is important to note that growth zoning predicted by THERIA_G is highly sensitive to the modeled P-T path. For instance if the pressure at initial garnet growth were 1.0 kbar higher, the resulting predicted core X_{grs} would be 0.06 higher and the X_{alm} would be 0.06 lower than that observed. X_{grs} was used to determine the P-T path as it is the least modified by intracrystalline diffusion, and the good match that was obtained is specific to the modeled P-T path. It would not be possible to achieve the same results along a

different P-T path with different rates as intracrystalline diffusion, even in small porphyroblasts, has little affect on X_{grs} .

3.5.3 Timescales of metamorphism and regional context

Rates of $1\text{-}2^{\circ}\text{C Ma}^{-1}$ for the change of temperature during metamorphism provide the best fit between the predicted and observed chemical zoning in the analyzed garnet population. Considering that the Ottawa Orogeny is thought to have been active between 1080 and 980 Ma (Easton, 1992; Rivers, 2009), a heating rate of $1^{\circ}\text{C Ma}^{-1}$ is unlikely as the corresponding timescale for garnet growth would be 106 Ma. The $2^{\circ}\text{C Ma}^{-1}$ rate provides a relative timescale of approximately 53 Ma for garnet crystallization during prograde heating (Table 3.2).

McCarron et al. (2013) provided absolute metamorphic ages for sample 12TM5E from in situ U-Pb monazite geochronology. Monazite was commonly found included in the outer 200 μm of garnet and as a phase in the rock's matrix. A major age population at 977 ± 4 Ma was interpreted to represent monazite formation at the expense of allanite and apatite late in garnet's growth history (McCarron et al., 2013). In their communication the P-T conditions of monazite formation were constrained to $540\text{-}620^{\circ}\text{C}$ and 4.5-6.8 kbar from phase equilibria modeling. The P-T conditions can be further constrained in this study by coupling THERIA_G modeling with the U-Pb monazite ages. The portion of garnet that THERIA_G is unable to predict corresponds to the symmetrical yttrium annulus inwards of the rim (Figs. 3.6, 3.7, 3.8). It is suggested that the rim of garnet could not be predicted by THERIA_G due to the breakdown of allanite, an unconsidered phase in the thermodynamic database. The peak P-T conditions predicted by THERIA_G,

615°C and 5.9 kbar, correspond to allanite breakdown, the development of a Y annulus and the formation of monazite. The monazite population at 977 ± 4 Ma is interpreted to have formed at these P-T conditions. Using the 977 ± 4 Ma age as an anchor for the P-T-t path and relative timescale determined through garnet growth simulations with THERIA_G, initial garnet growth is predicted at 1030 Ma (Fig. 3.10a). Using the size of the largest garnet porphyroblast identified with XR- μ CT and the timescale over which garnet was predicted to have formed, a corresponding average garnet growth rate of $30 \mu\text{m Ma}^{-1}$ can be obtained.

The P-T-t estimates provided in this study compliment those of McCarron et al (2013). Corfu & Easton (1995) identified a major period of metamorphism and deformation in the Mazinaw Domain between 1110 and 980 Ma associated with the Ottawa Orogeny or “Grenville” Orogeny. The 977 ± 4 Ma obtained by McCarron et al. (2013) puts peak metamorphism at the tale end of the Ottawa Orogeny in this locality of the Mazinaw Domain. The age fits well into a regional context given that detrital zircons put Flinton Group deposition after 1150 Ma (Sager-Kinsman & Parish, 1993) and $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende cooling ages from Flinton Group yield 950-940 Ma (Cosca et al., 1991). Using the cooling data of Busch et al. (1996) and the metamorphic constraints from this study an average cooling rate of 3°C Ma^{-1} can be calculated over the temperature interval 615-500°C. The cooling rate is remarkably similar to that predicted through THERIA_G modeling (2°C/Ma) and the $1\text{-}4^\circ\text{C Ma}^{-1}$ cooling rates calculated by Cosca et al. (1991) for the Grenville Orogen as a whole.

3.5.4 Limitations of THERIA_G modeling

THERIA_G was rigorously tested in this study and was successful at predicting the chemistry in a garnet population characterized with XR- μ CT and EPMA. THERIA_G was unable to predict the observed sizes of garnet using the observed CSD. On average THERIA_G grew the grains 100-200 μ m smaller than that observed. A potential explanation might be the presence of mineral inclusions in garnet, which are not considered during calculations with THERIA_G. The model grows garnet as spheres, adding shells to co-crystallizing garnet porphyroblasts. In sample 12TM5E the garnet porphyroblasts have inclusion rich cores and inclusion free rims (Fig. 3.4). The radius and volume that inclusions contribute to garnet would potentially account for some of the difference between the predicted and observed radius/volume. The largest porphyroblast centrally sectioned for this study has a radius of 1558 μ m. If the corresponding inclusion volume of garnet were 5, 10, 15, 20, 25 and 30%, the radius of the crystal would diminish by 26, 54, 82, 112, 142 and 175 μ m respectively.

Alternative reasons to explain the radius discrepancy may be shortcomings in the thermodynamic database or the major element chemistry used for calculations. The rock sample crushed and fused for WDXRFA was similar in size and originally attached to that shown in Figure 3.3a. It was noted that the analyzed garnet population grew from the same equilibrium domain however if there were compositional differences across the original sample than it may be possible that the whole rock chemistry used for phase equilibria calculations belonged to a different equilibrium domain than that of the analyzed garnet population.

THERIA_G was able to predict reasonably well the chemical zoning in X_{alm} , X_{sps} and X_{grs} from core to rim along the specified P-T-t path. However, issues were encountered for predicting X_{pyr} and the compositional changes for X_{alm} and X_{grs} in the outer 200 μm of garnet. The fit between the predicted and observed zoning for X_{pyr} is rather poor, and the discrepancy increases with a decrease in garnet size. Changes to the whole rock chemistry during garnet resorption at the staurolite in reaction may have played an important role at causing the X_{pyr} discrepancy. The inability of THERIA_G to accurately predict X_{pyr} may represent limitations in the internally consistent thermodynamic database or limitations of the diffusion parameters used to model multi-component diffusion in garnet. Based on the observations presented in this study, the diffusivities of Mg in almandine garnet may be too slow.

The inability of THERIA_G to predict the compositional changes in X_{alm} and X_{grs} in the outer 200 μm of garnet may represent a resorption event that interrupts periods of garnet growth or the influence of an unconsidered phase in the thermodynamic database. It is interesting to note that the point at which THERIA_G can no longer accurately predict X_{alm} and X_{grs} corresponds to an yttrium annulus (Figs. 3.6, 3.7, 3.8). The yttrium annuli in 12TM5E correspond to a small shoulder in X_{grs} before decreasing toward the rim and a small trough in X_{alm} before increasing toward the rim. It has been well documented that yttrium strongly partitions into garnet (Jaffe, 1951; Lanzirotti, 1995). Enrichment of yttrium in metamorphic garnet commonly results from breakdown of Y-rich accessory phases such as xenotime and allanite (Pyle & Spear, 1999; Yang & Pattison, 2006), or from resorption and regrowth of garnet (Pyle & Spear, 1999; Yang &

Rivers, 2002). In sample 12TM5E, McCarron et al. (2013) documented allanite inclusions in garnet on the core side of the yttrium peak and monazite inclusions on the rim side of the yttrium peak. They interpreted these observations to represent monazite growth at the expense of allanite and the formation of a Y annulus in garnet. The breakdown of epidote family minerals has been shown to cause a sharp decrease in X_{grs} and increase in X_{alm} (e.g., Hickmott & Spear 1992; Spear & Menard, 1993). These observations are consistent with the chemical trends observed in garnet porphyroblasts of 12TM5E. However, knowledge of the thermodynamic properties of allanite are scarce and not considered in our calculations. This may be a likely cause for mismatches with THERIA_G in the outer 200 μm of garnet.

3.6 Conclusions

This is the first successful analysis of the chemistry of an entire garnet population that couples thermodynamic and diffusion modeling to reconstruct the P-T-t path associated with an orogenic event. EPMA analysis on the centrally sectioned garnet porphyroblasts reveals decreasing X_{sps} and X_{grs} and increasing X_{alm} and X_{pyr} from core to rim consistent with a prograde zoning. A strong positive correlation between the X_{sps} content of the core and the size of garnet was identified, suggesting that the timing of crystallization reflects the P-T-X conditions and not the local availability of reactive components. Garnet growth simulations with the THERIA_G software provide a clockwise P-T path over the interval 3.7 to 5.9 kbar and 512 to 615°C for metamorphism associated with the Grenville Orogeny. Intracrystalline diffusion was particularly efficient at relaxing initial compositional gradients in relatively small garnet porphyroblasts and was used to infer an

average heating/cooling rate of ca. $2^{\circ}\text{C Ma}^{-1}$. Equilibrium mineral assemblages predicted by THERIA_G match petrographic observations well. In situ monazite geochronology coupled with THERIA_G modeling constrains peak metamorphism at the locality to 977 ± 4 Ma, initial garnet growth at 1030 Ma and an average garnet growth rate of ca. $30\mu\text{m Ma}^{-1}$. It is suggested that the volume mineral inclusions contribute to garnet should be considered during crystallization simulations with THERIA_G. It is concluded that a better understanding of the physio-chemical properties of accessory phases such as allanite and xenotime and their impact on phase relations with garnet is required to fully understand the chemical zoning of a garnet population as a record of the host rock's metamorphic evolution.

CHAPTER 4:

Overall conclusions

The Flinton Group was deposited after 1150 Ma (Sager-Kinsman & Parrish, 1993), metamorphosed during the Grenville Orogeny between 1080 and 980 Ma, and was in the initial stages of cooling by 950-940 Ma (Busch et al., 1996; Cosca et al., 1991).

Petrographic observations suggest that all porphyroblastic phases overgrew an initial fabric, S_0 , that was subsequently wrapped around the porphyroblasts, S_1 , and then crenulated, S_2 , during later deformation events. Phase equilibria modeling suggests an increase in pressure and temperature across the study area from 5.6 to 7.9 kbar and 615 to 715°C. Evidence for partial melting was not observed in the higher grade samples in the northeast portion of the field area. Isopleth thermobarometry applied to the cores of garnet porphyroblasts from different points along the study area revealed similar P-T conditions of initial garnet growth at 3.7 kbar and 515°C with corresponding geothermal gradients of 40°C km⁻¹. Such a high geothermal gradient is suggested to represent elevated geotherms in response to crustal delamination following the Shawinigan Orogeny, the Midcontinent rift system or the extensional basin in which the Flinton Group was deposited. Non destructive three-dimensional analysis of a population of garnet porphyroblasts characterized using high-resolution X-ray micro-computed tomography revealed a unimodal slightly positively skewed crystal size frequency distribution. Garnet porphyroblasts ranging from 4000 to 200 µm were centrally sectioned and analyzed with the electron probe micro-analyzer to reveal a prograde zoning characterized by decreasing X_{sps} and X_{grs} and increasing X_{alm} and X_{pyr} from core

to rim. Garnet growth simulations with the THERIA_G software program provided a clockwise path over the P-T interval 3.7 to 5.9 kbar and 513 to 615°C. Diffusional modification of growth zoning in relatively small porphyroblasts of the population were used to infer an average heating/cooling rate of 2°C Ma⁻¹. A major monazite age population at 977 ± 4 Ma was determined via in situ laser ablation - inductively coupled plasma - mass spectrometry U-Pb geochronology. From the distribution of accessory phases and major and trace element zoning in garnet, the age was interpreted to represent monazite growth at the expense of allanite near the peak conditions of garnet growth. Coupling the average heating rate of 2°C Ma⁻¹ with the age obtained from monazite U-Pb geochronology, initial garnet growth was predicted at 1030 Ma and an average growth rate of garnet of 30µm Ma⁻¹ was determined. The relationships between core chemistry, compositional gradient and crystal radius suggest that interface-controlled crystallization is a good approximation of the crystallization mechanism for garnet in the studied sample. Mineral inclusions, resorption processes and the associated change in the effective bulk rock composition, and unconsidered phases such as xenotime and allanite in the thermodynamic database are identified as important sources of error, which, to improve results with THERIA_G in the future, should be considered during garnet growth simulations.

In order to test the robustness of the metamorphic rates determined through diffusion modeling in the population of garnet porphyroblasts in this study detailed allanite and xenotime geochronology could be coupled with the monazite geochronology presented in this study. Additional garnet populations from the Flinton Group could also be analyzed

in a similar fashion to this study to determine if the metamorphic rates are similar or dissimilar. Detailed garnet geochronology could be performed on the different size classes of the population to determine when each individual size class nucleated along the prograde path. A novel approach could be adopted where a garnet-bearing sample would be crushed and sieved to separate the different garnet size classes for detailed Lu-Hf or Sm-Nd geochronology.

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APPENDIX

A.1 Solution Models

Grt [garnet, Holland & Powell (1998)]

Chl [chlorite, Holland et al., 1998]

AbPl [albite-rich side of the plagioclase solvus, Newton et al., (1980)]

AnPl [anorthite-rich side of the plagioclase solvus, Newton et al., (1980)]

Bt [biotite, Powell & Holland (1999), extended to cover Fe, Mn and Ti solutions]

St [staurolite, Holland & Powell (1998) extended to cover Mn-solutions]

Cld [chloritoid, White et al., (2000), extended to cover Mn-solutions]

Ph [muscovite, Holland & Powell (1998)]

Ilm [ilmenite, (Holland & Powell (1998)]

COH fluid [Carbon-oxygen-hydrogen fluid, Evans & Powell (2006)]

A.2 Mineral abbreviations

After Whitney & Evans (2010)

Mineral Name	Abbreviation
Garnet	Grt
Biotite	Bt
Staurolite	St
Chlorite	Chl
Chloritoid	Chd
Kyanite	Ky
Andalusite	And
Sillimanite	Sil
Clinozoisite	Czo
Plagioclase	Pl
Akali Feldspar	Afs
Cordierite	Crd
White mica	Ph
Sanidine	Sa
Ilmenite	Ilm
Magnetite	Mag
Rutile	Rt
Graphite	Gph
Allanite	Aln
Xenotime	Xtm
Monazite	Mnz
Zircon	Zrn
Apatite	Apa

A.3 Whole rock chemistry for additional samples

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	MgO	MnO	CaO	Fe ₂ O ₃	Na ₂ O	K ₂ O	P ₂ O ₅	L.O.I	Total
11TM5A	56.67	17.28	1.06	2.31	0.13	0.43	16.44	0.32	3.25	0.14	1.47	99.52
11TM5B	57.90	19.09	1.19	1.33	0.03	0.22	13.49	0.46	3.98	0.08	1.23	98.99
11TM5C	57.68	18.49	1.13	1.40	0.08	0.41	14.52	0.50	3.54	0.13	1.10	98.99
11TM5D	58.1	18.87	1.20	1.47	0.13	0.62	11.73	0.55	3.86	0.35	1.92	98.80
11TM5F	55.06	20.77	1.27	1.36	0.05	0.35	13.39	0.62	4.30	0.10	1.70	98.97

A.4 Equilibrium phase diagrams for additional samples

(A) 11TM5A, (B) 11TM5B, (C) 11TM5C, (D) 11TM5D and (E) 11TM5F. Garnet-bearing assemblages are highlighted in light grey while the observed mineral assemblages are highlighted in dark grey. The observed mineral assemblages are overlapped in Fig. 2.10f.

A.5 LA-ICP-MS monazite data

Analysis 1A-4.1 = thin section 5E2-1A, monazite 4, analysis 1

Analysis	²⁰⁷ Pb/ ²³⁵ U	207/235 Prop2SE	²⁰⁷ Pb/ ²³⁵ U Final age	²⁰⁶ Pb/ ²³⁸ U	206/238 Prop2SE	²⁰⁶ Pb/ ²³⁸ U Final age	Error Correlation	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb Prop2Se	²⁰⁷ Pb/ ²⁰⁶ Pb final age	% discordance	U (ppm)	Th (ppm)	Pb (ppm)
1A-4.1	1.600	0.063	971	0.162	0.005	971	0.161	0.072	0.003	966	-0.518	2160	5120	534
1A-9.2	1.599	0.059	972	0.163	0.004	970	0.494	0.072	0.002	996	2.610	3490	10860	1058
1A-9.1	1.595	0.052	967	0.163	0.004	971	0.259	0.071	0.002	976	0.512	3140	9930	991
1A-11.2	1.605	0.068	971	0.163	0.006	971	0.334	0.073	0.002	1018	4.617	3180	7830	787
1A-11.1	1.598	0.063	968	0.162	0.004	965	0.518	0.072	0.002	975	1.026	3420	14700	1380
1A-12.2	1.608	0.055	971	0.162	0.004	969	0.674	0.071	0.002	963	-0.623	3800	8440	837
1A-6.1	1.575	0.061	958	0.161	0.004	960	0.680	0.071	0.002	977	1.740	3080	9800	1010
1A-1.1	1.718	0.085	1017	0.167	0.006	993	0.342	0.078	0.004	1131	12.202	689	1990	213
1A-12.1	1.759	0.071	1029	0.172	0.006	1025	0.425	0.075	0.002	1033	0.774	3580	21800	2180
1A-8.1	1.561	0.063	957	0.158	0.005	944	0.333	0.072	0.003	1009	6.442	1459	5530	563
1A-14.3	1.960	0.360	1095	0.187	0.022	1100	0.543	0.075	0.013	1122	1.961	1050	2590	291
1A-3.1	1.860	0.130	1064	0.178	0.008	1055	0.487	0.075	0.004	1061	0.566	625	1350	145
1B-9.2	1.538	0.056	947	0.158	0.003	945	0.454	0.071	0.001	954	0.943	2650	7000	671
1B-9.1	1.622	0.067	979	0.164	0.003	978	0.649	0.072	0.002	982	0.407	2580	5400	549
1B-6.1	1.607	0.071	973	0.163	0.004	971	0.645	0.072	0.002	977	0.614	2640	14600	1540
1B-5.2	1.533	0.069	942	0.157	0.003	939	0.505	0.071	0.002	980	4.184	3350	9300	912
1B-5.1	1.716	0.093	1012	0.171	0.005	1015	0.494	0.074	0.003	1029	1.361	3260	26500	2470
1B-4.2	1.614	0.095	975	0.165	0.007	985	0.345	0.071	0.003	969	-1.651	4010	11970	1120
1B-4.1	1.626	0.073	979	0.165	0.004	984	0.259	0.072	0.002	987	0.304	3445	19170	1855
1B-2.1	1.534	0.065	944	0.155	0.003	930	0.266	0.072	0.002	982	5.295	3390	8590	814
1B-1.2	1.621	0.063	977	0.164	0.003	980	0.197	0.071	0.002	976	-0.410	3480	8230	806
5-10.1	1.521	0.077	937	0.157	0.005	942	0.365	0.070	0.002	950	0.842	3890	7040	587
5-9.1	1.623	0.092	977	0.168	0.005	1000	0.259	0.072	0.003	982	-1.833	2000	6820	632
5-8.2	1.651	0.069	988	0.173	0.004	1026	0.498	0.071	0.002	972	-5.556	2630	4840	502
5-8.1	1.655	0.060	990	0.167	0.003	992	0.518	0.073	0.001	1008	1.587	3260	16400	1680
5-7.1	1.709	0.067	1015	0.175	0.004	1037	0.371	0.072	0.002	983	-5.493	3570	23200	2180
5-6.1	1.656	0.063	991	0.170	0.004	1011	0.439	0.071	0.001	971	-4.119	4260	19300	2000
5-5.2	1.688	0.068	1006	0.171	0.003	1016	0.259	0.072	0.002	970	-4.742	4470	26000	2610
5-5.1	1.681	0.076	999	0.159	0.004	950	0.456	0.076	0.002	1108	14.260	2780	7850	807
5-4.2	1.616	0.069	980	0.164	0.005	977	0.468	0.072	0.002	950	-2.842	5930	15020	1401
5-4.1	1.682	0.097	1006	0.174	0.006	1034	0.590	0.073	0.003	989	-4.550	2010	7470	771
5-3.2	1.625	0.110	977	0.167	0.008	997	0.531	0.071	0.002	967	-3.102	5110	10620	1079
5-3.1	1.668	0.071	994	0.170	0.005	1012	0.600	0.072	0.002	977	-3.582	5490	17900	1780
5-2.2	1.728	0.068	1017	0.174	0.003	1031	0.403	0.071	0.002	986	-4.564	2260	5270	627
5-2.1	1.641	0.062	985	0.165	0.004	984	0.295	0.071	0.002	977	-0.716	3290	8400	858
5-1.1	1.645	0.063	988	0.169	0.003	1004	0.626	0.072	0.001	975	-2.974	2940	12700	1330
6-3.1	1.628	0.086	980	0.165	0.006	983	0.241	0.071	0.002	956	-2.824	3310	7410	712
6-1.1	1.624	0.055	979	0.164	0.003	978	0.319	0.072	0.002	999	2.102	2690	15600	1560
1-11.2	1.497	0.060	929	0.160	0.005	956	0.206	0.069	0.003	906	-5.519	1674	11690	1118
1-10.2	1.568	0.038	955	0.160	0.003	956	0.309	0.072	0.002	968	1.240	2820	6060	596
1-10.1	1.635	0.044	983	0.166	0.003	988	0.094	0.071	0.002	965	-2.383	3709	11700	1026
1-7.2	1.590	0.053	967	0.162	0.005	970	0.455	0.072	0.002	989	1.921	2230	4540	453
1-7.1	1.602	0.035	970	0.162	0.003	967	0.381	0.072	0.001	981	1.427	3630	17570	1641
1-5.2	1.600	0.050	968	0.163	0.004	972	0.390	0.071	0.002	960	-1.250	2160	4820	514

1-5.1	1.561	0.043	956	0.159	0.003	948	0.315	0.072	0.002	987	3.951	2140	10500	1100
1-4.2	1.560	0.053	953	0.159	0.005	951	0.608	0.070	0.002	946	-0.529	1490	4190	427
1-4.1	1.686	0.064	1001	0.166	0.005	993	0.508	0.074	0.004	1043	4.794	2200	5050	494
1-3.1	1.553	0.068	951	0.160	0.006	956	0.480	0.071	0.003	947	-0.950	4310	24800	2210
1-2.2	1.657	0.052	994	0.166	0.004	990	0.630	0.072	0.002	1007	1.688	2890	5250	519
1-2.1	1.644	0.039	988	0.165	0.003	984	0.513	0.072	0.001	986	0.203	2470	11300	1166
1-1.1	1.623	1.800	978	0.164	0.021	981	0.330	0.072	0.037	972	-0.926	2990	7170	594
1-3.2	1.642	0.230	985	0.168	0.017	999	0.289	0.069	0.007	945	-5.714	2520	6570	582
8-6.1	1.641	0.120	985	0.167	0.007	997	0.002	0.072	0.003	985	-1.218	3890	12000	1070
8-6.1	1.719	0.170	1014	0.169	0.010	1007	0.434	0.073	0.003	1027	1.947	3270	8450	823
8-5.2	1.691	0.073	1003	0.170	0.005	1009	0.584	0.073	0.002	987	-2.229	2780	7310	727
8-5.1	1.648	0.065	992	0.162	0.005	968	0.482	0.074	0.002	1043	7.191	3170	15500	1480
8-4.2	1.636	0.084	982	0.159	0.006	948	0.493	0.075	0.004	1050	9.714	2240	8650	750
8-4.1	1.662	0.066	992	0.165	0.005	986	0.469	0.073	0.002	993	0.705	2010	5730	552
8-3.2	1.735	0.075	1026	0.170	0.005	1010	0.327	0.073	0.002	1021	1.077	3280	11810	1104
8-3.1	1.614	0.060	977	0.166	0.004	989	0.547	0.070	0.002	950	-4.105	3270	13700	1290
8-2.3	1.647	0.077	987	0.165	0.006	984	0.490	0.073	0.001	980	-0.408	3480	16900	1710
8-2.2	1.626	0.100	979	0.164	0.006	977	0.107	0.072	0.004	986	0.913	3587	7920	739
8-2.1	1.605	0.079	970	0.164	0.005	977	0.389	0.071	0.002	965	-1.244	3200	8700	940
8-1.1	1.697	0.430	1006	0.168	0.020	1003	0.203	0.075	0.010	1020	1.667	3300	8200	800
14-7.2	1.608	0.061	971	0.165	0.005	984	0.641	0.072	0.002	973	-1.131	3610	10300	999
14-7.1	1.627	0.061	981	0.165	0.004	983	0.401	0.072	0.002	988	0.506	2160	4010	449
14-6.2	1.715	0.140	1018	0.174	0.008	1034	0.423	0.072	0.005	976	-5.943	3380	7000	612
14-6.1	1.622	0.094	977	0.165	0.006	985	0.552	0.071	0.003	968	-1.756	4040	7920	689
14-4.2	1.626	0.061	982	0.165	0.004	982	0.620	0.072	0.002	981	-0.102	2700	5920	633
14-4.1	1.751	0.055	1027	0.178	0.004	1058	0.475	0.071	0.001	971	-8.960	3850	24000	2500
14-3.2	1.842	0.790	1058	0.172	0.014	1021	0.310	0.076	0.018	1109	7.935	2320	5360	487
14-3.1	1.703	0.150	1008	0.170	0.006	1013	0.610	0.072	0.005	1012	-0.099	3980	15300	1410
14-2.1	1.756	0.150	1027	0.176	0.008	1045	0.361	0.072	0.006	970	-7.732	3290	7300	674
14-1.2	1.750	0.490	1021	0.176	0.027	1043	0.628	0.071	0.015	993	-5.035	975	2080	215
14-1.1	1.647	0.056	987	0.170	0.006	1014	0.197	0.071	0.002	947	-7.075	3220	13800	1390

A.6 THERIA_G input files

theriag_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

theriag_CSD:

5 158 Thickness of successive garnet shells (Delta r_shell) [mue] and size of radius class [mue]
0.0444 no. of garnets in radius class 1 [grt/ccm] of the rock volume (add a line for each radius class)
0.1422
0.5246
1.6717
2.9878
3.4235
2.8811
3.0589
2.1697
1.6272

therin:

SI(58.280)TI(1.113)AL(23.924)FE(6.710)MN(0.051)MG(2.166)CA(0.445)NA(1.399)K(5.912)O(167.6995)H(100)O(50)C(100) *

thermodynamic database of Holland & 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	0.000000
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	0.000000
VH2	10.0000	4.0000	-0.000219750		
Fe-chloritoid	SI(1)AL(2)FE(1)O(7)H(2)	fctd	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	0.000000
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	0.000000
VH2	10.0000	4.0000	-0.000219750		
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	0.000000
VH2	10.0000	4.0000	-0.000168000		
Fe-epidote	SI(3)AL(1)FE(2)CA(2)O(13)H(1)	fep	2nh		
ST	0.0	-6002180.000	357.0000	14.1900	
C3	520.10000	0.0314990	-15426000.0	218.800	0.00
VHP	0.000050500	1294.0	0.0000	0.00	0.000000
VH2	10.0000	4.0000	-0.000199280		
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	0.000000
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)	fcrd	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)	mnrd	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		
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	NI(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		
clinocllore	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		
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		
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			
graphite	C(1)		gph	1nh		
ST	0.0	0.000	5.8500	0.5298		
C3	51.00000	-0.0044280	488600.0	-805.500	0.00	
VHP	0.000048400	390.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000058500			
sylvite.liq	K(1)CL(1)		syvL	1nh		
ST	0.0	-416490.000	95.3000	3.8570		
C3	66.90000	0.0000000	0.0	0.000	0.00	
VHP	0.000500000	59.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000008850			
halite.liq	Na(1)CL(1)		hltL	1nh		
ST	0.0	-393420.000	79.7000	2.9650		
C3	72.00000	-0.0032230	0.0	0.000	0.00	
VHP	0.000500000	66.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000009900			
forsterite.liq	Si(1)MG(2)O(4)		foL	2nh		
ST	0.0	-2225160.000	-55.0000	4.2430		
C3	267.90000	0.0000000	0.0	0.000	0.00	
VHP	0.000145000	730.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000109500			
fayalite.liq	Si(1)Fe(2)O(4)		faL	2nh		
ST	0.0	-1459210.000	102.5000	4.6950		
C3	239.70000	0.0000000	0.0	0.000	0.00	
VHP	0.000169000	410.0	0.0000	0.00	0.00000	
VH2	10.0000	4.0000	-0.000061500			
sillimanite.liq	Si(1)Al(2)O(5)		sillL	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		
enstatite.liq SI(2)MG(2)O(6) enL 1nh					
ST	0.0	-3091760.000	-2.0000	6.9000	
C3	354.90000	0.0000000	0.0	0.000	0.00
VHP	0.000129000	260.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000039000		
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		
diopside.liq SI(2)MG(1)CA(1)O(6) diL 1nh					
ST	0.0	-3208180.000	23.8000	7.3400	
C3	345.30000	0.0000000	0.0	0.000	0.00
VHP	0.000129000	300.0	0.0000	0.00	0.00000
VH2	10.0000	4.0000	-0.000045000		
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		
!					
***** GAS DATA *****					
Water H(2)O(1) H2O nh					
SPC HHP98					
ST	0.0	-241810.000	188.8000	0.0000	
C3	40.10000	0.0086560	487500.0	-251.200	0.00
Carbon-dioxide C(1)O(2) CO2 nh					
SPC CHP98					
ST	0.0	-393510.000	213.7000	0.0000	
C3	87.80000	-0.0026440	706400.0	-998.900	0.00
CO	C(1)O(1)		CO	use	
ST	0.0	-110530.000	197.6700	0.0000	
C3	45.70000	-0.0000970	662700.0	-414.700	0.00
CS2	0.03498700	132.900			
CH4	C(1)H(4)		CH4	use	
ST	0.0	-74810.000	186.2600	0.0000	

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C3      150.10000    0.0020620    3427700.0    -2650.400        0.00
CS2      0.046000    190.600
**** SOLUTION DATA ****
FLUID3 (SITE,MARGULES) M(1):H2O,H2S,CH4,CO2,S2,O2,H2,CO
  Water   H2O    -1.0  0.0  0.0
  H2S     H2S    -1.0  0.0  0.0
  CH4     CH4    -1.0  0.0  0.0
  Carbon-dioxide CO2  -1.0  0.0  0.0
  S2      S2     -1.0  0.0  0.0
  O2      O2     -1.0  0.0  0.0
  H2      H2     -1.0  0.0  0.0
  CO      CO     -1.0  0.0  0.0
****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]
OHM-BUFFER O(2)  OHM   *OHM
  ST      0.000  000000.000  000.000000  0.000000
  CP1     0.000000  0.00000  0.00  0.0
  COM     hematite[6]magnetite[-4]  0
-OHM-BUFFER O(-2) -OHM   *OHM
  ST      0.000  000000.000  000.000000  0.000000
  CP1     0.000000  0.00000  0.00  0.0
  COM     OHM-BUFFER[-1]  0
***** SOLUTION DATA *****
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

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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

clinochlore 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

clinochlore - daphnite

12 2500.0 0.0 0.0

clinochlore - amesite

12 18000.0 0.0 0.0

daphnite - amesite

12 13500.0 0.0 0.0

*****MINERAL DATA***** phng

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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****
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

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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
***** SOLUTION DATA *****
LIQtc  (EXT,MARGULES)
Silica8.liq
albite.liq
K-feldspar.liq
anorthite.liq
sillimanite8.liq
forsterite8.liq
fayalite8.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

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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
!
forsterite8.liq - fayalite8.liq
12 18000.0  0.0  0.00
forsterite8.liq - H2O.liq
12 11000.0  0.0 -0.50
!
fayalite8.liq - H2O.liq
12 12000.0  0.0  0.00
!

```

A.7 EPMA element distribution maps for size classes 2, 5, 6, 8 and 10

EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 2. EPMA results along the dotted line in (B) are shown in Fig. 3.7b.

EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 5. EPMA results along the dotted line in (B) are shown in Fig. 3.7d.

EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 6. EPMA results along the dotted line in (B) are shown in Fig. 3.7e.

EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 8. EPMA results along the dotted line in (B) are shown in Fig. 3.7f.

EPMA element distribution maps for (A) Ca, (B) Mn, (C) Mg, (D) Fe and (E) Y for a garnet porphyroblast from size class 10. EPMA results along the dotted line in (B) are shown in Fig. 3.7g.

A.8 Example garnet formula calculation based on 24 oxygens

Oxide	Analysis (Wt%)	Molecular proportion of oxides	Molecular proportion of oxygen from each molecule	Number of anions on the basis of 24 oxygen	Number of cations	Endmember
SiO ₂	37.03	0.62	1.23	12.02	6.01	
Al ₂ O ₃	20.90	0.20	0.61	5.99	3.96	
TiO ₂	0.01	0.00	0.00	0.00	0.00	
FeO	38.81	0.54	0.54	5.27	5.27	0.87
MgO	2.29	0.06	0.06	0.55	0.55	0.09
CaO	0.90	0.02	0.02	0.16	0.16	0.03
MnO	0.08	0.00	0.00	0.01	0.01	0.01
Total	100.02	2.46			15.95	
	Oxygen factor	9.74		X site total	5.98	

Oxygen factor = (24/column 2)
X site total = (Fe+Mn+Mg+Ca)

All garnet spot analysis are provided on the accompanying CD.