TRACE ELEMENT ZONING IN GARNETS:

IMPLICATIONS FOR METAMORPHIC PETROGENESIS

by

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ABSTRACT

Trace element zoning has been measured in garnets from a variety of metamorphic environments using a Cameca IMS-3F ion microprobe. Trace element variability is shown to be a sensitive tracer of metamorphic processes during garnet growth, and hence provides insights into metamorphism unavailable from major element studies.

An amphibolite garnet from the western Tauern window, Austria exhibits: 1) a rimward decreasing Ti zoning profile, and 2) humps in element abundance of Na, Sc, V, Y and heavy REE that roughly correlate with a Ca variation interpreted as a P-T reversal. Coexisting amphibole shows humps in V, Sc and Y at a pleochroic break. The humps suggest a brief interval of open system behavior during garnet growth. Open system components were derived either externally, from trace element enriched metasomatic fluids, or internally, from the trace element enriched cores of zoned refractory minerals. Similarities between the humps for garnet and amphibole suggest that the two minerals grew at the same time. The trace element signatures of the amphibole core (flat Y and Sc) suggest that it formed prior to garnet nucleation.

Two garnets from the contact metamorphic terrain of the Kwoiek Area, British Columbia show: 1) 'bell shaped' Mn zoning, 2) a rimward decrease-increase-decrease Ti profile, and 3) inflections in Li, Na, Ca, Sc, V and some HREE at the point of abrupt Ti increases. Only Mn can be fit easily by a simple Rayleigh fractionation model, suggesting that Rayleigh fractionation is not a successful paradigm for garnet zoning. The zig-zag Ti zoning profile suggests non-equilibrium behavior during isobaric contact metamorphism in a Ti-oxide bearing assemblage. A possible explanation for the Ti zoning is solute trapping of surface segregated Ti during two episodes of rapid mineral growth.

Phase equilibria, inclusion relations, and major and trace element zoning in garnets were used to investigate reaction histories in a suite of calcareous pelites from the NW Shelburne Falls quadrangle of western Massachusetts.
Ferromagnesian components in garnet were produced primarily through a reaction involving chlorite as a reactant. The most Fe-rich sample also produced ferromagnesian garnet through magnetite breakdown. Involvement of magnetite in garnet producing reactions is suggested by: 1) the presence of magnetite inclusions in garnet, but not in the rock matrix, and 2) strong rimward increases in the magnetite-compatible trace element Co in garnet.

Grossular component in garnet was produced by different reactions in rocks of varying Ca/Al and Fe/Mg whole-rock ratio. Low CaO, high SiO₂, high FeO/MgO rocks developed grossular component via reactions in which plagioclase was the Ca source. Involvement of plagioclase in grossular producing reactions is suggested by: 1) the presence of plagioclase inclusions in garnets, and 2) rimward zoning toward more Na-rich plagioclase. High CaO, intermediate SiO₂ rocks first produced grossular component by reactions involving clinzoisite. Evidence for clinzoisite involvement in garnet growth is provided by: 1) the presence of clinzoisite inclusions solely in portions of garnet in which phase equilibria constraints on Ca-zoning are compatible with increased T metamorphism, 2) the development of Y and HREE enrichments in growing garnet due to breakdown of refractory Y and HREE enriched clinzoisite, and 3) zoning of plagioclase toward high Ca. High Ca, low SiO₂, low Fe/Mg rocks developed grossular component in part through amphibole breakdown. Amphibole involvement in garnet growth reactions is suggested by: 1) the presence of diamond shaped pseudomorphs solely in low Fe/Mg rocks, 2) increases in MREE near the rims of garnets.

Trace element zoning is particularly useful for tracing phase relations in the calcareous subsystems of metamorphic rocks because the Ca-rich phases (amphibole, clinzoisite, plagioclase, garnet) have distinctive trace element signatures.

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Chapter 1: Introduction
1.0 Introduction

It is evident that the primary goal of metamorphic petrologists is shifting from the determination of conditions of peak metamorphism to understanding the dynamics of metamorphic processes. To understand thoroughly the development of orogenic terrains it is necessary to characterize the changes in temperature, pressure, deformation field, mineral assemblage, chemical environment, heating rate, uplift rate, mineral growth rate, and degree of approach to chemical equilibrium that occur during a metamorphic event. Substantial progress on several of these fronts is evident. Reaction histories - changes in mineral assemblage and mineral composition during metamorphism - have been divined through studies of mineral inclusions and pseudomorphic textures (Loomis, 1972; Thompson et al., 1977; Selverstone et al., 1984; Spear and Rumble, 1986; St. Onge, 1987). P-T paths for some regional metamorphic terrains are now relatively well characterized (Hollister et al.; 1979; Tracy and Robinson, 1980; Hollister, 1982; Selverstone et al., 1984; Spear et al., 1984; Schenk, 1984; Droop 1985; Bucher-Nurminen and Droop, 1984; Selverstone and Spear, 1985; Spear and Franz, 1986; Spear and Rumble, 1986). Uplift and heating/cooling histories have been determined through kinetic modeling (Lasaga et al., 1977; Tracy and
Dietsch, 1982), Ar^{40}/Ar^{39} geochronology, (Harrison et al., 1979; Cliff et al., 1985), and integrated petrologic and geochronologic investigations (Hollister, 1982; Selverstone, 1985). Changes in deformation field have been ascertained through studies of rotated porphyroblasts (Rosenfeld, 1970). Research into the dynamic aspects of metamorphism using traditional petrologic techniques continues apace.

Other aspects of the dynamics of metamorphism have not been addressed in as much detail: (1) changes in chemical environment (open system behavior) during metamorphism, except the gross characterization of metasomatism (Brady, 1977; Joesten, 1983), oxygen isotope infiltration (Wickham and Taylor, 1986) and fluid-rock ratios (Ferry, 1986), (2) changes in degree of equilibration/overstepping during metamorphism, (3) changes in heating rate during orogenesis, and (4) changes in mineral growth and nucleation rates during metamorphism.

A common thread in many of the studies referenced above is their reliance on textures and inclusions preserved within zoned porphyroblasts, particularly garnets, to provide information on both physicochemical and kinetic aspects of metamorphism. Garnets are crucibles that can store the history of metamorphic rocks
prior to matrix equilibration; the inclusions and zoning of garnets provide a record of processes during mineral growth (Hollister, 1966; Rosenfeld, 1970; Tracy et al., 1976; Loomis, 1975; Loomis, 1979; Holland and Richardson, 1979; Spear and Selverstone, 1982; Spear et al., 1984; Baker, 1985; Spear and Rumble, 1986).

Thusfar, petrologists have essentially limited their attentions to the four major elements, Fe, Mg, Ca, and Mn, in their studies of element zoning in garnet. Use of both major and trace element zoning may tighten the constraints that can be placed on the dynamic aspects of metamorphism. Trace elements have a variety of geochemical properties, so they may provide information on a wide range of metamorphic processes. The coupling of trace element and major element geochemistry has provided important insights into igneous processes. Trace element abundances in successive growth zones in garnet provide a continuous record of processes during garnet growth, just as lavas extracted from a subsurface magma reservoir provide a record of events in the magma chamber. Trace elements may provide information on the occurrence of the following processes during garnet growth: 1) elemental fractionation or internal metasomatism caused by mineral growth or breakdown, 2) changes in P-T conditions, 3) the operation of disequilibrium processes, and 4) open system
behavior. Study of trace element zoning in garnets may help elucidate poorly-constrained metamorphic processes, and provide additional constraints on problems that are already tractable.

1.1 Mineral zoning studies - literature review

Major element zoning in garnet and other minerals provides important insights into the dynamics of metamorphic terrains prior to peak metamorphism (Spear et al., 1984). Garnets are ideal to study because they have slow diffusion rates at metamorphic temperatures (Freer, 1981; Cygan and Lasaga, 1985; Elphick et al., 1985), they are common in a wide-range of pelitic and mafic bulk compositions and they have fairly well-known thermodynamic properties (Ganguly and Kennedy, 1974; Ganguly and Saxena, 1984; Geiger et al., 1987). Coupling of major and trace element zoning should provide additional constraints on the evolution of metamorphic assemblages, P-T conditions and chemical environments early in the history of metamorphic terrains prior to rim equilibration. This information is particularly important because both the structural development of many orogenic belts and the mobility of metamorphic fluids, trace elements, and isotopes are often coeval with garnet growth.
Recent reviews of major element garnet zoning studies are provided by Tracy (1982) and Loomis (1983). Garnet zoning studies can be divided into those which assume local, surface equilibrium between zoned porphyroblast rims and their surrounding matrix, and those that assume surface disequilibrium. Studies of each type are highlighted below.

1.1.1 Prograde growth zoning - with surface equilibrium

A large number of studies of amphibolite facies rocks have interpreted garnet zoning as a feature developed during mineral growth accompanying heating and/or decompression (Hollister; 1966, 1969; Harte and Henley; 1966; Tracy et al. 1976; Trzcienski, 1977; Silverstone et al. 1984; Banno et al, 1986; Spear and Rumble, 1986). Preservation of growth zoning requires that the diffusion coefficients in a growing porphyroblast be small; each layer of the mineral is effectively removed from subsequent reactions within the metamorphic system. The details of zoning in a garnet depend on the bulk composition (assemblage) and the P-T path during growth. The vast majority of amphibolite facies garnets have high-Mn \((X_{\text{Spessartine}})\) and high-Ca \((X_{\text{Grossular}})\) cores, and are zoned toward lower \((\text{Fe}/\text{Fe+Mg})\) from core to rim (Tracy, 1982). The overall similarity between the garnet zoning profiles from many medium-grade
schists reflects: (1) the movement of the AFM three-phase assemblage, garnet-biotite-chlorite to lower (Fe/Fe+Mg) with increased temperature (Thompson, 1976; Loomis, 1986; Spear, in press), and (2) the high compatibility of Mn in garnets (Hollister, 1969). Prograde growth zoning provides information on changes in effective bulk composition (Hollister, 1966; Atherton, 1968), changes in assemblage (Thompson et al., 1977; Karabinos, 1984, 1985), and changes in pressure and temperature during garnet growth (Selverstone et al., 1984; Selverstone and Spear, 1985; Spear and Rumble, 1986; St. Onge, 1987). This information can be used to constrain the tectonic and chemical histories of metamorphic terrains (Spear et al., 1984).

1.1.2 Retrograde diffusion zoning - with surface equilibrium

Upper-amphibolite and granulite facies garnets are generally characterized by unzoned cores and zoned near-rim regions (Grant and Weiblen, 1971; deBethune et al., 1975; Lasaga et al., 1977; Woodsworth, 1977; Crowley and Spear, 1987; Spear et al., in prep). This zoning differs from growth zoning; it develops by diffusion during cooling, rather than by heterogeneous reactions during growth, although garnet growth during cooling is not uncommon (Cygan and Lasaga, 1982). Retrograde, diffusion-
induced zoning is most commonly towards higher (Fe/Fe+Mg) and higher $X_{\text{Spessartine}}$ at garnet rims. The retrograded rims are often interpreted in terms of cooling processes (Lasaga et al., 1977; Crowley and Spear, 1987; Spear et al. in prep). The diffusion-induced zoning profiles can be deconvoluted to provide constraints on the cooling rates of high-grade terrains (Lasaga et al., 1977; Spear et al., in prep), or on retrograde P-T paths (Bohlen et al., 1985; Spear, in press).

1.1.3 Disequilibrium zoning - no surface equilibrium

In contact metamorphic environments garnet zoning is occasionally interpreted as a disequilibrium feature. Loomis (1982, 1983) investigated theoretically the disequilibrium zoning of metamorphic garnets, and suggested that features observed by Hollister (1969) could be rationalized by assuming the operation of disequilibrium processes. Loomis related the inverse correlation between bulk rock Mn and $X_{\text{Spessartine}}$ in garnet cores to a reaction-controlled-growth model in which nucleation of garnet is delayed to a temperature higher than that at which garnet would nucleate under equilibrium growth conditions.
1.2 Trace elements in metamorphic rocks - a literature review

Trace element geochemistry is not widely utilized in high-grade metamorphic petrogenetic studies. To date, studies of the trace element geochemistry of high-grade metamorphic rocks can be divided into three categories: (1) whole-rock studies of the mobility of trace elements in metamorphic environments, (2) igneous or chemical-sedimentological investigations of high-grade metamorphic rocks, and (3) studies of the distribution of trace elements between metamorphic minerals.

Each of these three categories of study is reviewed below. Trace element investigations of mid-crustal level greenschist to amphibolite facies material are highlighted. The more extensive literature on trace elements in granulites is summarized by Taylor and McClennan (1985), and is not considered below.

1.2.1 Trace element mobility during crustal metamorphism

Geochemists are concerned with the mobility of trace elements during prograde metamorphism for three reasons: (1) to evaluate whether crustal budgets for trace elements determined through analyses of surficial sedimentary rocks can be extended validly to depth in the continental crust (a particularly important question is
the vertical distribution of the heat-producing elements (K, Th, and U) (Sawka and Chappell, in press), (2) to assess the applicability of trace element discriminant diagrams for tectonic setting (Pearce and Cann, 1973) to metamorphosed volcanics, and (3) to understand the ore-forming potential of metamorphic processes (Haack et al., 1984).

Commonly, large suites of samples from a single metasedimentary formation are analyzed, lumped together according to metamorphic grade and the mean concentrations of trace elements at the different grades are compared. Studies that advocate trace element immobility generally sample a large enough suite of rocks of each grade that they are able to prove that a large, heterogeneous suite of samples at low grade remains heterogeneous at higher grades. Those that favor substantial mobility demonstrate that the mean of a heterogeneous population of element concentrations at low grade is different from the mean of a heterogeneous population of element concentrations at high grade.

Shaw (1954) suggested that the abundances of the majority of trace elements (including Ga, Cr, V, Co, Sc, Zr, Y and Sr) in metapelitic rocks of the Littleton Formation in western New Hampshire did not change with progressive metamorphism from garnet to sillimanite
grade. Exceptions were Ni, Cu, Li, and Pb, which appeared to diminish in abundance at highest metamorphic grade.

Results postdating Shaw's classic study are equivocal. Most investigations suggest little mobility of trace elements (Schwarcz, 1966; Cullers et al., 1974; Muecke et al., 1979; Ronov et al., 1977) except for the alkali-metals (Muecke et al., 1977). Haack and co-workers (1984) claim significant mobility of Cu, Tl, Ba, Pb, Bi, Hg, Sr, Zn and Cd, and suggest that metamorphic fluids are excellent mineralizing agents. Rosler and Beuge (1983) also claim to demonstrate widespread mobility (generally a decrease in element abundance with increased grade) of virtually all trace elements. The latter study is difficult to evaluate; no sample localities, petrographic descriptions, analyses, or standard deviations on averaged analyses are provided.

A second type of trace element mobility study examines a single outcrop, for example a metamorphosed basaltic pillow or lava flow, and relates variability between portions of the outcrop to metamorphic processes. Such studies are most commonly undertaken in low-grade hydrothermally altered basalts; an example from a high-grade terrane is the study of Hynes (1980). Hynes attributed unusual Ti/Zr and Ti/Y ratios of metamorphosed basalts to movement of Ti down chemical potential
gradients cause by difference in $\mu(\text{CO}_2)$ between metamorphic mineral assemblages.

The mobility of trace (and major) elements during metamorphism remains a controversial issue. The studies that demonstrate mobility are often of questionable statistical rigor. Few studies make a convincing case for the variable abundance of any elements at a two-sigma confidence level. Observed differences in trace elements with grade may reflect initial bulk compositional effects. Neither the whole rock investigations of progressive metamorphic sequences nor the small scale studies of local element mobility adequately characterize the petrogenetic controls on trace element mobility.

1.2.2 Sedimentological/igneous studies of metamorphic rocks

Investigators convinced that trace elements, particularly Sc, Y, Zr, P, Ti and the rare earth elements, are immobile during diagenesis and metamorphism treat metasediments and metavolcanics as if they were pristine sediments and volcanics. They make lithologic correlations of metapelites or attempt to pinpoint the tectonic affinity of the basaltic precursor of an amphibolite using techniques applied to unmetamorphosed rocks.
A few authors have used the trace element chemistry of pelites to investigate sedimentological processes (Senior and Leake, 1978), or to make stratigraphic correlations between high-grade metasediments in complexly folded terrains (Holland and Winchester, 1983).

The petrogenesis of the basaltic precursors of amphibolites are also investigated using immobile trace elements. Aleinekoff (1977), Muecke et al. (1979), Drury (1983), Winchester and Floyd (1984) and Coish et al. (1985), among many others, use trace element signatures of metavolcanics to fingerprint the tectonic settings of amphibolites. Discriminant diagrams for tectonic environment are suspect, even in fresh basalts (Wood et al., 1976; Prestvik, 1982; Arculus, 1987); the added complications of small-scale 'immobile' element mobility (Hynes, 198.) limit the usefulness of this approach in metamorphic rocks.

1.2.3 Trace element distributions between metamorphic minerals

The heyday for determinations of the partitioning of trace elements between amphibolite facies minerals was the late 1950's and early 1960's (deVore, 1955; Engel and Engel, 1960; Turekian and Phinney, 1962; Albee, 1965; Schwarcz, 1966; Hunzicker, 1967; Hietanen, 1969),
although Russian researchers present more recent analyses (Krylova et al., 1970; Kremenetskiy and Samdurova, 1979; Lebedev and Nagaytsev, 1982). The reasons for this decline in interest are twofold: 1) the mineral-separate data were difficult to collect, and 2) little useful petrogenetic information was derived from the data. Mineral-mineral trace element partitioning is not systematic with metamorphic grade (Albee, 1965; Hietanen, 1969), except for the ilmenite/biotite Cr, V, Co and Zr distributions described by Schwarcz (1966), so trace element variations did not appear to be promising as geothermometers or geobarometers. Relatively low data quality and the zoning of trace elements in the mineral separates used for these early studies may have complicated recognition of any systematics of element partitioning between metamorphic minerals.

1.2.4 Summary - trace elements in metamorphic rocks

Traditional trace element geochemical study of metamorphic rocks and minerals has not yielded significant petrogenetic information. The results obtained in the 1960's were curiosities, but did not provide answers to important petrologic questions. In the next section I will detail how in situ analysis of trace element zoning in metamorphic minerals may provide insights into important petrologic controversies.
1.3 Trace element zoning - metamorphic garnets

Mineral zoning and inclusion studies provide important constraints on the dynamic aspects of metamorphism. The in situ analytic capability of the ion microprobe provides a new means to examine the trace element evolution of single hand samples during porphyroblast growth (Shimizu and LeRouex, 1986). If trace element geochemists turn their attentions from the large scale (hand samples and mineral separates) to the small scale (points in zoned crystals) they may better understand metamorphic processes and hence the evolution of the continental crust.

The prime advantages that trace elements have over major elements in petrogenetic studies is the wide-range in chemical properties they exhibit. Ion size, charge, degree of formation of ionic bonds, crystal field stabilization energy and other chemical properties all vary significantly among the elements that can be measured in situ with the ion microprobe. Thus, the zoning of elements of varying properties will elucidate different metamorphic processes during garnet growth. Each of the elements chosen for ion-probe analysis will be informative about different aspects of the metamorphic process. In conjunction with each other, and the major elements, they should provide a more complete understanding of metamorphism. The trace element
abundance in the surface of a growing garnet will reflect the physicochemical environment during garnet growth. Just as in igneous systems, where specific trace elements are more sensitive monitors of distinct igneous processes than major elements, specific trace elements in garnets may be sensitive monitors of distinct metamorphic processes.

Titanium, sodium and zirconium are all found in trace levels in metamorphic garnets, yet all are essential structural constituents of common (almost ubiquitous) metamorphic minerals such as ilmenite, rutile, plagioclase, paragonite, and zircon. The activities of Ti\(^{4+}\), Na\(^{1+}\), and Zr\(^{4+}\) in metamorphic fluids may often be buffered by equilibria between the aforementioned phases and other metamorphic silicates and oxides. Analogously, the presence of rutile, zircon, and apatite buffer the titanium, zirconium, and phosphorus activities in evolved igneous melts (Harrison and Watson, 1985). Thus the variation of Na, Ti and Zr in a zoning profile across a garnet grain will reflect primarily the pressure, temperature, and fluid compositional dependences of their partitioning into the garnet structure. Non-ideal solid solution effects associated with changes in the major element composition of the
minerals involved in the buffering equilibria may also be important (Kretz, 1959).

Selectively compatible trace elements should reveal the involvement of specific metamorphic minerals in garnet growth reactions, just as certain trace element variations are diagnostic tracers of igneous minerals in magma chamber processes (i.e. Ni for olivine (Hart and Davis, 1978); Eu and Sr for plagioclase (Drake and Weill, 1975); and Sc for clinopyroxene (Ray et al., 1983)). For example, Li and Zn zoning may reflect involvement of staurolite in metamorphic processes during garnet growth (Dutrow et al., 1986), Co, Cr, and V zoning may illuminate behavior of oxides during garnet growth (Schwarcz, 1966), and the rare earth elements and Y should be sensitive to involvement of REE-rich phases such as epidote in garnet growth reactions (Gromet and Silver, 1984).

Major elements are not good indicators of open system behavior during metamorphism of chemically complicated bulk compositions such as pelites. In such systems many major elements stabilize a phase (the phase rule variance is low). Infiltration of a cation-rich fluid merely changes the modal abundance of the minerals in the rock, and does not change the phase chemistry. Thus trace elements - like stable isotopes - can provide
information on open system processes during metamorphism unavailable from major element studies.

Trace elements reveal disequilibrium partitioning between phases, and hence variations in kinetic parameters such as growth rate in igneous environments (Grove and Bence; 1977; Shimizu, 1983). Similarly, trace element zoning (particularly of high-charge elements such as Ti) may provide the best evidence for disequilibrium partitioning during garnet growth.

1.3.1 Previous work - trace element zoning in garnets

Bollingberg and Bryhni (1972) examined the zoning of several trace elements (Ba, Co, Cr, Cu, Ni, Sc, Sr, Ti, V, and Zr) in an eclogitic garnet. They dissected a large (20 mm) garnet grain and analyzed three fractions - core, mantle and rim - by spectrographic methods. Mg rose in abundance to the rim, whereas Fe, Mn and Ca all decreased in abundance. Trace elements Ti (505-138 ppm.), Sc (97-69 ppm), and V (63-53 ppm) were zoned to low rim values, Co (54-124 ppm), Cr (183-429 ppm) and Ni (7-17 ppm) rose to high rim values, and Sr and Zr displayed fluctuating patterns. Garnet contained the most Sc, Mn, Co and Zr of any primary mineral in the eclogite; co-existing rutile contained the most Ti, Cr and V, amphibole the most Cu and Ni, and clinopyroxene the most Sr. Late-stage talc was enriched in Co and Ni.
1.4 What is to be done?

This thesis consists of five chapters and two appendices. Chapters II through IV present trace element zoning data for garnets previously described in the literature from a variety of metamorphic environments. By examining trace element zoning in garnets from a diverse set of well-characterized environments the behavior of trace elements in metamorphic systems is illuminated. Chapter V is a petrologic and trace element study of a suite of polymetamorphic calcareous pelites from western Massachusetts.

Chapter II and III describe trace element zoning in garnets from two thoroughly investigated metamorphic terrains. The Kwoiek area (chapter III) is an extremely well-understood contact metamorphic terrain (Hollister, 1966; 1969a, 1969b, 1970), and the western Tauern window (Chapter II) is one of the best-characterized high-P amphibolitic terrains (Selverstone et al., 1984, Selverstone and Spear, 1985; Selverstone, 1985; Droop, 1985; Cliff et al., 1985; Selverstone and Munoz, 1987). Each region was subject to a single prograde metamorphic event producing garnet, and each have well-constrained petrologic and thermal histories. Insights into the degree of metamorphic disequilibrium during garnet growth in a rapidly heated environment are provided by the
Kwoiek area study. The assumption of closed system
metamorphism is investigated in the Tauern sample.

Chapter IV examines garnets from a range of
metamorphic environments. Each garnet has either been
described in a previous electron microprobe study or is
from an archetypal metamorphic environment. Samples
studied include two polymetamorphic garnets (Karabinos,
1984; Rumble and Finnerty, 1974), a rapidly-cooled
granulite facies pelite (Spear and Chamberlain, 1986;
Spear et al., in prep), a sample characterized by a
reaction change during garnet growth (Selverstone and
Munoz, 1987), a sample in which the fluid compositions
differed on either side of a single garnet (Burton,
1986), and a high-pressure, eclogitic garnet (Cloos,
1986).

Chapter V combines petrographic investigations,
phase equilibria results, and major and trace element
zoning studies to constrain the reaction histories during
garnet growth in a complex terrane in western
Massachusetts.

Chapters II and III are designed to stand alone as
individual papers - and there is thus a bit of repetition
between chapters. A slightly abbreviated version of
Chapter II was published in Geology, and Chapter III is
slated for submission to Contributions to Mineralogy and
Petrology. Chapter IV will either be expanded upon and be
submitted to the Journal of Metamorphic Geology, or will be used as a pilot study for future projects. Chapter V will be purged of some of its minutiae, and submitted to Journal of Petrology as two papers.
Chapter II: Trace element zoning in coexisting metamorphic minerals, Tauern Window, Austria - Implications for open system behavior during metamorphism
Abstract

Trace element zoning has been measured in co-existing minerals from an amphibolite from the Tauern window, Austria, using an ion microprobe. Humps in the zoning profiles of Sc, V, Y and the heavy rare earth elements (HREE) in both garnet and amphibole mark a period of open system behavior. These humps correspond to a portion of the garnet major element zoning profile that is interpreted as a P-T reversal. The source of the mass excesses of these elements remains somewhat ambiguous: they were derived either on a thin section scale by the breakdown of refractory minerals enriched in trace elements, or externally from unusual trace element enriched fluids. Sympathetic trace element zoning in co-existing amphibole and garnet is used to correlate episodes of mineral growth. P-T paths determined from garnet zoning may require modification if open system behavior is unrecognized during garnet growth.
2.0 Introduction

The major element zoning of metamorphic porphyroblasts has been used to investigate variations in the P-T conditions in metamorphic terrains prior to the final equilibration of matrix minerals and porphyroblast rims (Tracy et al., 1976; Holland and Richardson, 1979; Spear and Selverstone, 1983). Garnets are the most frequently studied zoned porphyroblasts (Tracy, 1982; Loomis, 1983; Spear and Selverstone, 1983). The chemical signatures of early metamorphism are assumed to be preserved in garnet cores up to the amphibolite facies because chemical diffusion in garnet is slow at low to moderate metamorphic temperatures (Woodsworth, 1977; Freer, 1981; Cygan and Lasaga, 1985). Ubiquity of garnet in a wide range of bulk compositions contributes to its importance as a probe of metamorphic processes. Accurate interpretation of chemical zoning in garnet leads to significantly improved understanding of P-T paths of metamorphism and hence of the tectonics of mountain belts; therefore, it is essential to develop techniques that elucidate metamorphic processes during garnet growth. One important assumption made in many studies of garnet zoning is that of closed system metamorphism. Zoning in garnets is ascribed primarily to P-T variation, and not to metasomatic effects.
The process of metasomatism is a controversial topic in the metamorphic petrologic literature (Thompson, 1959, 1970; Weill and Fyfe, 1964, 1967; Korzhinskii, 1966, 1967; Frantz and Mao, 1976, 1979; Brady, 1977; Rumble, 1982). High-variance, mono- and di-mineralic zones at the contacts between distinct lithologic units form by metasomatism accompanying metamorphism (Joesten, 1974; Thompson, 1975; Brady, 1977). Documentation of metasomatic processes in the more common pelites and amphibolites of regional metamorphic terrains is problematic. Metamorphism of pelites is considered to be isochemical for major elements other than the volatile constituents H₂O and CO₂ (Shaw, 1956), although a few studies (i.e. Ferry, 1983) demonstrate substantial alkali metal mobility. Trace element mobility during amphibolite facies metamorphism of pelites and amphibolites is also a controversial issue (Shaw, 1954; Ronov et al., 1977).

In this chapter we investigate trace element variation during mineral growth (trace element zoning) with an ion microprobe to provide additional constraints on the processes affecting major element zoning profiles in medium-grade amphibolites. We use a well-studied rock from the Tauern Window, Austria (Selverstone et al., 1984; Selverstone, 1985) as an example. This example demonstrates that trace elements are sensitive indicators of the occurrence of open system metasomatic behavior.
during garnet growth. Elements such as Sc, Y, and the heavy rare earth elements (HREE), all normally considered to be immobile during prograde metamorphism, appear to exhibit open system behavior on the scale of a thin section.

2.1 Ion microprobe analysis

Ion-microprobe techniques used to investigate the zoning in more abundant trace elements (i.e. Sc, Ti, V, Cr, Y) are similar to those described elsewhere (Shimizu et al., 1978; Shimizu and Allegre, 1978; Shimizu and Hart, 1982). Based on repeated analysis of a working standard (Appendix I), element over silicon ratios are reproducible to < +/- 10%. REE analysis techniques are delineated by Shimizu and LeRouex (1986). Machine conditions and working curves for garnets are provided in Appendix I. No adequate working curves for most trace elements in amphibole or plagioclase are available; only relative element zoning for these minerals is depicted below. A single amphibole (Kakanui hornblende) of known REE content was analyzed. It showed similar REE ion yields to garnet, so the garnet working curves were used for the amphibole REE analyses.

2.2 Geologic Setting

The sample investigated, FH-1M, is an amphibolite from the Lower Schieferhulle of the Tauern window, Austria. Details of geologic setting, phase relations,
petrography and P-T conditions of metamorphism can be found elsewhere (Selverstone et al., 1984; Selverstone, 1985; Selverstone and Munoz, 1987). The sample contains the assemblage hornblende + kyanite + staurolite + garnet + biotite + chlorite + epidote + plagioclase + ankerite + quartz + rutile + ilmenite + late-stage margarite. The garnets are large (2-4 mm) and euhedral, and they contain inclusions of plagioclase, epidote, ankerite, ilmenite and rutile. Garnet growth occurred by continuous reaction in a constant divariant assemblage that included chlorite, epidote and ankerite as reactants. On the basis of geothermometry, geobarometry, and thermodynamic modeling of garnet zoning, Selverstone et al. (1984) suggested that garnets grew during decompression to rim equilibration conditions of 550° C and ≈ 7 kbar (Fig. 2.1). They also stated, on the basis of major element zoning, that a P-T reversal of 300-400 bars occurred during garnet growth as a result of a brief interval of burial during the uplift-dominated P-T path.

2.3 Mineral zoning

Fig. 2.2 shows the locations of the zoning traverses portrayed in Figs. 2.3 through 2.8. The minerals studied are zoned approximately concentrically in both major and trace elements. It is imperative to understand the interrelation between major and trace element variations because accurate interpretation of metamorphic processes
is facilitated by a sound knowledge of the development of major element zoning. Gaps in the traverses indicate the locations of inclusions.

2.3.1 Garnet zoning

Garnet zoning in one traverse from a single garnet depicted in Fig. 2.2a and three traverses in a garnet depicted in Fig. 2.2b are shown in Figs. 2.3 and 2.4 respectively. The garnet in Fig. 2.2a is a near-center cut, that in Fig. 2.2b is an oblique cut investigated in order to delineate element behavior within the hump region. Major element zoning (Fe, Ca, Mn, Mg) (see Figs. 2.3a and 2.4a) in garnets mirrors that presented by Selverstone et al. (1984) (see their Fig. 11). The overall details of the traverses presented in Figs. 2.3 and 2.4 are similar; however, variations do occur on a local scale. As growth occurs from the core to point 4 (Fig. 2.2a, Fig. 2.3) almandine and pyrope components increase, whereas grossular and spessartine decrease. Selverstone et al. (1984) interpret this part of the zoning profile as a period of garnet growth during heating and decompression. During the next interval, from point four to point five, $X_{Alm}$ dips, $X_{Gross}$ peaks slightly, and $X_{Pyr}$ continues to increase. This portion of the growth history corresponds to Selverstone et al.'s P-T reversal. Near the rim $X_{Alm}$ decreases, $X_{Gross}$ drops off, and $X_{Pyr}$ increases. Selverstone et al. describe this
as a final period of garnet growth during decompression from 9 to 7 kbar. The P-T path reflects primarily the pressure dependence of Ca partitioning in the assemblage garnet-aluminosilicate-plagioclase-quartz (Ghent, 1976).

Trace elements can be divided into two categories based on their zoning patterns: elements that exhibit humps in the region of the garnet where the Ca zoning defines the P-T reversal (Fig. 2.2a, ≈ point 5) and elements that display roughly continuous increases or decreases in abundance from core to rim. The former include Na, Sc, V, Y and the HREE, the latter Ti and Co. (Fig. 2.3 and 2.4). Minor fluctuations in the profiles may reflect real petrogenetic processes, but also may be due to the influence of microinclusions. In this chapter we concentrate on the interpretation of major features in the zoning profiles that are clearly reproducible in several garnet grains from the sample. Ti/Si decreases and Co increases by almost a factor of two from core to rim. Cr remains fairly constant, although there is a slight rimward Cr increase. Na/Si (factor of almost 2), Sc (factor of 2), and Y (factor of > 10) all decrease from the core to point 4 (Fig. 2.2a). At this point they, as well as V/Si, exhibit strong abundance increases over a distance of 30-40 microns in the garnet depicted in Fig 2a. Each then decreases in abundance to rim values less than the values at point 4 (Fig. 2.2a).
Significant differences in trace element abundances in the hump region exist both between the garnets in Fig. 2.2a and Fig. 2.2b, and between the three traverses from the single garnet in Fig. 2.2b. The Na/Si ion intensity at the hump varies from ≈ 0.0008 in the garnet in Fig. 2.2a to almost 0.0016 in traverse B in the garnet in Fig. 2.2b. (note the change in y-axis scale between Figs. 2.3 and 2.4). Sc/Si ion intensity is slightly higher at the hump in the garnet depicted in Fig. 2.2b, and the Sc/Si baseline value prior to the hump is also higher in this garnet. Less dramatic variability is also seen between the humps for V and Y. The garnet in Fig. 2.2b displays an ill-defined Cr hump, which was not evident in the garnet from Fig. 2.2a. There is no interpretable correlation between minerals abutting the four traverses or proximity of the traverses to particular minerals (i.e. amphibole). Additional traverses would be required to determine whether large humps are systematically correlated with the foliation direction.

Based on the disparities between element abundances at the hump in contiguous garnet zoning profiles, it is suggested that the scale of equilibration for trace elements during the hump forming period was on the order of tens to hundreds of microns rather than millimeters.

The REE exhibit systematic zoning, which complements that of the abundant trace elements (Fig. 2.5). The heavy
REE (Gd–Yb) all behave coherently and similarly to Y save for the innermost point. For example, Dy falls from > 70 ppm near the core to 20 ppm at point 4. The other HREE display similar variation throughout this interval. Gd maintains a fairly constant abundance while Eu, Sm and Nd all increase in abundance (except for the Nd core point). At point 5 the heavy REE are all enriched, each by a factor of about 1.2, Gd remains constant and the light REE remain constant. The final REE point shows a light REE enrichment (factor of 2 compared to point 5) and a final heavy REE decrease to a level almost identical to that at point 4. An interesting aspect of the REE zoning is the absence of a strong negative Eu anomaly in a plagioclase-rich rock.

2.3.2 Amphibole zoning

Amphibole zoning is displayed in Figs. 2.6 and 2.7. Two parallel traverses across a c-axis section (Fig. 2.2b) are depicted. The traverses cut across a distinct discontinuity where both pleochroism and birefringence change abruptly.

The major element zoning roughly parallels that of garnet. From core to rim both XFe (Fe/Fe+Mg) and Mn content drop. Although (Fe/Fe+Mg) is smoothly zoned, there is an inflection in the profile at the pleochroic break. Ca increases slightly, as opposed to the Ca decrease in garnet, as does SiO₂ content.
Trace elements in amphibole can also be subdivided into two categories: elements displaying humps, and those with smooth profiles. There is a strong correspondence among the two groups between garnet and amphibole. Titanium and cobalt have smooth profiles, although titanium is inflected at the pleochroic break. Sc, V, Cr, and Y all display humps in element/silicon ratio rinward of the pleochroic break. Na has irregular profiles in the amphibole, displaying no obvious hump. The magnitudes of the humps in garnet and amphibole are compared later in this chapter.

Partial rare earth element patterns in amphibole for the four points indicated in Fig. 2.2b are shown in Fig. 2.7 (Yb is not plotted due to GdO⁺ interferences). The amphibole is enriched in the middle REE (Sm and Eu) (Fig. 2.7). The amphibole core has higher HREE abundances (Er/Sm ratios) than the rim, and the rim and middle have high light REE abundances (Fig. 2.7). No evidence for a heavy REE hump was discerned; the narrow width of the Y-trough coreward of the hump, as shown in Fig. 2.6, suggests that the wide beam (≈ 20 microns) used to analyze the REE could not resolve the narrow hump region. No portion of the amphibole zoning profile displays a negative Eu anomaly.
2.3.3 Plagioclase zoning

Plagioclase zoning in major and trace elements is presented in Fig. 2.8. The core of the grain is albite rich; Selverstone et al. (1984) report rim plagioclase compositions of An 35 and core values as low as An 12. Trace element zoning is non-systematic. It is difficult to delineate zoning trends on grains as small as 50 microns when the ion probe beam is 5 microns in diameter, and when small microinclusions of ferromagnesian minerals can severely interfere with measured abundances of Mg, Fe and Mn.

2.4 Discussion

The trace element data, used in concert with the major element results, allow us to address the assumptions in the garnet zoning modeling: that garnet grew in a closed system, in a low-variance assemblage and with no change in garnet growth reaction.

Prior to evaluating the closed system assumption for FH-1M, it is necessary to define the size of the 'system' during metamorphism, a daunting task. For purposes of this chapter the system is defined as the effective bulk composition (EBC) that chemically communicates with the surface of a growing mineral (or with a metamorphic intergranular medium) over a specific time interval. The system does not equal the total mass of all elemental components in a hand sample. The interior of a zoned
(refractory) mineral is not part of the equilibrating metamorphic system.

The abundance of a trace element on the surface of a growing porphyroblast in equilibrium with a surrounding metamorphic mineral assemblage is controlled by two factors: (1) the effective bulk composition (EBC) and (2) the bulk distribution coefficient (D) for partitioning of the element between the porphyroblast and the other matrix phases. The zoning of elements that exhibit smoothly decreasing (Mn), roughly flat (Cr) or increasing profiles (Co) can probably be explained in terms of equilibrium partitioning models (Hollister, 1966; Cygan and Lasaga, 1982). The elements exhibiting humps require either: (1) a large fluctuation in bulk partition coefficient, or (2) strong metasomatic enrichment of the EBC, over a narrow growth interval. Each of these two possibilities is addressed in turn; quantitative evaluation of the relative importance of the two processes hinges on accurate mineral-mineral partition coefficients, and these are unavailable at the present time (see Appendix II of this thesis).

2.4.1 Variations in bulk D - Can they cause the humps?

The rough correlation between the trace element humps and the P-T reversal immediately suggests that they are genetically related. Could variability of mineral-
mineral distribution coefficients with changes in P and T during the reversal produce the trace element humps?

The bulk distribution coefficient D is defined as D = \Sigma X_i D_i where X_i is the weight fraction of phase i in equilibrium with garnet and D_i is the garnet-mineral (phase I) distribution coefficient (McIntyre, 1963; Gast, 1968).

The D_i terms are functions of pressure, temperature and mineral composition (McIntyre, 1963). Temperature changed by less than 30° during garnet growth, so T effects on the D_i are probably small.

Several lines of evidence suggest that pressure effects on D_i of the P-T reversal cannot have produced the humps: (1) the ΔV of trace element substitutions into silicates are generally small. Equilibrium constants for element solubility reactions are not pressure sensitive. For example, Na abundance in a metamorphic fluid co-existing with the mineral assemblage of FH-1M is not pressure sensitive. The Na⁺ activity in any fluid in FH-1M is defined by the hydrolysis reaction: 2

NaAlSi_3O_8(plag) + 2 H⁺(fluid) = 2 Na⁺(fluid) +
Al_2SiO_5(kyanite) + 5 SiO_2(quartz) + H_2O(fluid).

Na⁺(fluid) activity in FH-1M, and hence Na⁺ in garnet, cannot change unless pressure or temperature varies, plagioclase composition changes, pH varies, or the activity of water changes. The logarithm of the
equilibrium constant \((\log K_{eq})\) for the above reaction calculated at 500° C between 2 and 10 kbar using data in Helgeson et al. (1978) and Helgeson et al. (1981) (assuming pure end-member phases) varies by less than a log unit (8.7 to 9.6). Thus, a pressure change of 500 bars, such as that calculated at the P-T reversal (Selverstone et al., 1984) is unlikely to cause significant change in the mineral-fluid partition coefficient for an element \((\text{Na}^+)\) between a silicate and a metamorphic fluid.

(2) The two buffered trace elements (Na and Ti) are decoupled at the hump, yet exhibit roughly parallel decreases outside the hump region (core to point 4; point 5 to rim). Ti does not exhibit a hump whereas Na does. Ti activity in the matrix is buffered by the presence of rutile; garnet thus contains the maximum Ti allowable at the P and T of growth under equilibrium conditions (see also Chapter IV). Na forms a major component in plagioclase, hornblende, and paragonite (a mineral that may have been present early in the sample's history (Selverstone, personal communication, 1987)) so the concentration of Na in garnet reflects the activity of Na imposed on the system by the aforementioned sodic phases. Assuming that the overall decompression trend of the calculated P-T path is genuine, both Ti solubility and Na solubility in garnet appear to decrease with lowered P.
(see also chapter IV). An added complication is the observed decrease in albite component of plagioclase with garnet growth along the early P-T path. Provided the buffering assemblage did not change, the decoupling of Na and Ti cannot be reconciled with the apparent parallel pressure dependences of Na and Ti solubility into garnet.

(3) Both a garnet incompatible element (V) and garnet compatible trace element (Sc) have abundances at the hump that are higher than at the core of garnet. In a closed system, an increase in pressure to a value higher than that calculated for the core would be required to increase the V and Sc abundances to a level higher than that observed in the garnet core (ignoring any effects of changes in modal mineralogy on bulk D).

Bulk D also changes as a result of changes in \( X_i \). The \( X_i \) for metamorphic minerals change during metamorphism as product minerals grow and reactant minerals break down (Hollister, 1969). Additionally, for a refractory mineral, the effective \( X_i \) increases with temperature. That is, at low temperatures a refractory mineral not explicitly involved as a participant in metamorphic reactions is inert because diffusion coefficients are low enough that virtually none of the mineral reacts with other minerals over metamorphic time-scales. As temperature increases, and diffusion coefficients increase in magnitude, a larger fraction of
the refractory mineral can participate in the reacting metamorphic system over reasonable metamorphic time scales (Spear, in press). At still higher temperature, such as in igneous systems, diffusion coefficients are large enough that the entire mineral can be effectively in equilibrium with other phases of a reacting system, and $X_i$ corresponds directly to weight fraction.

A large change in modal mineralogy could alter the bulk Ds of several elements. In order to enrich elements such as Sc and V by up to a factor of 2 at the hump in a closed system, D must increase by a similar amount at constant EBC. A simple calculation demonstrates that a change in modal mineralogy in which ten percent of a mineral that strongly incorporated ($D(\text{gar/min}) \ll 1.0$) the elements exhibiting humps was replaced by a mineral in which these elements are incompatible ($D(\text{gar/min}) \gg 1.0$) could lead to factor of two increase in the bulk D. However, it is unlikely that the decrease following such an increase in bulk D could be produced in garnet for compatible (Sc), incompatible (V), and buffered (Na) elements in a single mineral-out reaction (see Appendix II for element compatabilities).

2.4.2 Enrichment of the EBC (Metasomatism)

Because fluctuation of bulk distribution coefficient is unlikely, the element humps must be primarily due to an increase in the EBC of the trace elements Sc, V, Y and
the heavy REE. The two means by which the EBC may be increased are (1) introduction of a pulse of trace element-enriched fluid into the system, and (2) breakdown of a refractory mineral (Hollister, 1969) enriched in trace elements. Either one of these mechanisms can be considered to be open system metasomatism; the fundamental question is whether the open system components were derived locally (on a hand sample scale) or externally (on an outcrop or regional scale). In this chapter, the former process is referred to as internal metasomatism, and the latter process is called external metasomatism.

External metasomatism, which is the process traditionally referred to as metasomatism, is called on as an explanation for anomalous trace element behavior in many geologic environments (Menzies and Murthy, 1980; Jones et al., 1982). Studies of REE mobility in low-grade regional metamorphic, ocean floor and hydrothermal regimes generally show enhanced mobility of light REE compared with heavy REE (Wood et al., 1976; Ludden and Thompson, 1979), although F and CO₂ complexing appear to enhance the solubility of the heavy REE relative to the light REE (Haskin et al., 1966). Thus, an external metasomatic cause for the trace element humps may require introduction of an unusual, perhaps F-rich, trace-element-bearing fluid into the system. A qualitative ion
microprobe traverse across FH-1M garnet for the elements C, F, and Cl revealed no humps correlating with the cation humps described above. If F- and Cl-rich fluids infiltrated FH-1M, they did not leave a chemical record in the garnets.

Internal metasomatism enriches the EBC in elements that are compatible in refractory minerals broken down during metamorphism. A refractory mineral that grew in a closed system prior to garnet would probably exhibit core to rim elemental depletions in elements highly compatible in that mineral. Any refractory mineral that grew during garnet growth would exhibit the same core to rim elemental depletions as garnet. In this case Sc, Mn, Y and the HREE should all decrease in abundance concomitant with their fractionation into garnet cores. Trace element zoning in hornblendes from FH-1M is partially in accord with this prediction (Figs. 2.3-2.7): Y and the heavy REE decrease significantly from core to rim, although Sc does not. Plagioclase cores are enriched in Na (An 12) and depleted in Mn (Fig. 2.8). On the basis of results described in other chapters, ilmenite, rutile, staurolite, and epidote are also refractory minerals in FH-1M. Relative to garnet, ilmenite is enriched in V (chapter V), staurolite is rich in Li and Zn (chapter III and V), and epidote is rich in V, Sc, Y, Zr, and the REE (chapter V).
A P-T-\(\mu(H_2O)\) reversal during the path of metamorphism would transfer minerals involved in a metamorphic reaction from products to reactants, provided the kinetics of the reverse reactions were favorable. Refractory porphyroblasts would be resorbed, subject to the availability of fluids to drive hydration (and/or carbonation) reactions. It is likely that ilmenite and plagioclase would be transferred from the product to reactant sides of the whole rock reaction in FH-1M during a P-T-\(\mu(H_2O)\) reversal because each is a product on the low pressure side of an anhydrous, shallow dP/dT reaction: the reaction almandine + rutile = ilmenite + kyanite + quartz (Bohlen et al., 1983) for the former and grossular + kyanite + quartz = anorthite (Ghent, 1976) for the latter. Consideration of these water-absent reactions does not necessarily imply that they took place in FH-1M because whole rock reactions depend strongly on the nature of the dehydration and decarbonation reactions in a rock. They are listed to indicate the identity of some low molar volume phases in the sample. The humps in the elements Na, Sc, V, Y, and the REE can perhaps be explained by a change in reaction mechanism at the P-T reversal in which refractory plagioclase + ilmenite +/- amphibole and/or trace element enriched minor phases such as epidote were transferred from products to reactants, exposing their trace element and Na enriched cores to the
matrix in equilibrium with garnet and amphibole during a restricted mineral growth interval. Garnet itself may have switched from product to reactant during the P-T reversal, leading to minor garnet resorption followed by re-incorporation of garnet compatible trace elements into porphyroblasts during a second mineral growth episode.

Resorption of garnet followed by re-incorporation of trace elements during a second garnet growth episode is an attractive hypothesis that could help explain humps in garnet compatible elements Sc, Y and the HREE although not garnet incompatible elements V or Na. In addition, mass balance constraints (for the garnet in Fig. 2.2a) reveal that garnet resorption cannot sufficiently enrich even the garnet-compatible trace elements in the hump region. For example, graphical integration of the Sc profile rimward of point 4 reveals that a minimum of 0.7 mm of garnet of the Sc concentration at point 4 are required to supply the mass excess rimward of point 4. This distance extends beyond the present rim of the garnet; no petrographic evidence for garnet resorption beyond the rim of the garnet is visible in thin-section. Garnet resorption followed by trace element reincorporation may be an important process contributing to the formation of humps, but cannot be the sole process.
2.4.3 Internal or external metasomatism?

The evidence presented in the last two sections suggests that the trace element humps are due to a brief increase in the EBC for Sc, V, Y and the heavy REE. External metasomatism cannot be ruled out as a cause for the humps, although a metasomatic fluid carrying V, Sc, Y and the heavy REE would be unusual. Internal metasomatism, in which the trace element mass excesses are derived from the cores of refractory minerals, is a plausible process that could produce mass excesses for Na (from albite-rich plagioclase cores), Sc (from Sc-rich garnet and amphibole cores), V (from V-rich ilmenite cores), and Y and the heavy REE (from heavy REE-enriched garnet, amphibole, and perhaps epidote cores). The P-T reversal would cause minor resorption of minerals that had been continuously growing along the early clockwise P-T path of the terrane. The hand-sample scale differences between element abundances at the humps suggest that a localized process, such as resorption, was involved in hump formation.

2.4.4 Trace elements: Effective monitors of metasomatism

The trace elements such as Sc, V, Y and the REE appear to be good indicators of the influx of a metasomatic component, derived either externally or internally, into the reacting metamorphic system of FH-1M
during garnet growth. Will trace elements generally be useful for recognizing open system metasomatism?

In a low-variance sample, such as FH-1M, virtually all the chemical potentials of major element phase components within the minerals in the system are specified by equilibria among minerals in the rock (Thompson, 1970). Influx of a fluid enriched in such 'buffered' components increases the modal abundance of phases rich in those components but does not change the activity of the mineral end members containing that component (at constant temperature, pressure and fluid fugacity). In contrast, trace elements that are not essential structural constituents of minerals do not have locally 'buffered' activities in metamorphic systems. Influx of fluids enriched in non-buffered trace elements results in concomitant increases of those elements in all equilibrated phases, or portions of phases, in the rock. Additionally, trace elements have a smaller mass inertia than major elements. It is difficult to affect the abundance of an element present in a rock at the 10 wt % level by influx of a 100 ppm fluid, whereas a 100 ppm trace element fluid could overwhelm the original trace element signature of a 1 ppm trace element. Thus, trace elements (and isotopes) can indicate the operation of metasomatic processes in low-variance systems whereas buffered major elements cannot.
2.4.5 The nature and timing of mineral coexistence

The co-occurrence of Sc, V, and Y humps in garnet and amphibole suggest that the hump points in each mineral formed contemporaneously.

Figure 2.9 shows trace element/silicon (ion intensities) plotted versus Fe/Mg (ion intensity) for Sc, Ti, Y, and Mn. Fe/Mg is a monotonically decreasing compositional variable from core to rim in both garnet and amphibole, hence, it is a convenient monitor of reaction progress. If garnet and amphibole grew coevally and in equilibrium, then their trace elements should show sympathetic variability of similar magnitude (as represented by variability parallel to the ordinate of Fig. 2.9) as a function of Fe/Mg, provided both garnet/amphibole Fe/Mg \( K_d \) and trace element bulk D's did not change significantly during porphyroblast growth. Fe/Mg fractionation between garnet and amphibole is temperature dependent (Graham and Powell, 1984). However, temperature during garnet growth in FH-1M varied by only 30° (Selverstone et al., 1984), so little Fe/Mg variability can be attributed to temperature effects. Effects of changing pressure on \( K_d \) 's are also likely to be small.

Mn, Sc and Y are all highly compatible in garnet, and should therefore decrease from core to rim in garnet and any mineral growing coevally with it in a closed
system. As detailed earlier, open system metasomatism should lead to concurrent humps in metasomatized non-buffered elements in growing porphyroblasts. Correlations of metamorphic events on the basis of trace element zoning should be feasible.

Examination of Fig. 2.9 suggests that the garnet profiles can be divided into three regions on the basis of zoning in the garnet compatible elements (Mn, Sc, Y): (1) 1 to 2, from garnet cores to the base of the hump, (2) 2 to 3, from the base of the hump to the top of the hump, and (3) 3 to 4, from the top of the hump to the rim. The amphibole profiles are divisible into four intervals, three corresponding to those described above for garnet, and an interval (0-1) at the core of the amphibole. The extra interval is evident as a region of constant Mn and Sc and increased Y, in amphibole. The three compatible elements, Mn, Sc and Y all display roughly similar behavior in the final two intervals (2-3 and 3-4) in both minerals, and it appears that garnet and amphibole both grew during this interval. The core interval in amphibole (0-1) displays no decreases in the garnet compatible elements (Mn, Sc, Y), and intervals 1-2 in the two minerals exhibit different degrees of fractionation, particularly for Y. This evidence suggests that the core of the amphibole grew prior to garnet nucleation. It is also possible that all the garnets
studied were not center cuts, that the traverses missed the garnet core; however, the Y rise observed in the amphibole core suggests that amphibole indeed nucleated before garnet because it is difficult to produce Y increases in the assemblage of FH-1M in the presence of growing garnet. This conclusion is in accord with Selverstone et al.'s (1984) observation of lawsonite pseudomorphs in the cores of amphiboles in other samples from the Lower Schieferhulle of the western Tauern Window implying that amphibole initially grew in the lawsonite stability field, prior to the nucleation of garnet at ≈ 520°C, 10 kbar.

2.4.6 Implications for garnet zoning modeling

It is impossible to evaluate unequivocally the assumption of constant mineral assemblage during garnet growth based on the trace element data. The continued presence of plagioclase, ilmenite, and other reactive phases throughout the hump interval cannot be proved. Amphibole existed throughout garnet growth. It appears that the whole-rock reaction changed across the hump. Open-system metasomatism, either internal (on a thin-section scale) or external (on an outcrop or regional scale) has occurred. The zoning of several trace elements (Sc, V, Y, and the heavy REE) and at least one major element (Na) require a modification of simple closed system models of prograde metamorphism. The overall shape
of the P-T path derived by Selverstone et al. is not inconsistent with this analysis, including the existence of a small P-T-µ(H₂O) reversal; however, the details of the P-T reversal may not be as depicted by Selverstone et al. (1984) if garnet did not grow continuously throughout the reversal.

2.5 Summary

This example demonstrates that trace element zoning in metamorphic minerals exists, can be more pronounced than major element zoning, and can provide information on metamorphic processes unavailable from major element investigations. Garnet compatible trace elements are particularly useful for monitoring processes during garnet growth, just as melt compatible elements are useful for monitoring the evolution of magmatic systems. If various metamorphic minerals and the metamorphic fluid phase have different characteristic trace elements, variation in these elements can be used to interpret the reaction histories of metamorphic assemblages, the histories of fluid-rock interactions during metamorphism, and hence the P-T-µ(H₂O) paths experienced by the rocks.
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Figure 2.1. P-T diagram showing the P-T paths calculated from major element garnet zoning profiles in FH-1M using the techniques of Spear and Selverstone (1983) (from Selverstone et al., 1984). Note P-T reversal at 9 kbar. Details of calculation provided in Selverstone et al. (1984).
Figure 2.2A. Sketch map of a garnet from FH-1M showing locations of ion microprobe traverses and REE points depicted in Figs. 2.2 and 2.4. Stippled pattern = amphibole, black grains = ilmenite, colorless = garnet and matrix (plagioclase + biotite + chlorite + kyanite + staurolite + epidote + ankerite + quartz + rutile + late-stage margarite). Note that the ilmenite grains roughly define the foliation.
Figure 2.2B. Sketch map of garnet, amphibole and plagioclase from FH-1M showing the locations of ion microprobe traverses and REE points depicted in Figs. 2.3, 2.5, 2.6, and 2.7. Stippled pattern = amphibole, black = ilmenite, star = plagioclase. Ilmenite grains define the foliation.
Figure 2.3. Zoning profiles in garnet depicted in Fig. 2.1A for major and more abundant trace elements. Depicted are ion intensities normalized to Si. Concentrations are estimated from working curves determined for pyrope-rich garnets and must be considered approximate. Error bars represent total range of four determinations of element/Si ratio. Errors based on counting statistics are smaller than the symbol size if error bars are not shown. Large numbers represent approximate locations of REE analyses relative to the traverse. Scale bar is 100 microns.
Figure 2.4. Zoning traverse in a second garnet depicted in Figure 2.2B. Garnet is not cut through its center. Element over silicon ratios are presented. Errors based on counting statistics are generally smaller than the symbol size. Shown are traverses A (triangles), B (squares), and C (circles). Gaps in the traverses occur where microinclusions were intersected by the primary ion beam. Note the differences between the element abundances at the humps.
Figure 2.5. Rare earth element patterns for garnet depicted in Fig. 2.2A in sample FH-1M. Concentrations estimated from working curve derived for pyrope rich garnets. Patterns normalized to chondrites. Error bars for each element are smaller than the symbols for the middle and heavy REE. Nd errors are up to three times the size of the symbols.
Figure 2.6. Major and abundant trace element zoning in amphibole sketched in Fig. 2.2B. Depicted are ion intensities normalized to Si ion intensity. Because Si (molar) varies between core and rim this value cannot directly correspond to concentration. Arrows and circles represent two parallel traverses shown in Figure 2.2b. Errors are roughly the size of the symbols. PB represents a break in pleochroism.
Figure 2.7. Rare earth element zoning in amphibole from FH-1M. Location of analysis points are shown on Fig. 2.2B. Concentrations derived from garnet working curves. Yb values not shown due to interferences of abundant GdO⁺ on Yb mass spectra. Errors based on counting statistics are generally smaller than the symbol size. Patterns normalized to chondrites.
Figure 2.8. Major and trace element zoning in element/Si in plagioclase from FH-1M. Grain location is shown of Fig. 2B. Si/8 cations varies as a function of anorthite content, so element/Si does not correspond linearly to element concentration. Errors based on counting statistics are usually smaller than the symbol size. Note that these plots are roughly rim-to-rim, as opposed to the core-to-rim plots shown for the larger amphibole and garnet porphyroblasts.
Figure 2.9. Log (element/silicon) vs. log (Mg/Fe) for four garnet traverses and two amphibole traverses. Points 0, 1, 2, 3, and 4 all represent distinct points on the traverses. Points 2 represent the base of the humps, Points 3 represents the top of the humps, and points 4 represents the rims.
Chapter III: Trace-element zoning in garnet from the Kwoiek Area, British Columbia: Possible influences of interface segregation in metamorphism
3.0 Abstract

Trace element zoning in garnets from two samples from the contact metamorphosed Kwoiek area, British Columbia (Hollister, 1969), was measured with an ion microprobe. Zoning profiles are tripartite with chemical breaks defined by co-variation of major and trace elements. Important features of the trace element zoning profiles are: (1) roughly 'bell-shaped' zoning profiles for Y and the HREE, (2) an abrupt Ti rise at a point midway through each garnet, (3) inflections in the zoning profiles of other elements (Li, Na, Cr, V, Y, Zr, and the HREE) at this point, and (4) irregular Cr and V profiles.

'Bell-shaped' Mn zoning formed by Rayleigh fractionation has become paradigmatic in amphibolite facies garnets, and was first observed in Kwoiek garnets. However, the zoning profiles of most other trace elements cannot be easily modeled using simple Rayleigh fractionation models.

Ti activity in the two samples should be buffered by phase relations with ilmenite. Garnets from a continuously heated contact metamorphic environment should display continuous Ti zoning profiles if equilibrium was maintained throughout garnet growth. The irregular Ti profiles suggest disequilibrium partitioning.
Several elements (Cr, V) may indicate internal metasomatism during metamorphism. The source for the mass excess of these elements is probably the refractory cores of ilmenite grains.

Either a model requiring differing matrix transport rates of trace elements or an interface kinetic based model could explain the unusual trace element behavior at the element inflection point. An interface model in which electrostatically segregated elements in the interface of the garnet were trapped during the initial pulses of rapid garnet growth is the preferred model.
3.1 Introduction

The assumption of equilibrium between co-existing minerals during prograde metamorphism is a fundamental but incompletely evaluated assumption in metamorphic petrology (Goldschmidt, 1911; Eskola, 1915). Geothermometry (Essene, 1982), geobarometry (Newton, 1983), modeling of fluid-rock interactions (Ferry, 1986) and garnet zoning modeling (Spear and Selverstone, 1983) all assume chemical equilibrium between metamorphic mineral rims.

In many cases there is good evidence for attainment of local chemical equilibrium between grain rims during prograde metamorphism: 1) phase equilibria studies of natural assemblages in restricted geologic regions are often interpretable in terms of simple, equilibrium facies types, particularly if the chemical potentials of fluid species are internally buffered (Rumble et al., 1982; Spear, 1982); 2) thermobarometric studies of multiple samples from restricted areas often yield internally consistent P-T conditions within the precision of well-calibrated geothermometers and geobarometers (Hodges and Spear, 1982; Bohlen et al., 1985; Hodges and McKenna, 1987); 3) isograds and calculated metamorphic temperatures are often progressively and regularly distributed within regional and contact metamorphic
terrains; and 4) textural equilibrium is attained in many metamorphic samples (Zen, 1963).

Documented occurrences of prograde chemical disequilibrium are few, although Loomis (1976, 1982) and Hollister (1969; 1970) describe non-equilibrium behavior during prograde contact metamorphism. Experimental studies of the kinetics of metamorphic reactions are presented by several authors, but do not address chemical-partitioning aspects of metamorphic disequilibrium (Tanner et al., 1985; Schramke et al., 1987).

Minerals nucleate and grow when a metamorphic reaction is overstepped (Fyfe et al., 1958). The degree of attainment of chemical equilibrium appears to correlate inversely with the degree of overstepping; slightly overstepped reactions are close to chemical equilibrium (Aagaard and Helgeson, 1982; Walther and Wood, 1984). Under conditions near equilibrium, mineral growth rate increases with the degree of overstepping (Walther and Wood; 1984; Rubie and Thompson, 1984). Walther and Wood (1984) suggest small temperature oversteps (< 10° C) of regional metamorphic dehydration reactions whereas Ridley and Thompson (1986) advocate larger reaction overstepping (10-50° C) in both contact and regional environments. Ridley and Thompson calculate that the theoretically determined exponential dependence
of nucleation rate on overstepping leads to rapid nucleation following a critical degree of overstepping (10-50°), independent of heating rate. If Ridley and Thompson are correct, there may be chemical and textural evidence for large degrees of reaction overstepping prior to nucleation in both contact and regional metamorphic rocks.

As shown by studies in both natural igneous environments (Shimizu 1981) and experimental systems (Grove and Bence, 1976), trace elements are more sensitive monitors of disequilibrium behavior during geologic processes than are major elements. Ti and Cr in clinopyroxene are particularly effective indicators of disequilibrium behavior (i.e. rapid growth) in igneous rocks. Because Ti is soluble at trace levels in garnets, and because its activity in metamorphic environments is buffered by equilibria between silicates and Ti oxides (Ghent and Stout, 1984), Ti zoning may provide evidence of disequilibrium partitioning during garnet growth. Zoning of other trace elements may provide constraints on other processes, such as P-T changes or open system metamorphism (Hickmott et al., 1987), occurring during garnet growth, although interpretation of their profiles in terms of non-equilibrium processes is complicated because their activities are not buffered by mineral equilibria in a metamorphic rock.
Trace element zoning was investigated in two samples from a region that has become a paradigm for contact metamorphic environments – the Kwoiek area of British Columbia (Hollister, 1969) – with a goal of characterizing the trace element signatures imprinted on garnet zoning by rapid metamorphic processes. Zoned porphyroblasts are common in this terrain and disequilibrium features, formed in a prograde metamorphic environment, are ubiquitous. For instance, staurolites from the region are sector-zoned (Hollister, 1970), and textural relations between aluminosilicates suggest initial metastable crystallization of andalusite (Hollister, 1969). The Kwoiek area is a well-studied locale in which to undertake a preliminary study of the disequilibrium incorporation of trace elements into garnet.

If trace element zoning signatures similar to those of the Kwoiek garnets are found in regional metamorphic rocks, they may alert petrologists to the possibilities of significant reaction overstepping, rapid mineral growth, and non-equilibrium partitioning. Determination of dimensionless parameters arising during consideration of disequilibrium partitioning models allows evaluation of situations in which disequilibrium metamorphic processes are likely to operate. Thus, it may be possible
to evaluate metamorphic models predicated on the assumption of rim equilibrium in metamorphic terrains.

3.2 Geologic setting

3.2.1 Geology and petrography - Hollister (1969) redux

The two samples, KLH 350B and KLH 350F, (kindly provided by L.S. Hollister) are from a single, staurolite-grade outcrop within a large roof pendant of metamorphic rocks in the Coast Range Batholith in the Kwoiek area, British Columbia (Hollister, 1969). These samples were collected and described by Hollister (1966, 1969, 1969b, 1970) in his seminal works on the metamorphism of the region. Aspects of Hollister's studies pertinent to this investigation are reviewed below.

The samples are fine- to medium-grained, foliated meta-graywackes consisting of pods and layers of light-colored, quartzofeldspathic and dark, graphitic, pelitic to semi-pelitic schists. The mineral assemblage (mode 350B, mode 350F) in both samples is biotite (29.6, 23.8)-chlorite (4.3, 0.6)- garnet (4.1, 1.4)- staurolite (2.5, 8.2)- [quartz + plagioclase] (58.5, 65.2)- ilmenite (1.0, 0.8)- graphite (trace, trace). Sample 350F contains significantly more modal staurolite, and less modal garnet and chlorite, than sample 350B; hence, sample 350F is from a more aluminous layer of the graywacke and 350B
is from a more ferruginous layer. Partial mineral analyses, petrographic descriptions, and petrogenetic interpretations are provided by Hollister (1969).

Detailed mapping, petrographic studies and electron microprobe analyses led Hollister to conclude that the Kwoiek area was subject to a single, prograde metamorphic episode related to emplacement of the Coast Range Batholith. Hollister estimated that the peak temperature at outcrop 350 was 575°C. Pressures were estimated to be slightly higher than the alumino-silicate triple point. (Hollister, 1969).

Staurolite-grade garnets grew by two AFM reactions (generalized) (Hollister, 1969):

(I) chlorite + muscovite + qtz = garnet + biotite + H₂O and

(II) muscovite + chlorite +/- ilmenite = staurolite + biotite + garnet + quartz + H₂O.

The relative importance of each reaction depends on whole-rock bulk composition. Muscovite is not found in samples 350B or 350F; the latter of these two reactions has eliminated muscovite from the assemblage.

3.2.2 Evidence for rapid - major element constraints

The existence of rapid, disequilibrium metamorphic processes in this contact metamorphic terrain is documented by two compelling lines of evidence: 1) the
presence of strongly sector-zoned staurolites, and 2) the existence of metastably crystallized andalusite.

Sector-zoning is strongly developed in staurolites from this terrain (Hollister, 1970), with [001] sectors enriched in Al and depleted in Ti, Si, and Mg relative to [010] and [110]. The development of sector-zoning is a disequilibrium process produced by rapid mineral growth rates (Kouchi et al., 1983). Sector-zoned minerals are generally restricted to contact metamorphic terrains and igneous magma chambers, both regimes in which rapid transfers of heat and mass predominate.

Hollister (1969) demonstrated that andalusite crystallized metastably in the contact aureole of the Coast Range Batholith, prior to nucleation of kyanite and finally sillimanite. Regional distributions of the aluminosilicates concentric to the Coast Range Batholith, overgrowth relations of kyanite on andalusite, and the distribution of polymorphic sequences in two traverses near the batholith all strongly support a scenario in which andalusite crystallized metastably in the kyanite stability field.

3.3 Analytical

Analytical conditions and working curves are presented in Appendix I.
3.4 Results - Element zoning

Element zoning profiles for garnets from the two samples are shown in Figs. 3.1 and 3.2 as the ratio of the ion intensity of each element to that of silicon. Several traverses were made in each sample; traverses exhibiting maximum Mn variations are depicted to ensure that the thin sections were cut through the cores of the grains. The overall features of each traverse are similar and no consistent difference between traverses from dark and light layers of the graywacke was observed. However, as suggested by the asymmetry of several profiles in Figs. 3.1 and 3.2, particularly for the REE, the details of different traverses are not identical. Concentrations are provided (semi-quantitatively) for those trace elements with adequate working curves (Sc, Cr, Co, Y). Breaks in slope, or abrupt increases in element abundance for a number of the elements, are found at the points designated by A and B.

3.4.1 Major elements

Iron, magnesium, manganese, calcium and titanium zoning patterns are described by Hollister (1966, 1969) and interpreted in those papers and in works by Crawford (1974), Loomis (1982) and Cygan and Lasaga (1982). Fig. 3.1 and Hollister's (1969) Figs. 7 and 15 show that MgO/FeO rises from 0.10 to 0.14 in 350B and remains
constant at about 0.12-0.13 in 350F to a point
approximately 40 microns from garnet rims (point B).
There MgO/FeO reverses, dropping rapidly to 0.10 in each
sample. Hollister (1969) interpreted the decreased
(Fe/Fe+Mg) in terms of growth through reaction (I), and
the latter growth as due to reaction (II).

The outstanding feature of the major element zoning
is the 'bell-shaped' Mn profile. Hollister (1966, 1969)
successfully reproduced most of this profile using a
Rayleigh fractionation model. Cygan and Lasaga (1982)
duplicated it via a non-linear fractionation model,
Loomis (1982) mimicked it using a disequilibrium-reaction
model, and Spear (in press) has reproduced similar
profiles using an equilibrium growth model. Mn zoning is
somewhat of a red-herring. Because Mn is highly
compatible in garnet (Hollister, 1969), its zoning can be
replicated by a variety of thermochemical and kinetic
models.

Ca varies irregularly, between 2-2.5 wt% CaO.
Crawford (1974) interprets the irregular Ca-zoning in
garnets from the Kwoiek area in terms of equilibria with
plagioclase.

3.4.2 Trace elements

Trace element zoning is depicted in Figs. 3.1 and
3.2. The outstanding feature of the zoning profiles is
their roughly tripartite nature. A distinct break in
trace element abundance exists at point A, whereas minor effects are visible at point B. The break at point B primarily affects major elements. The trace element break at point A is pronounced and is not evident in the zoning profiles of Fe, Mg, or Mn. The discovery of the large trace element break at point A correlating with a small Ca break (< 0.5 wt %) is a principal discovery of this work; Hollister's electron microprobe analyses for Ti hinted at the existence of the trace element break, and the ion probe results confirm it.

Trace elements are divided into two groups on the basis of presumed site occupancies: cubic-site trace elements (Li, Na, Sc, Co, Y and the REE) and octahedral-site trace elements (Ti, V, Cr, Zr). Site assignments are based on results summarized by Meagher (1982). Conveniently, this designation separates ions on the basis of cation size.

The cubic-site cations all developed smooth – albeit inflected – profiles on the scale depicted. Li/Si decreases steeply in both 350B and 350F, levels off near point A and drops in the rims to similar levels (Li/Si ≈ 0.0002) in both samples. Na/Si has different core values (0.0012 in 350F and 0.0008 in 350B) and rim values (0.0004 in 350F and 0.0002 in 350B) in the two samples. Sc behaves differently in the two samples. Each exhibits
a relatively flat Sc profile in the core (Sc/Si ≈ 0.003), but antithetic variability rimward of point A. Y/Si comes closest of the cubic-site trace elements to duplicating the 'bell-shaped' behavior of Mn. It fluctuates somewhat in the core of sample 350B, drops precipitously to point A, and then levels off rimward. Cobalt maintains a constant concentration of roughly 0.00005 Co/Si in each sample.

The REE display two-stage growth profiles with a break at point A. All the middle and heavy REE (Lu, Yb, Er, Ho, Dy and perhaps Tb) in 350B exhibit core-to-rim depleted profiles in the region coreward of point A, whereas only the heavy REE (Lu, Yb, Tm, Er, and perhaps Ho) are core-to-point A depleted in 350F. At point A, each of the heavy REE elements displays an inflection; the scale of this figure clouds interpretation of this portion of the profiles for the heaviest REE (Er, Yb and Lu). The middle REE (particularly Dy and Tb in sample 350F) display relatively flat profiles in the core region, then begin decreasing slightly, rimward of point A. The differences in absolute abundance of these elements between the two samples probably reflects variability in bulk compositions.

The octahedral-site trace elements (Ti, V, Cr and Zr) exhibit more exotic behavior. In each sample, Ti and V begin at intermediate levels in the cores, and drop
slightly to point A; there, Ti increases abruptly by a factor of 2 to 3 in sample 350B and a factor of 2 in sample 350F, and V begins a gradual increase. In each case, the total V enrichment is smaller than the Ti enrichment. Cr exhibits the least systematic behavior of any element examined. Zr has a constant composition in the core of 350F, increases slightly at the trace element break at point A, then drops fairly abruptly to a low concentration at the rim (Zr was not measured in the traverse in 350B).

The most important feature of the trace element zoning profiles is the break at point A. The cubic-site trace elements (Li, Na, Sc, Y, and the HREE) all exhibit either inflections or increases in element abundance and the octahedral-site trace elements (Ti, V, Cr, Zr) also exhibit increases in abundance or inflections at this point. In the remainder of this paper a variety of questions regarding the trace element behavior at point A are considered: 1) Can the humps and inflections be rationalized with equilibrium behavior? 2) If disequilibrium is required, what is the nature of the process controlling that non-equilibrium partitioning? and 3) If the process can be identified, in what geologic environments is the process important?
3.5 Partitioning models

In this section we evaluate a number of partitioning models from the geologic and materials science literature in terms of their consequences for metamorphic mineral zoning. Specifically, we examine which type of partitioning model is appropriate to explain the minor element zoning in the Kwoiek garnets. It is emphasized that different models may apply to different elements.

Both equilibrium and disequilibrium models are included. Examining a wide variety of trace elements ranging from compatible to incompatible allows evaluation of the most important controls on trace element distributions during garnet growth.

3.5.1 Constraints on models

The activities of Ti and Na are controlled by phase equilibria involving ilmenite and plagioclase respectively, as well as other silicates. Assuming that Ti enters the octahedral site in garnets by a $M^{+2}_2 TiAl_{-2}$ exchange (Huggins et al., 1977), the titanium activity in the garnet during growth will be defined by equilibria such as:

\[
(III) \ 3SiO_2(qtz) + Fe_3Al_2Si_3O_{12}(garnet) + 2FeTiO_3(ilm) + KFe_3AlSi_3O_{10}(OH)_2(biot) = 2Fe_3(FeTi)Si_3O_{12}(garnet) + KAl_3Si_3O_{10}(OH)_2(musc).
\]
Similarly, if sodium enters garnet through a NaSiCa_A1_ exchange the Na activity in garnet is defined by the equilibria:

\[ \text{NaSiCa}_A_1_\text{ (garnet)} = \text{NaSiCa}_A_1_\text{ (plag)} \]

At equilibrium, variations in Ti and Na in garnet will reflect changes in equilibrium constant for these reactions as a function of P, T and mineral composition.

Accurate distribution coefficients are not available for partitioning of trace elements between metamorphic minerals; however, rough groupings of elements into categories based on compatibility relative to garnet can be constructed based on published mineral separate data (see Appendix II). Y, Sc, Mn and probably the HREE are compatible elements relative to the other minerals in the Kwoiek area assemblage. Co and Zr are intermediate elements, and Cr and V are incompatible elements. Li is probably also an incompatible element because it is strongly concentrated in micas and staurolite (Dutrow, Holdaway and Hinton, 1984) in metamorphic environments (see Appendix II). In a closed system characterized by depletion zoning the steepness of observed profiles may reflect the compatibility of a given element in garnet relative to the matrix minerals; reference to Figure 3.2 suggests Lu and Yb are the most compatible REE in each sample. The above categories are restricted; for an element to qualify as compatible, D(gar/mineral) was
required to be greater than two for every known garnet/mineral pair described in the literature. The behavior of generalized 'compatible' and 'incompatible' elements according to different partitioning and growth models is easily calculated.

The bulk distribution coefficient $D$ is defined as $\Sigma X_i D_i$, where the $D_i$ are mineral-mineral distribution coefficients and the $X_i$ are weight fractions. The $D_i$ are $f(P, T, X)$. We cannot predict the temperature and pressure dependence of the $D_i$, but we can use the data in Appendix II and the reaction models and modal data in Hollister (1969) to estimate changes in bulk distribution coefficient during garnet growth due to changes in mineralogy. The principal mineralogic changes are the breakdown of chlorite and muscovite and the growth of garnet, staurolite and biotite. No strong fractionation of trace elements exists between micas (Appendix II and de Albuquerque, 1975) except for a slight enrichment in Li, Cr, V and Co of biotite relative to muscovite (de Albuquerque, 1975). Thus, the bulk partition coefficients for Li, V and Cr decrease during garnet growth by reaction (I).

In addition to the effect of changing modal mineralogy on bulk partition coefficients, participation of refractory phases in the metamorphic reactions affects the trace element zoning of garnet by changing the
effective bulk composition (see Chapter II). Refractory phases are defined by Hollister (1969) as minerals that are zoned at metamorphic temperatures, thus shielding the equilibrating matrix from interaction with them. Hollister suggested that staurolite and ilmenite are refractory in these assemblages. Staurolite is refractory for Li, and ilmenite is refractory for V, Mn and perhaps Cr, but not for Ti.

3.5.2 Rayleigh Fractionation?

An equilibrium partitioning model can be applied to major or trace element incorporation into a growing porphyroblast if equilibrium between the porphyroblast rim and the matrix minerals existed during mineral growth. Examples of equilibrium partitioning models include: one-stage, isothermal, Rayleigh fractionation models (Hollister, 1966, 1969); multi-stage, polythermal, 'Rayleigh type' fractionation models (Atherton, 1968); fractionation models that allow bulk distribution coefficients to be a function of P, T and composition (Cyganski and Lasaga, 1982) as well as more complicated equilibrium thermodynamic models such as those of Spear (in press) and Loomis and Nimick (1982). The Mn profile in sample 350B has been modeled explicitly using single-stage models, compositionally dependent models, and the integrated form of the thermodynamic equations (Loomis and Nimick, 1982).
The simplest method for modeling a zoning profile such as 'bell shaped' Mn is to use a Rayleigh fractionation expression. Simple Rayleigh fractionation incorporates three constraints: 1) mass balance within a closed system, 2) constant partitioning during the modeled process, and 3) complete removal of the fractionating element from the reacting system by mineral growth processes. The second requirement generally means that the modeled element must be a trace element, distribution coefficients are usually strong functions of major element composition (Cygan and Lasaga, 1982). Simple Rayleigh fractionation is an idealized process in both igneous and metamorphic systems; nonetheless, it has been widely used to model mineral zoning in metamorphic rocks (Hollister, 1966, 1969; Atherton, 1968; Tracy, 1982), and fractional crystallization in igneous systems (Gast, 1968; Zielinski and Frey, 1970; Allegre et al., 1977; Haskin, 1983). Rayleigh zoning for compatible elements is the simplest mathematical form of what can more generally be called depletion zoning: the formation of decreased core to rim zoning by segregation of compatible trace elements into the cores of porphyroblasts at higher weight fractions than are present in the equilibrating system. A simple Rayleigh fractionation expression was used by Hollister to duplicate the Mn profile of the Kwoiek garnets, thus by
comparing Mn with other elements in the garnets, we can evaluate the assumptions in the simple Rayleigh models for other elements.

The simple Rayleigh fractionation equation is:

\[ \text{Mn}_{\text{gar}} = K_{\text{Mn}} \text{Mn}_0 (1 - W_{\text{gar}}/W_0) (K_{\text{Mn}})^{-1} \]  

(Hollister, 1969) where \( \text{Mn}_{\text{gar}} \) is the weight fraction of Mn in garnet rim, \( K_{\text{Mn}} \) is the bulk distribution coefficient for partitioning of Mn between garnet and matrix, \( \text{Mn}_0 \) is the initial weight percent of Mn in the system, and \( W_{\text{gar}}/W_0 \) is the weight fraction of garnet in the system. (Note that the \( (1 - W_{\text{gar}}/W_0) \) term is equivalent to \( f \), the fraction of melt, in the igneous Rayleigh fractionation expression).

Any element obeying simple Rayleigh fractionation during garnet growth will also follow a distribution equation of the form:

\[ \text{El}_{\text{gar}} = K_{\text{El}} \text{El}_0 (1 - W_{\text{gar}}/W_0) (K_{\text{El}})^{-1} \]  

Thus, the ratio of Mn concentration to the concentration of another trace element governed by a Rayleigh distribution law is:

\[ \frac{\text{Mn}}{\text{El}}(\text{gar}) = \frac{K_{\text{Mn}}}{K_{\text{El}}} \frac{\text{Mn}_0 (1 - W_{\text{g}}/W_0) (K_{\text{Mn}})^{-1}}{K_{\text{El}} \text{El}_0} \]  

(3)

Assuming \( (1 - W_{\text{gar}}/W_0) \) is equivalent for each element (this assumption is tantamount to assuming equal system sizes for different elements) and taking logarithms yields:
\[
\log(Mn/El)_{\text{gar}} = (K(Mn)_{\text{gar}} - K(El)) \log(1 - \frac{W_{\text{gar}}}{W_0}) + \log(K(Mn)_{Mn_0}/K(El)_{El_0})
\]

Taking the log of equation (1), and combining with (4) we obtain:

\[
\log(Mn/El)_{\text{gar}} = \left(\frac{(K(Mn)_{\text{gar}} - K(El))}{K(Mn) - 1}\right) \log((Mn)_{\text{gar}}) + \text{a constant}
\]

Thus, if K's are constant any trace element that follows an exponential fractionation law during garnet growth will yield a straight line on a log(Mn) vs. log(Mn/El) plot (Fig. 3.3). The slope of this line is proportional to \(\frac{(K(Mn)_{\text{gar}} - K(El))}{K(Mn) - 1}\), provided the scale of equilibration for the two elements is similar, and the intercept reflects the influence of the bulk composition and the ratio of distribution coefficients. An element with a bulk distribution coefficient identical to Mn yields a horizontal vector pointed left on Fig. 3.3, an infinite K yields a vertical upwards vector, and a small K yields a down and leftward vector approaching 45 degrees from the horizontal.

Any vector oriented between a downward vertical vector and a vector oriented down and to the left at 45° requires either disequilibrium partitioning or open-system behavior (this region will henceforth be referred to as the DEOS region (Disequilibrium/Open System)). The DEOS region is entered whenever the abundance of the element in the denominator (El) increases in abundance
(relative to Mn) to a greater degree than an element with
K≈0 would increase during simple Rayleigh fractionation.
Partition coefficients cannot be negative; thus, to enter
the DEOS region one must change either MnO, the effective
bulk composition for Mn, or ElO, the effective bulk
composition for any other element.

As shown by the tripartite profiles (Fig. 3.1 -
3.3), none of the trace elements in the studied samples
can be explained by a single-stage Rayleigh fractionation
models, with the sole exception of cobalt. More complex
mechanisms such as two-stage growth, open-system
behavior, or disequilibrium partitioning are required.

An abrupt change in distribution coefficients for an
element leads to a kink in the log (Mn/El) plot of Figure
3.3; presumably a gradual change leads to a smooth curve.
The derivation of equation (1) assumes a constant K;
however, two episodes of garnet growth with differing K's
can be treated as two distinct Rayleigh events.
Conclusions based on comparisons to Mn are valid because
Mn zoning displays one-stage Rayleigh behavior (except in
the profiles' outermost sections). Portions of the
profiles on Fig 3 may reflect these multi-stage Rayleigh
processes. For example, the Sc profile for sample 350B
could reflect an initial growth interval where K(Sc) ≤ 1,
followed by a period where K(Sc) approached K(Mn).
Based on the above arguments and Figures 3.1-3.3, it is suggested that DEOS behavior is possible for the following trace elements: Li in 350F early in its growth history, Sc coreward of point A in 350F, Ti at point A in both samples, V late in the growth profile on one side of 350B only, Cr in its outermost growth profile in 350B, and Y near the rim of each garnet. It is important to emphasize that a vector in the forbidden region strongly suggests DEOS behavior, but a vector outside the region does not preclude such behavior. For example the steepening of Sc (350B) may be similar to the clearer evidence for DEOS for Sc in 350F. Titanium is somewhat of a special case. Rayleigh fractionation is inappropriate for Ti because it is a buffered element; nonetheless, the presence of the Ti vector of Fig. 3.3 in the DEOS region is evidence for disequilibrium during garnet growth.

Because Ti activity is buffered at a high level by phase equilibria with ilmenite at a given pressure, temperature and mineral compositions (i.e. by reaction III) the titanium zoning profile strongly suggests that disequilibrium partitioning was operative during garnet growth. Open system behavior cannot produce a Ti fluctuation (see Chapter II); influx of a Ti-rich fluid into an ilmenite-bearing rock changes the modal amount of ilmenite, but not the activity of titanium (provided mineral compositions or Ti substitution mechanisms do not
change radically). In an equilibrium growth model in Kwoiek assemblages the Ti profile would reflect only variations in intensive parameters. The observed zig-zag pattern in Ti (Figures 3.1 and 3.2) implies a repeated and drastic fluctuation in temperature or mineral composition during garnet growth, which seems unlikely during isobaric contact metamorphism. Furthermore, based on evidence from a rapidly cooled high-grade terrain (Chapter IV) and on data for mineral separates from ilmenite bearing gneisses from the Adirondacks (Engel and Engel, 1960), Ti solubility in garnet rises with increasing temperature. Thus, at equilibrium, the Ti zoning implies two episodes of garnet growth during declining temperature, an unlikely scenario.

Other elements that show breaks in their profiles at point A (i.e. Sc, Li, Na, V in 350F, Zr, and the REE) may also display disequilibrium effects. In particular, the Li and V (in 350F) log(Mn/E1) vs. log(Mn) plots (Figure 3.3) are in the DEOS regime at the same point as Ti.

Evidence for DEOS behavior appears elsewhere in the profiles other than at the point where Ti increases. The steepening of the V profile on one side of 350B's profile, and the anomalous Cr behavior, may represent the breakdown of ilmenite during garnet growth. Ilmenite is highly enriched in V relative to garnet on the basis of qualitative measurement of ion yields of a western
Massachusetts ilmenite (Chapter V). Fractionation into a refractory phase, or breakdown of the trace element enriched core of a refractory phase can be considered open-system behavior on a thin-section scale (Chapter II; Hollister, 1969; Hickmott et al., 1987).

In this section it has been suggested that:

1) Rayleigh fractionation is an overly simplistic model for trace element zoning in the Kwoiek garnets.

2) The Ti zoning suggests disequilibrium partitioning. Other elements may also have experienced disequilibrium partitioning, but the evidence is somewhat equivocal.

3) Small scale open-system behavior may have affected the late-stage growth profiles of V and Cr as a result of ilmenite breakdown.

3.5.3 Disequilibrium partitioning models

In this section, two categories of disequilibrium models are examined to explain anomalous element behavior: diffusion-controlled partitioning models and interface-controlled partitioning models. The goal of the discussion is to predict the trace element signatures imprinted on garnet zoning profiles by these two types of disequilibrium processes and to compare those predictions to the zoning profiles of Hollister's garnets. We do not consider whether diffusion control, interface control, or heat flow control is the rate determining step during
garnet crystallization (Fisher, 1978; Rubie and Thompson, 1984). A number of these scenarios have been previously considered in the geological literature; these are discussed briefly. Those that have appeared only in the materials science literature are discussed in greater detail.

Many of these models were derived for binary metal or glass systems. Thus, some cannot be easily applied to multicomponent, multiphase, silicate systems such as those found in metamorphic rocks. Nonetheless, with this caveat in mind, we apply the simplified models, assuming that the Kwoiek samples can be approximated as two-phase (garnet and 'matrix') assemblages, and attempt to gain insights into the processes affecting these and other rapidly crystallized metamorphic rocks.

5.3.1 Diffusion controlled models

Infinite reservoir, diffusion-controlled growth models have been discussed extensively in both the geological (Albarede and Bottinga, 1972; Shimizu, 1983; Loomis, 1982; Tracy and McClellan, 1985; Lasaga, 1986) and materials science literature (Burton et al., 1953; Smith et al., 1955). The primary assumption in infinite reservoir diffusion-controlled growth models is that transport, either diffusive or convective, in the matrix is slow enough that the concentration of an element in the matrix in equilibrium with the surface of the crystal
differs from that in the bulk matrix. The simplest model of this sort is that described initially by Tiller et al. (1953) and Smith et al. (1955) and applied to igneous processes by Albarede and Bottinga (1972) and Shimizu (1983). This isothermal model assumes that transport of material to the interface is matrix diffusion-limited, that the radius of curvature of a growing grain is large enough that a one-dimensional model can be used, that the matrix diffusion coefficient \((D)\) is a constant value and much larger than the diffusion coefficient in the growing mineral, and that growth is at a constant velocity. These assumptions are restrictive, but do not significantly detract from the major conclusions derived from this analysis. The constant velocity solution to the appropriate differential equation for concentration in a growing mineral as a function of growth distance \((\approx \text{grain size})\) is (Shimizu, 1983):

\[
C^S = C_0/2[1 + \text{erf}(\sqrt{VX/D}/2) + (2K_i-1)\exp(K_i(K_i-1)\sqrt{VX/D})\text{erfc}((2K_i-1)\sqrt{VX/D}/2)]
\]

(6)

where \(C^S\) is the concentration of element \(i\) in refractory mineral \(S\), \(C_0\) is the initial concentration of that element in the system, \(x\) is the half-width of the growing mineral, \(V\) is growth velocity, and the other terms are as defined previously. Fig. 3.4 depicts \(C^\text{gar}/C_0\) for different values of reduced grain size. The most important implications of this figure for trace element
zoning in garnet are: 1) incompatible elements appear to become more compatible (they increase in abundance relative to Rayleigh fractionation) whilst compatible elements appear to become less compatible (they decrease in abundance relative to Rayleigh fractionation) when growth velocity increases, 2) compatible elements are affected at lower (by a factor of 100) growth velocities than are incompatible elements, 3) all trace elements should be affected unless matrix diffusion coefficients vary significantly for the different elements, and 4) element concentrations approach a steady state (see also Lasaga, 1986, Fig. 1). Garnet growth dominated by diffusion controlled disequilibrium would show: 1) parallel depletion of compatible elements (Sc, Y, HREE) and enrichment of incompatible elements (Li, Ti, V, Co) during episodes of rapid mineral growth, and 2) much more significant depletions of compatible elements than enrichments of incompatible elements.

The trace element behavior at point A in Hollister's garnets violates these two predictions. The HREE and Sc, defined earlier as compatible or highly compatible elements, do not show a steep drop-off in abundance at point A. Co and Li, both incompatible elements, do not strongly increase in abundance at point A, as would be predicted for a matrix diffusion-controlled model.
A model calling for rapid Mn, Co and Li matrix transport compared to Ti and other elements showing evidence for disequilibrium partitioning, could potentially explain the decoupling of incompatible trace elements at point A. The arguments of Brady (1983), however, suggest that grain-boundary diffusion of different cations in metamorphic environments is similar due to similar complexing in the diffusional medium. A model dependent on radically different matrix transport rates is possible, but seems unlikely.

Brady (1983) and Frantz and Mao (1976), among others, point out that differential transport of cations along grain boundaries is controlled by cation solubilities (either in the grain boundaries or in an intergranular fluid) rather than intrinsic grain boundary diffusion coefficients. Conceivably, Ti could be significantly less soluble in an intergranular fluid or grain-boundary region than the other trace elements, leading to depletion near rims during garnet growth. This hypothesis is unlikely for two reasons: 1) there is no consistent depletion of ilmenite near the garnet rims and 2) Ti content of biotite does not vary systematically as a function of distance from garnet.

If we assume that expression (6) roughly approximates the physics of a situation in which matrix transport, rather than lattice diffusion, dominates, it
can be written in terms of a dimensionless number \((Vx/D)\) that allows estimation of the circumstances in which diffusion-controlled partitioning will be significant in metamorphic processes. Values of this dimensionless number are plotted in Fig. 3.5 for various reported values of grain boundary diffusion coefficients \(D\) and a range of crystal growth rates appropriate to metamorphic environments. \(V\) in contact metamorphic environments is estimated to range from \(10^{-2}\) to \(10^{-6}\) cm/year (Loomis, 1982). Estimates of mineral growth rates in regional terrains are not common. A first order approximation can be made using data presented by Selverstone et al. (1984) and Selverstone (1985). The \(P-T-t\) path during growth of Selverstone's garnets is well-constrained. The grain radius of her sample FH-1M was divided by the time of garnet growth as extracted from the known \(P-T-t\) path to obtain an average garnet growth rate. Calculated growth rates range from \(1.0\times10^{-8}\) to \(2.5\times10^{-9}\) cm/year. The length-scale \((x)\) utilized is 10 microns, a grain size appropriate to the early stage of garnet growth. As both velocity and the length-scale appear in the numerator of the dimensionless number the effects of most early rapid growth will be counterbalanced by the smaller grain sizes during this interval (see Fig. 11 of Loomis, 1982).

This dimensionless number provides rough insights into the growth rates required to observe the chemical
effects of diffusion limited matrix disequilibrium. Matrix diffusion-controlled partitioning will be significant when the dimensionless number \( \approx 1.0 \). Based on this criterion, diffusion controlled disequilibrium partitioning at rapid growth rates is predicted using Brady's (1983) hydrothermal grain-boundary diffusion coefficient for SiO\(_2\) \((10^{-9}/\text{a cm}^2/\text{sec where a is grain size in microns})\). Using Joesten's (1983) dry grain-boundary value for oxygen \((5.2 \times 10^{-15} \text{ cm}^2/\text{sec at 600}^\circ \text{C})\), diffusion controlled partitioning is predicted in most contact metamorphic environments. Matrix transport controlled disequilibrium trace element zoning in garnets is unlikely to be an important process in prograde regional metamorphic environments.

5.3.2 Interface kinetics controlled models

Hall (1953) proposed that processes within the interface during crystallization of solids could lead to disequilibrium trace element partitioning. Beyond a critical growth velocity, impurity atoms located on a grain's surface cannot equilibrate with their growth environment prior to attachment of a new lattice plane. Dowty (1976) utilized a similar model in the geological literature; he attributed the phenomenon of sector-zoning to crystal-face-dependent adsorption of small, highly charged cations into exposed protosites of sector-zoned crystals.
Such interface field effects have been observed and modeled by numerous authors, particularly in rapidly grown materials. Interface field effects are most noticeable in elongate crystals in which solute concentrations differ between crystallographic faces. This phenomenon is observed in: ceramic/semiconductor materials - As, Sb and Ga in Ge (Hall, 1953; Wang et al., 1982), Ga in Si (Leamy et al., 1980), and igneous minerals - trace elements in sector-zoned augite (Shimizu, 1981). Other sector-zoned minerals probably owe their zoning to similar effects (Dowty, 1976; Burton and Hickmott, i.e. prep).

Interface field effects on trace element partitioning arise because the chemical potential of an ionic species can be significantly different in an interface region than it is in a bulk ionic solid (Yan et al., 1983). Interaction potentials exist in interface regions between solute atoms and grain interfaces. These interactions include: 1) an electrostatic potential between solutes and interfaces, 2) an elastic potential due to misfit between solute and solvent cations in a solid matrix, 3) dipole interactions between solute-vacancy pairs and interface electric fields, 4) an entropy of mixing, and 5) long-range coulomb interactions (Yan et al., 1983; Kingery, 1974; Kingery, 1984). The most important of these forces in ionic ceramics and
minerals are probably electrostatic and elastic forces (Kingery, 1974).

Electrostatic interactions in solvent interfaces are due to forces of the space-charge region that exist near interfaces in ionic solids. Discussions of the nature of this space-charge region are presented by a number of authors (Frenkel, 1946; Lehovec, 1953; Kliwer and Koehler, 1965; Kingery, 1974; Yan et al., 1983). To a first approximation, grain interfaces act as infinite sources or sinks for vacancies. Generally there is a difference in the free energy of formation of cation and anion vacancies in a solid interface leading to an excess of cation vacancies over anion vacancies in the surface of a material (Yan et al., 1983). The excess cation vacancies have a localized negative space-charge penetrating the crystal and a positive charge-compensating region in the grain-boundary itself. The gradient in vacancy concentrations leads to an electrostatic potential difference between interface regions and bulk solids. Aliotropic solutes (i.e. Sc$^{+3}$ for Mg$^{+2}$) are also associated with cation vacancies; thus the nature of electrostatic potentials at interfaces is controlled both by temperature-dependent, Schottky vacancy formation and solute content. Experimentally, it has been shown that this potential difference leads to segregation of aliovalent cations near interfaces
compared to bulk solids in some ionic ceramics. In particular, highly charged cations segregate in surface regions of many ionic oxides.

Electrostatic interactions are of primary importance for segregation of aliovalent cations in ceramics. $\text{Sc}^{+3}$, which has a cation radius in six-fold coordination similar to $\text{Mg}^{+2}$, is strongly segregated in MgO interfaces due to electrostatic interactions (Chiang et al., 1981). Chiang and co-workers demonstrate that a multi-layer approximation to the electrostatic potential effectively duplicates the Sc segregation seen in their experiments. Aluminum segregation in ($\text{MgAl}_2\text{O}_4$) spinel grain boundaries is also attributed to electrostatic interaction of solutes with an interface electrostatic field (Chiang, 1985).

Extrapolation from simple oxide systems ($\text{MgO}$, $\text{MgAl}_2\text{O}_4$) to complex silicates such as garnet is a potentially difficult endeavor. Both the sign of the electrostatic potential at metamorphic temperatures and the nature of defect substitutions in garnet are unknown. Homogeneous chemical equilibria and charge balance constraints will also influence the distribution of cations in the surface of a solid. If garnet interfaces are negatively charged, as are many ceramic oxides such as MgO, $\text{Al}_2\text{O}_3$, and MgAl$_2$O$_4$, highly charged cations ($\text{Ti}^{+4}$, $\text{Zr}^{+4}$) will be attracted to the octahedral or tetrahedral
sites, and these same cations plus $V^{+3}$, $Cr^{+3}$, and $REE^{+3}$ will be attracted to the cubic site. Local heterogeneous defect equilibria could lead to complex solute coupling in interface regions.

The enrichment of $Ti^{+4}$ and inflections in many other aliovalent cations observed at point A (Figure 3.1 and 3.2) suggest that electrostatic segregations may be important in garnets.

Elastic energy in ceramic interfaces arises due to the size misfit between solute atoms and solvent atoms on the same lattice sites. This misfit leads to a lower heat of solution in the more open structure of the interface than in the bulk solid. Theoretical consideration of metallic systems suggest that the degree of elastic solute segregation in interfaces will show a logarithmic dependence on solute misfit $((r_2-r_1)/r_1)$ where $r_1$ and $r_2$ are the ionic radii of the solvent and solute ions (Li and Kingery, 1984).

$Al_2O_3$ (corundum) exhibits solute segregation at interfaces of $La^{+3}$, $Y^{+3}$, $Sc^{+3}$, $Zn^{+2}$, $Ni^{+2}$ $Si^{+4}$, $Ti^{+3}$ (Li and Kingery, 1984) in which the natural log of solute enrichment correlates with $((r_2-r_1)/r_1)^2$, suggesting that elastic-strain influences grain-boundary segregation in this material. $Ti^{+4}$ appears to be the only segregant in $Al_2O_3$ for which significant electrostatic interaction also contributes to segregation.
Calculation of \((r_2-r_1)/r_1\) for trace elements in garnet predicts that significant segregation of large cations such as Na and the LREE would be expected based primarily on elastic constraints. Additionally, enrichment of Zr would be larger than that of Ti if elastic effects dominated over electrostatic effects. These calculations are predicated on the assumption that interface cations display similar site occupancies to their equilibrium occupancies.

In the previous paragraphs we have detailed the types of solute distributions expected in the interfaces of ionic solids. Solutes can be enriched by a factor of \(>10\) in the interface region of alkali halides and oxides (Yan et al., 1983; Kingery, 1984). The enrichments and inflections of aliovalent solutes, particularly Ti\(^{4+}\), at point A, suggests that electrostatic segregation may influence the disequilibrium trace element signatures preserved in the Kwoiek garnets.

3.5.4 Solute trapping of interface segregants

The solute enriched/depleted region in grain interfaces is carried along with the interface during slow crystal growth (Tiller and Ahn, 1981). Figure 3.6 schematically depicts the solute profiles possible in a crystal interface. Under conditions of slow grain growth \(K_i=K_{\text{bulk}}\), where \(K_i\) is the interface distribution coefficient; the bulk solid can communicate with the
matrix through the interface layers of the solid and the growth medium (Tiller and Ahn, 1981; Tiller, 1986). Diffusive communication will generally be slow in the solid, and diffusion coefficients in garnets, even in an interface region, are undoubtedly much smaller than matrix diffusion coefficients at mid-amphibolite facies conditions. For equilibrium to exist, cations must be able to migrate through the interface region of thickness $\delta_{xs}$ more rapidly than mineral growth traps the interface solute. There will a critical interface velocity $V_{crit} \approx \frac{p_{solid}}{\delta_{xs}}$ at which communication between bulk matrix and growing solid is lost, and interface solute trapping becomes important (Tiller and Ahn, 1981, Tiller, 1986). Rough calculation of $V\delta/D$ allows estimation of the metamorphic environments in which interface solute segregants will be entrapped in growing metamorphic minerals.

The width of the interface region ($\delta$) for garnets is not known, but can be estimated by analogy with ceramic and alkali halide interfaces. The scale lengths of the electrostatic interface and elastic interface differ, with the electrostatic interface penetrating more deeply than the elastic interface (Chiang et al., 1981). The former is defined as the depth to which surface electrostatic fields are present, the latter is the depth to which interface elastic strain exists. Observations
summarized by Kingery (1984) suggest that interface thicknesses range from 0.5-10 nm in oxide materials although Tiller (1986) believes that surface-segregant-rich layers extend to depths up to 1 micron. The detailed Auger profiles of Chiang et al. (1981) demonstrate that electrostatically induced segregation of Sc exists to a depth of 2.0 nm whereas elastic segregation of Ca reaches a depth of less than 0.5 nm.

Calculations of $V\delta/D$ assuming an interface width of 1 nm, diffusion coefficients in garnet of Cygan and Lasaga (1982) and a range of growth velocities can be read from Fig. 3.5. The interface width utilized is at the low end of interface widths reported for ceramics; therefore preservation of solute enrichment may occur at slower growth velocities than those estimated in Fig 5. A major assumption of this rough calculation is that diffusion coefficients determined for bulk solids are appropriate in the more open structure of a grain surface; it is possible that the higher defect concentrations in the surface would lead to diffusion rates more rapid than those in the bulk solid. Critical growth velocity occurs when $V\delta/D \approx 1$ (Tiller and Ahn, 1981).

Interface controlled partitioning is predicted to be trapped at growth rates ($10^{-2}-10^{-6}$ cm/year) and temperatures appropriate for contact metamorphic environments (Loomis, 1982). At growth rates estimated
for regional terrains, interface solutes in garnet may be trapped at the lowest calculated temperatures (400°C), or if mineral growth rates are extremely rapid. A growth rate an order of magnitude faster than that calculated for Silverstone's garnet would exceed critical trapping velocities at temperatures approaching 500°C. Interface controlled disequilibrium is significant at slower growth rates than diffusive/transport controlled disequilibrium.

The rapid growth rates in the Kwoiek area provide a mechanism for entrapment of surface segregated Ti and other trace elements. An important question remains: Why do we see two episodes of high-Ti to low-Ti zoning? The high Ti level in the core is anticipated at the rapid growth rates immediately after nucleation, but what caused the Ti jump at point A?

3.5.5. What happened at point A? A discussion

In the previous two sections it has been suggested 1) that enrichments of trace elements, such as Ti, occurred due to electrostatic and/or elastic segregation at garnet interfaces, and 2) that solute trapping of surface segregants is expected at rapid mineral growth rates. In this section these conclusions are related to the thermal and petrologic history postulated by Hollister.

The three-stage growth history inferred from the zoning profiles for the garnets is interpretable in terms
of two periods of growth in the AFM+Mn trivariant assemblage garnet-biotite-chlorite and an episode of growth in the divariant AFM+Mn assemblage garnet-biotite-chlorite-staurolite (Hollister, 1969).

It is likely that nucleation of garnet was delayed and significant overstepping of reaction (I) occurred (Hollister, 1969; Loomis, 1982); thus the initial stage of garnet growth occurred at rapid velocity with significant trapping of interface solutes. As the compositions of the minerals approached their equilibrium compositions due to mass transport, the affinity of the reaction decreased, the garnet growth velocity slowed, and the incorporation of trapped solute diminished.

It is postulated that at point A the affinity of the whole-rock growth reaction increased abruptly, and rapid garnet growth, accompanied by significant solute trapping occurred again. The nature of the event that initiated the second episode of rapid growth is not well-constrained.

Near equilibrium, an increase in growth velocity is caused by either a linear (Fisher, 1978) or non-linear (Lasaga, 1986) increase in the affinity of a reaction. The affinity of a continuous reaction could be increased by: 1) a rapid change in temperature, 2) a change in metamorphic fluid composition, 3) an abrupt change in mineral composition, or 4) nucleation of a new phase. The
exponential dependence of growth rate on affinity
(n=2.69) determined by Schramke et al. (1987) would favor
rapid changes in growth rate over small changes in
overstepping.

A change in heating rate is unlikely; there are two
generations of plutons in the Kwoiek area, but the later
stage stocks appear to be of only local thermal
importance (Hollister, 1969). A fluid composition change
is possible, but difficult to quantify. Mineral or fluid
composition could change isothermally through exposure of
the core of a mineral grain to the equilibrating
environment that was far from equilibrium with growing
garnet.

Nucleation of a new phase such as staurolite at
point A is unlikely for three reasons: (1) If staurolite
and garnet grow concurrently, similar 'bell-shaped'
zoning profiles develop in each mineral (Hollister,
1969). Because staurolite is unzoned in Mn (D. Hickmott
unpub. ion probe data; Hollister, 1970), staurolite
probably did not nucleate at point A. Staurolite and
garnet did not grow together during interval AB. (2)
Garnet does not exhibit Li or Zn (see Chapter V)
fractionation between points A and B, and (3) garnet
between point B and the rim is zoned in a complementary
fashion to staurolite ((Fe/Fe+Mg) increase). Thus,
staurolite growth was probably initiated at point B, as
was concluded by Hollister. Based on Hollister's petrographic descriptions it is unlikely that a phase other than staurolite could have nucleated at point A.

Point A corresponds to a small change in the Ca-content of garnet. Crawford (1974) noted the correspondence between Ti increases and Ca upturns, and ascribed them (perhaps incorrectly) to miscibility gaps in the plagioclase solid-solution series. The overall affinity of reaction would increase after an abrupt change in plagioclase composition.

There is no entirely satisfactory explanation for the change in reaction affinity that may have produced the trace element behavior observed at point A. Despite this drawback, the trace element signatures of rapid growth processes appear to have been identified and ascribed to reasonable disequilibrium partitioning models.

3.6 Implications for metamorphic petrogenesis

Equilibrium between metamorphic minerals cannot be assumed automatically, particularly for trace elements, during rapid growth of metamorphic minerals. Phase equilibria studies and element partitioning experiments must beware of systematic non-equilibrium effects. For example, if growth rates for all the garnets in a suite of samples from the same outcrop were similar, then the magnitude of disequilibrium trace element incorporation
would probably be similar. Similar apparent partition coefficients would be measured for mineral-mineral pairs, but these values would not be equilibrium partition coefficients. Disequilibrium processes are not necessarily non-systematic processes; they are governed by thermodynamic, mass balance and kinetic equations, just as are equilibrium processes.

Walther and Wood (1984) suggest that rates of surface dissolution (surface processes) do not determine the rates of reaction in metamorphic systems. Lasaga (1986) emphasized the importance of interface kinetics in metamorphism, based on theoretical and experimental constraints. This study, and observations of sector-zoned minerals in both igneous and metamorphic systems (i.e. Hollister, 1970), suggest that the attainment of equilibrium of dissolution and attachment of major components at mineral interfaces does not imply that trace element adsorption and desorption are not rate limited by interface processes in metamorphic environments (DeVore, 1955). Trace elements may be excellent indicators of the operation of interface kinetics during metamorphism.

3.7 Conclusions

The trace element signatures of the Hollister garnets are consistent with disequilibrium trace element partitioning into garnets.
Preservation of disequilibrium partitioning due to interface field effects is likely to occur in contact metamorphic environments, and may occasionally occur in regional environments when mineral growth rates are rapid, particularly at low temperatures.

Highly charged ions, particularly Ti, are most useful for recognizing disequilibrium partitioning. Theoretical calculations also confirm that preservation of trace-element signatures in contact metamorphic environments is likely. Caution is urged in attempts to utilize mineral zoning to infer petrogenetic histories in regions in which rapid mineral growth took place.

The effects described above are not limited to garnets, although garnets are particularly susceptible due to their small diffusion coefficients at metamorphic temperatures. Both the interface field effects and the preservation of those effects will occur commonly in metamorphic, igneous and hydrothermal environments where mineral growth is rapid.

Examination of grain boundaries of natural samples and experimental charges using the auger, TEM and ion-probe techniques of Chiang et al. (1981) and Kingery (1984) may lead to insights into the nature of interfaces in both igneous and metamorphic environments.
Bibliography


Frantz, J.D. and Mao, H.K. (1976) Bimetamoratism resulting from intergranular diffusion I. A


Figure 3.1: Major and trace element zoning profiles in samples 350B and 350F. Errors based on counting statistics generally smaller than symbol size. The breaks in element zoning profiles are labeled by Points A and B. Asymmetry of profiles may reflect either real variations or off center cuts through the garnets.
Figure 3.2: Rare earth element zoning in samples 350B and 350F. These traverses are not through the same grains as the traverses portrayed in Fig. 3.1. These profiles do not traverse the entire grain.
Figure 3.3: Log Mn/El vs. log Mn plot. Slopes on this plot are proportional to D. A vertical upwards vector would be expected for an element with a bulk partition coefficient approaching infinity, a left-directed horizontal vector would be expected for an element with the same bulk partition coefficient as Mn, a left-directed vector at 45° to the horizontal would be expected for a bulk partition coefficient approaching zero. A vector directed leftward between the 45° from horizontal vector and a down-pointing vertical vector suggests disequilibrium partitioning/open system behavior (DEOS). Circles are for 350B; triangles are for 350F. High Mn in cores. Mn must be a compatible element and hence decrease from core to rim.
Figure 3.4: $C_s / C_o$ (initial bulk concentration in sample) versus reduced radius as calculated using expression 6. Generic compatible element is assigned a bulk D of five and generic incompatible element is assigned a bulk D of 0.2.
Figure 3.5: Log of dimensionless numbers versus temperature. Solid lines are growth rates appropriate to contact environments (see text). Dotted lines are growth rates appropriate to regional environments (calculated from P-T-t path of Selverstone et al., 1984). Diagonal lines appropriate for interface partitioning (I) (E's calculated from pre-exponential and activation energies of Cygan and Lasaga, 1985), flat lines for matrix (grain boundary (GB)) diffusion limited processes (grain boundary diffusion coefficient of Brady, 1983). C1 and C2 are contact metamorphic growth rates, R is for a regional metamorphic growth rate. Other details in text.
Figure 3.6: Schematic depiction of the types of solute segregation possible at a two-phase boundary. Nature of segregation depends on electrostatic potential and surface interface fields. After Tiller (1986).
Chapter IV: Trace element zoning in garnets from diverse metamorphic environments
4.1 Introduction

Trace element geochemistry has provided important insights into igneous petrogenesis (Gast, 1968; Kay and Gast, 1973; Frey et al., 1978), but has not yet been fully appreciated in metamorphic petrology. Trace element investigations have contributed significantly to geochemists' understanding of granulite facies petrogenesis (Pride, Muecke and Sarkar, 1979; Weaver and Tarney, 1980; Smalley et al., 1983), because systematic differences between element abundances are demonstrable between granulites and lower grade rocks. However, amphibolite facies rocks, in which zoned minerals are ubiquitous and element mobility is not well-understood, have not been successfully investigated using trace element geochemistry.

Whole-rock trace element investigations of amphibolite facies metapelites and amphibolites have examined the mobility of trace elements during metamorphism (Shaw, 1954; Schwarcz, 1966; Konoj et al., 1977; Muecke et al., 1979), used trace element signatures to correlate rock units in complexly deformed terrains (Holland and Winchester, 1983), and attempted to fingerprint the tectonic settings of the basaltic protoliths of amphibolites (Aleinekoff, 1977; Winchester and Floyd, 1984). The studies of trace element mobility are equivocal due to the unquantifiable heterogeneity of
the parental sedimentary or volcanic rocks. In addition, the latter two types of studies cannot adequately address the question of trace element mobility during metamorphism.

Mineral-mineral trace element partition studies of amphibolite grade metamorphic minerals were performed during the 1950's and 1960's (DeVore, 1955; Turekian and Phinney, 1962; Albee, 1965; Hietanen, 1969), and a few recent studies have appeared in the Russian literature (Krylova et al., 1970; Makrygina et al., 1980; Lebedev and Nagaytsev, 1982). Almost universally, these studies do not show mineral-mineral partition coefficients that change systematically with increased metamorphic grade. The recognition of the significant trace element zoning in metamorphic garnets analyzed with the ion microprobe (e.g. Hickmott et al., 1987) provides one explanation for non-systematic element partitioning between amphibolite facies minerals.

Major element zoning determined with the electron microprobe can be used to constrain the geologic histories of metamorphic terrains (Tracy, 1982; Loomis, 1983; Spear and Selverstone, 1983). The in-situ analytic capability of the ion microprobe permits the relative variability (zoning) of trace elements in porphyroblasts to be measured. The coupling of trace element variability studies with studies of major elements may help constrain
processes during garnet growth (see other chapters of this thesis).

The trace element zoning in six garnetiferous rocks from well-understood metamorphic terrains described in the literature is delineated in this chapter. The samples range from the upper-greenschist to lower-granulite facies and experienced a diversity of metamorphic histories. Samples include: polymetamorphic garnets (Karabinos, 1984, 1985; Rumble and Finnerty, 1974), garnets that experienced an assemblage change during metamorphism (Karabinos, 1984, 1985; Selverstone and Munoz, 1987), a garnet that re-equilibrated during isobaric cooling (Spear and Chamberlain, 1986; Spear et al., in prep), a garnet that grew across two distinct fluid composition regimes (Burton, 1986), and an eclogitic garnet (Cloos, 1986; Kinzler et al., in prep). In conjunction with results for garnets grown over a well-constrained clockwise P-T path (chapter II), and a garnet from a contact metamorphic environment (chapter III) these results provide a framework for interpreting trace element zoning in poorly-understood garnets (chapter V).

This study does not delve into the petrogenesis of any of the samples in great detail. The goal of the chapter is to provide a catalog of the types of trace element behavior to be expected in different metamorphic
environments. For each garnet are included: 1) a brief description of the geologic setting of the rock containing the garnet, 2) the trace element zoning in the garnet, and 3) ruminations on the significance of the trace element zoning.

Regional geologic settings, phase relations, mineral chemistries and petrogenetic interpretations of the studied samples are detailed in references listed in Table 4.1. For each garnet, petrologic and tectonic information directly relevant to interpretation of the trace element zoning is recapitulated. These sections are necessarily partisan—only highlights of the studies are provided.

Trace element zoning in a single traverse from each sample is provided in Figures 4.1 through 4.6. Sketches and electron microprobe zoning profiles are included in the original literature descriptions of many of these garnets. Zoning profiles, sketches and photos of the garnets from the cited papers are referenced directly in this chapter.

4.2 Analytical

Analyses were made using a Cameca IMS-4F ion microprobe. Descriptions of analytical conditions and procedures are in Appendix I. Zoning profiles are presented in (Element/Si) ion intensities, which are linearly related to concentration.
4.3 Western Tauern Window, Austria - PJ-9A

4.3.1 Western Tauern Window, Austria - geologic background

PJ-9A, a calcareous schist from the Furtschaglschiefer series of the western Tauern window, Austria (Selverstone and Munoz, 1987), is characterized by interstratified graphitic and non-graphitic layers. The graphite-free layers contain a hornblende + white mica bearing assemblage whereas the graphite-rich layers contain biotite + plagioclase + chlorite + epidote pseudomorphs after hornblende (Selverstone and Munoz, 1987). The stability of hornblende in the sample is a function of fluid composition. Graphite-rich layers are more CO₂-rich and graphite-free layers are more water-rich (Selverstone and Munoz, 1987). The garnet growth reactions in the two layers differed due to the differences in fluid composition between layers. Garnets (such as that examined in this study) from layers containing amphibole pseudomorphs exhibit abrupt discontinuities in Ca and Fe zoning profiles whereas garnets from pseudomorph-free layers are smoothly and continuously zoned (Selverstone and Munoz, 1987, Fig. 3).

4.3.2 PJ-9A - zoning profiles

The garnet depicted by Selverstone and Munoz (1987) in their Figure 2F was analyzed in this study. There is a
distinct break (the chemical unconformity, CU) in the major element zoning profile (Figure 4.1, and see also Selverstone and Munoz (1987), Figure 3B). $X_{\text{Almandine}}$ rises, and $X_{\text{Grossular}}$ drops at this point. Overall, the garnet is characterized by rimward increases in $X_{\text{Pyrope}}$ and $X_{\text{Almandine}}$, and by decreases in $X_{\text{Grossular}}$ and $X_{\text{Spessartine}}$. Mn also turns up slightly at the garnet rim.

Trace element zoning reveals a more complicated metamorphic history. Highlights of the trace element zoning are: the Ti, Na, Sc, Y, and Zr breaks at the chemical unconformity defined by the major elements, the low Y abundance in the garnet core, the overall decreasing Ti zoning profiles, and, perhaps of greatest interest, the Li, Na, Y and Zr humps coreward of the CU.

4.3.3 Regional correlations of garnet growth events

Garnets in PJ-9A exhibit humps in the elements Li, Na, Y, and Zr. Garnets from FH-1M (chapter II) from the an interbedded unit of the Lower Schieferhülle display humps in Na, Sc, V and Y. These two calcareous rocks have similar assemblages, but differ in several ways: 1) there are hornblende pseudomorphs in graphitic layers in PJ-9A as opposed to stable hornblende in FH-1M, 2) abundant graphite and phengite are present in PJ-9A, and 3) stable carbonate, staurolite, and kyanite are all found in FH-1M. The similarities between humps in the two rocks may
allow accurate correlation of metamorphism in two samples of different bulk composition. As detailed in chapter II, the humps are probably due to open-system behavior, either external or internal metasomatism, probably initiated by a P-T reversal. The primary difference between the two sets of humps is the lack of a Sc and V hump in PJ-9A. It is not clear how the difference in mineralogy produces a Sc and V hump in FH-1M, but not in PJ-9A. Based on the observation of Sc and V increases in garnet accompanying amphibole breakdown (see next section), a possible explanation is that amphibole partially broke down during the P-T reversal in FH-1M, but remained stable in PJ-9A.

4.3.4 Ca phase breakdown - amphibole in PJ-9A

Because of the strong correlation between garnets displaying chemical unconformities and layers containing hornblende pseudomorphs, the trace element zoning in PJ-9A between the chemical unconformity and the garnet rim may be interpreted in terms of amphibole breakdown and concomitant growth of biotite + plagioclase + epidote + chlorite + garnet. Na, Y, and Zr all rise in abundance at the CU. Between the CU and the rim the sense of zoning of Sc and V each reverse, and Cr, Y and Zr each maintain higher abundance levels than in the early stage of garnet growth. The increasing Sc and V profiles appear to be due to breakdown of zoned, refractory hornblende +/-
other minerals, leading to an enrichment of trace element in the effective bulk composition in equilibrium with garnet (Chapter II). Hornblende cores in FH-1M are enriched in Y and Sc (Chapter II).

4.4 Sulitjelma Area, Norway - R229

4.4.1 Sulitjelma Area, Norway - geologic setting

Sample R229, a metapelite from the Sulitjelma area, western Norway, is segregated into graphite-rich and graphite-free layers (Burton, 1986). The two layers each contain the same silicate mineral assemblage: garnet + biotite + muscovite + quartz + plagioclase. Burton (1986) noted that quartz rods were epitaxially aligned with [110] planes in garnet solely in graphite-bearing layers of the metapelites. This unusual textural feature was ascribed to the differential solubility of quartz in CO$_2$- and H$_2$O-rich fluids (Walther and Orville, 1983). The lower solubility of quartz in CO$_2$-rich fluids in the graphitic layers prevented SiO$_2$ from escaping from the rapidly-growing garnet. This scenario assumes that an intergranular fluid film controls cation transport in metamorphic systems (Walther and Orville, 1983). The morphologies of garnets from graphitic and non-graphitic layers also differ. Garnets in the graphitic layers are euhedral and devoid of inclusions other than the aforementioned quartz-rods, whereas garnets in the non-
graphitic layers are anhedral and rich in inclusions (Burton, 1986).

4.4.2 R229 - garnet zoning

Garnet G3-R229 (Burton, 1986, Figure 2) is a composite garnet grain - two garnet nuclei coalesced in a graphite-rich layer, and a portion of the garnet extended into a graphite-poor layer during garnet growth. Manganese descends from high values in the cores of the graphite-rich area ($X_{\text{spessartine}} \approx 0.07$) to virtually nil in the graphite-free zone. Ca zoning is complex. Values in the graphitic core are $X_{\text{grossular}} \approx 0.08$, rim values then range up to $X_{\text{grossular}} \approx 0.11$ with a grossular-poor trough separating the two regions. The graphite-free region exhibits closely-spaced Ca isopleths, and ranges from $X_{\text{grossular}}$ of 0.06 in its inner regions to $X_{\text{grossular}} \approx 0.25$ on the rim of the graphite-free zone. Note that the full complexity of the Ca zoning is not evident in Figure 4.2 because the ion probe traverse barely penetrated the graphite-free zone. $X_{\text{almandine}}$ in the graphite-rich zone ranges from 0.77 at the core up to > 0.81 and then down to $\approx 0.78$ at the rim. Fe-zoning is more complex in the graphite-free region, ranging from a high of 0.81 in its inner portions to a low of 0.63 in the outermost rim. Pyrope in graphitic zones rises from 0.05 to 0.10 then drops to $\approx 0.06$ in a narrow near-rim region, whereas the graphite-free zone is zoned up to
X_{pyrope} > 0.11 then down to 0.05 in the narrow near-rim zone (Burton, 1986). Note that the near rim zones were not penetrated by the ion probe traverse.

The outstanding features of the trace element zoning (Figure 4.2) are: 1) the difference in Ti/Si between the near-rims of the graphite-rich and graphite-poor zones of the garnet, 2) the lower Na content in the graphite-free zone and 3) the asymmetry of the Y profile.

4.4.3 Fluid composition effects

R229 may provide an opportunity to assess the differences in trace element partitioning behavior in H_2O-rich and CO_2-rich fluids in a single sample, provided bulk-compositional effects are well-understood. Assumptions in such an assessment include: 1) that garnet rims ceased growing at the same P-T conditions, 2) that the bulk compositions of the two layers were similar, 3) that transport within each layer was rapid enough that equilibrium was maintained between garnet rims and matrices, and 4) that no fractionation of trace elements into refractory minerals besides garnet has occurred. Assumption 2 may be flawed, thus no interpretation of non-buffered trace elements is attempted. Assumption 1 is reasonable, because calculated P-T conditions for rims of garnets in graphite-rich and graphite-poor layers are similar (Burton, 1986), although the lack of ion probe analyses in the nearest-rim zone is problematic. Thus the
buffered trace elements (Ti and Na), whose activity in a metamorphic fluid is not strongly controlled by bulk composition, may potentially be interpreted in terms of fluid behavior.

The higher Ti abundance in the graphite-free layer than anywhere in the graphite-rich layer suggests that Ti solubility in garnets is higher in H₂O-rich fluids than CO₂-rich fluids.

Further interpretation of this fascinating sample will require: 1) additional traverses in garnets to resolve the closely spaced compositional isopleths in the graphite-free zone and to examine differences in trace element zoning profiles as a function of distance from the graphite-rich/graphite-free contact, 2) accurate electron probe analyses of mineral compositions in the two layers (Burton, 1986, does not provide a table of mineral analyses), and 3) determination of trace element abundances in other minerals in order to formulate trace element distribution coefficients in the two layers and thereby investigate differences in partitioning as a function of fluid composition.

4.5 Jamaica, Vermont - 120

4.5.1 Jamaica, Vermont - geologic setting

The Jamaica, Vermont, sample is polymetamorphic (Karabinos, 1984). Karabinos described garnet inclusion relations, major element zoning and other petrographic
observations that implied that sample 120, and other
aluminous pelites from the Jamaica area, underwent an
early garnet growth episode by the reaction: (1) quartz +
chlorite + chloritoid = garnet + H₂O, followed by
retrograde resorption of garnet through the reaction: (2)
garnet + rutile + H₂O = ilmenite + chlorite + quartz, and
finally a second episode of garnet growth by reaction
(1). Ilmenite and rutile were stable during stage 1
growth. Ilmenite alone accompanied the second growth
episode.

4.5.2 120 - garnet zoning

A sketch of sample 120 is shown by Karabinos (1984)
in his Figure 3. Major element zoning in this garnet is
provided by Karabinos (1984) in his Figure 6. The
outstanding feature of the major element zoning is its
tripartite nature (Figure 4.3; Karabinos, 1984, Figure
6). It is divided into: (1) an inner-zone (core to point
CU) of rising Mg/Fe (≈0.08 to 0.10), declining MnO (3 to
1 wt %), and high and slightly declining (6.5 to 5.5 wt
%) CaO, (2) an intermediate zone (CU to TU) of
anomalously low Mg/Fe (0.08), high MnO (up to 4 wt. %),
and low CaO (< 3 wt%), and (3) an outer zone of sharply
rising Mg/Fe (up to >0.12), dropping MnO, and constant,
or slightly declining CaO (4-5 wt %). The major element
zoning and inclusion relations are consistent with the polymetamorphic history postulated by Karabinos.

The trace element zoning exhibits discontinuities and inflections at the same locations as the major element zoning. Ti shows a decrease by a factor of three across the chemical unconformity (CU). It then rises slightly while maintaining a low-abundance level out towards the rim. Sc also displays a pronounced drop at the chemical unconformity. Cr, and especially Y, jump abruptly at the CU and decline rapidly toward the TU, in a fashion similar to manganese. Na, V, and Co exhibit minor inflections at the chemical unconformity, Na declines gradually to a low-level at the rim.

4.5.3 Processes during retrogradation - Jamaica area

Karabinos (1984) was forced to call on diffusive re-incorporation of Mn into garnet during retrogradation to explain the Mn hump between the CU and the TU (Figure 9 of Karabinos, 1984). He also calculated that the diffusion coefficient required to produce the Mn excess in the region between the TU and the CU was over two orders of magnitude larger than the empirical Fe-Mg interdiffusion coefficient determined by Lasaga and co-workers (Lasaga et al., 1977). He stated that grain-boundary diffusion along inclusion boundaries "increased the penetration distance in garnet during retrogressive alteration". The decoupling of the garnet-compatible
element Sc from other compatible elements Y and Mn (Appendix II) suggest that Karabinos' model is incorrect in detail. The sharpness of the Y-Sc-Mn break at the Cu also precludes a resorption/diffusive re-equilibration origin for the Mn-Sc hump. The simplest explanation for the zoning profiles is to postulate garnet growth in three distinct episodes, at different temperatures, pressures and/or assemblages, rather than two. The relative pressures of metamorphism of the event are addressed qualitatively in a later section of this chapter.

4.6 Bradford, Vermont - 70-308

4.6.1 Bradford, Vermont - geologic setting

Sample 70-308 is from a polymetamorphic environment (Rumble and Finnerty, 1974). Early Ordovician (?) contact metamorphic almandine-rich garnet is overgrown by minute amounts of Devonian spessartine-grossular-rich garnet. The early garnet grade contact metamorphic assemblage almandine + andesine + biotite(I) + white mica (I) + ilmenite + K-spar + apatite + quartz was remetamorphosed to the biotite grade assemblage spessartine + albite + epidote + white mica (II) + biotite (II) + sphene + K-spar + apatite + quartz (Rumble and Finnerty, 1974).

4.6.2 70-308 - garnet zoning
Rumble and Finnerty (1974, Figure 2) provide a sketch of a garnet from 70-308 showing euhedral almandine-rich garnet overgrown by grossularite/spessartine formed during biotite-grade remetamorphism. Their Figure 3 and Figure 4.4 depict the abrupt major element break found in the garnet. From euhedral core to anhedral overgrowth, iron and magnesium decrease from over 37 wt % to less than 16 wt % and 1.8 wt % to < 0.1 wt. % respectively over a distance of less than 10 microns (point CB, Figure 4.4). Manganese and calcium rise concomitantly (2.0 wt % to > 12.0 wt %) for the former and (<2 wt % to over 14 wt % for the latter) (Rumble and Finnerty, 1974).

Trace element zoning across the polymetamorphic discontinuity (CB) is equally dramatic (Figure 4.4). From the euhedral, almandine-rich core, to the anhedral, spessartine-rich rim Sc, V, and Y all drop precipitously (by over a factor of 200 for Y), and Na and Ti rise abruptly.

4.6.3 Processes during polymetamorphism - 70-308

The major and trace element effects observed at point CB are due to: 1) the change in P-T conditions between early and late metamorphism, and 2) the change in assemblage between the two garnet growth events.
Major and buffered trace element (Na and Ti) differences between the two zones must reflect the differences in P-T conditions between the two garnet growth episodes. The early episode of growth was garnet-grade (moderate-T), the latter was at biotite-grade (low-T) - relative pressures of metamorphism are discussed in section 4.9.

The trace element behavior may reflect P-T effects on bulk distribution coefficients, but also segregation or release of trace elements from refractory phases during the interval separating the two episodes of garnet growth. The most important mineralogic changes for trace elements is probably the growth of sphene and/or epidote. Both of these minerals strongly partitions many trace elements (such as REE) relative to the other minerals in the rocks (except apatite) (Gromet and Silver, 1983). The factor of 200 drop in Y may represent segregation of Y into sphene or epidote during stage two metamorphism.

4.7 Franciscan Fm, northern California

4.7.1 Franciscan Fm, California - geologic setting

Sample 60-79, an eclogite from the Franciscan Fm, Ca, is not described in the literature. The matrix assemblage contains garnet + omphacite + sphene + rutile. Amphibole and clinzoisite are present as inclusions in garnet.
Detailed descriptions of phase-relations, geologic setting, and the tectonic significance of Franciscan eclogites are provided by Bailey et al. (1964), Ernst et al. (1970), Brown and Bradshaw (1979), and Cloos (1986).

4.7.2 Franciscan eclogite, CA. - sample 60-79

The Franciscan eclogite sample (60-79) is zoned toward higher Mg/(Mg+Fe) at its rims (from 0.09 to 0.15) and towards lower Mn (X_{Spess} > 0.05 to <0.01), except in the outermost point (Figure 4.5). The Ca-content remains essentially constant at X_{Gross} \approx 0.27 (unpub. microprobe data, D. Hickmott).

Titanium decreases from a high value (Ti/Si \approx 0.008) in garnet cores to a low-value of \approx 0.003 midway through the profile. Ti/Si then rises slightly before dropping to a low rim-value of \approx 0.003. The sodium profile parallels the Ti zoning, whereas Cr is grossly antithetic. The majority of the trace elements - Cr, Sc, V and Y, - display irregular zoning profiles. Y appears to increase in abundance near the rim of the garnet (Figure 4.5).

4.8 Bellows Falls, N.H - BF-9E

4.8.1 Bellows Falls, N.H. - geologic background

BF-9E, a coarse-grained pelite from the Bellows Falls area, N.H., cooled rapidly from peak metamorphic conditions (T > 700°C, P \approx 6 kbar) to temperatures around 500°C at 5 kbar (Spear and Chamberlain, 1986; Spear, in
press; Spear et al., in prep). The peak-grade assemblage is garnet-biotite-sillimanite-K-spar-quartz-plagioclase +/- accessory minerals, and the re-equilibrated matrix assemblage is garnet-biotite-muscovite-quartz-plagioclase +/- sillimanite +/- staurolite +/- chlorite +/- accessories. Garnets exhibit interdiffusion halos around biotite inclusions and minor near-rim resorption and diffusive re-equilibration that were generated during cooling.

The near-rim zoning profile is interpreted by Spear and co-workers (Hickmott et al., 1984; Spear and Chamberlain, 1986; Spear, in press; Spear et al., in prep) as due to retrograde diffusion, first in the Al₂O₃-FeO-MgO (AFM) (Thompson, 1957) assemblage garnet-biotite-sillimanite-K-spar and later in the AFM assemblage garnet-biotite-muscovite +/- sillimanite +/- staurolite +/- chlorite.

Finite difference modeling of the diffusion halos around biotites demonstrates that the cooling rate during retrogradation was rapid (25-100°C/my.) (Spear and Chamberlain, 1986; Spear et al., in prep.).

4.8.2 BF-9E – zoning profiles

A sketch of a portion of sample BF-9G (chemically similar to BF-9E) is shown in Spear and Chamberlain (1986; Figure 4).
In BF-9E, the Fe/(Mg+Fe) ratio increases from a homogeneous core value of about (0.86) to a rim value of (0.89). X_{Grossular} increases and X_{Spessartine} displays an unusual pattern, rising then declining at the garnet rim (D. Hickmott unpub. data).

Y and Na increase from the homogeneous garnet middle to the rim; Ti, Cr, and V all decrease from core to rim. Sc displays a humped profile rising to Sc/Si of 0.004 about 40 microns from the rim, then dropping to ≈ 0.003 at the rim. (Figure 4.6)

4.8.3 Temperature dependence - non-buffered trace elements

Deconvoluting the temperature, pressure, and chemical dependences of the incorporation of trace elements into garnet is a problematic endeavor.

Sample BF-9E provides an opportunity to estimate the temperature dependence of the trace element variations because its thermal history has been well studied (Spear and Chamberlain, 1986; Spear et al., in prep.). The garnet rim equilibrated at both high-temperature (> 700°C) and low-temperature (∼ 500°C). Thus, by making several assumptions, the relative direction of change in trace element solubility in garnet with temperature in the assemblage garnet-biotite-sillimanite-quartz-plagioclase +/- muscovite +/- K-spar +/- staurolite can be inferred. The initial assumptions are: 1) matrix diffusion was
sufficiently rapid that each element was equilibrated in the matrix during re-equilibration 2) each element closed with respect to diffusion at the same time in the rim of garnet, 3) open system behavior, either external metasomatism or internal metasomatism (see chapter II), did not occur, 4) garnet resorption did not occur during reequilibration; and 5) the change in assemblage did not seriously affect the partitioning.

The temperature dependence of Na and Ti (the buffered trace elements) incorporation into garnet are considered later in this chapter. V and Cr each diminish in abundance from the relatively homogeneous garnet middle to the rim and thus appear to have a negative temperature dependence. Y rises in abundance with decreasing grade and appears to have a positive temperature dependence. Sc shows a hump; it mimics the Mn profile, but at a shorter length scale. The Mn zoning is rationalized in terms of a change in slope in Mn isopleths across the sillimanite+K-spar+H₂O = muscovite+quartz univariant reaction curve (Spear, in press).

Given the petrographic and chemical observations, it appears that some of the above assumptions are violated. Matrix transport was not rapid enough that sillimanite could entirely break down. Based on the presence of late-stage muscovite and chlorite, water-rich fluids have
clearly infiltrated the sample. An infinite reservoir model may be inappropriate for compatible elements in garnets (Y and Sc) because the garnet is locally resorbed (although not particularly strongly in the traverse portrayed). Finally, the assemblage change reverses the direction of partitioning for both Mn and Sc in garnet. Nonetheless, the results presented above may provide rough constraints on the temperature dependence of trace elements partitioning into garnets in a common metamorphic assemblage.

The core-rim trace element variations in this garnet, cooled from granulite to amphibolite facies, parallel changes in Y (≈700 to ≈1800 average ppm from granulite to amphibolite), Ti (≈240 to ≈130 ppm), and Cr (≈ 50 to ≈ 15 ppm) exhibited in a suite of garnets from granulite to upper amphibolite facies rocks in the Adirondacks (Engel and Engel, 1960). This observation suggests that the temperature dependences inferred above are reasonable. Engel and Engel's garnets were presumably fairly homogeneous (see also Bohlen et al., 1985), as temperatures during metamorphism of the Adirondack granulites were higher than 650°C. Above this temperature most metamorphic garnets are homogeneous, except at their outermost rims (Tracy, 1982).
4.8.4 Diffusion length-scales – trace elements

The relative penetration depths of the trace elements in the diffusively re-equilibrated rims of BF-9E could be used to estimate relative values of diffusion coefficients during cooling if the retrogradation had occurred in a closed-system with a constant assemblage. It is somewhat misleading to attempt to extract relative diffusion coefficients in these samples because the assemblage changed during retrogradation. Moreover, fluids infiltrated the sample during cooling, and minor garnet resorption has occurred. However, given these caveats, the trace element diffusion coefficients integrated over the cooling path roughly follow the order $D(\text{Cr}) \approx D(\text{Y}) \approx D(\text{Cr}) < D(\text{Ti}) \approx D(\text{V}) < D(\text{Na}) \approx D(\text{Sc}) < D(\text{Mn})$.

4.9 P-T variability – buffered trace elements

Titanium and sodium occur in garnets at trace levels. They are also major structural constituents of minerals in the vast majority of metamorphic rocks. Because the activities of sodium and titanium in metamorphic fluids, and hence in metamorphic garnet, are buffered by silicate-silicate or silicate-oxide equilibria, the titanium and sodium contents of garnet may be useful P-T indicators (Ghent and Stout, 1984). In mantle assemblages Sobolev and Lavret'ev (1971) and
Ringwood and Major (1971) demonstrated that Na increases in garnet with increased pressure, whereas Green and Sobolev (1978) showed that the solubility of Ti in garnet rises with temperature in ilmenite-bearing assemblages. Engel and Engel (1960) demonstrated that the Ti-content of garnet in Ti-oxide bearing assemblages increased going from mid-amphibolite to granulite facies. Ghent and Stout (1984) showed that Ti in garnet from ilmenite bearing rocks ranged from 'undetectable' to 'detectable' from low- to high- grades in an electron microprobe study.

The three primary Ti-bearing phases in garnet-bearing pelites, calc-pelites and amphibolites are sphene, rutile, and ilmenite. The titanium activity in a metamorphic fluid (if it exists) will be buffered by reactions such as:

\[ \text{TiO}_2 + 4\text{H}^+ = \text{Ti}^{4+} + 2\text{H}_2\text{O} \quad \text{(rutile bearing)} \]

\[ 3\text{FeTiO}_3 + \text{Al}_2\text{Si}_3\text{O}_5 + 2\text{SiO}_2 + 12\text{H}^+ = 3\text{Ti}^{4+} + \]

\[ \text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 6\text{H}_2\text{O} \quad \text{(ilmenite bearing)} \]

\[ 3\text{CaTiSiO}_5 + \text{Al}_2\text{Si}_5\text{O}_5 + 12\text{H}^+ = 3\text{Ti}^{4+} + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \]

\[ \text{SiO}_2 + 6\text{H}_2\text{O} \quad \text{(sphene bearing)} \]

The Ti activity in a metamorphic fluid will depend on T, P, and fluid composition (\(\mu(\text{H}_2\text{O})\), pH, fO₂). An additional complication is the unknown nature of Ti substitution into metamorphic garnets. Fe and Ti site-occupancies in garnet are controversial (Huggins et al., 1977; Schwartz et al., 1980; Amthauer, 1986). There is
spectroscopic evidence that Ti$^{+4}$ can be found in
tetrahedral sites in garnets, and that both Ti$^{+3}$ and Ti$^{+4}$
are found in octahedral coordination (Huggins et al., 1977; Schwartz et al., 1980).

Figure 4.7 is a P-T diagram showing facies
boundaries (from Ernst, 1976) on which the Ti/Si values
of the rims and select cores of the garnets investigated
in this study are plotted at their estimated P-T
conditions. Because some samples contain assemblages
unsuitable for geothermometry and geobarometry (125, 70-
308, 60-79) they can only be assigned to a facies rather
than to explicit P-T conditions.

To first order there is a rough correlation between
high values of Ti/Si (0.003-0.006) in garnets co-existing
with Ti-oxides, and high pressure (P > 8 kbar) (Recall
that the pressures for the garnets merely assigned to
facies series are unconstrained). However, the Ti-
saturating phase in the high-pressure assemblages is
rutile rather than ilmenite. The activity of TiO$_2$ is
higher in these assemblages than in low-P environments.
The isobarically cooled sample, BF-9E, suggests a
negative temperature dependence of Ti solubility in
garnet in Ti-saturated assemblages, although this
correlation is not fully supported by consideration of
all of the data.
The most anomalous garnet is the overgrowth on 70-308, a sphene-bearing greenschist facies assemblage. Its Ti/Si value (≈ 0.006) is higher than values obtained in presumably high-pressure garnets (including the eclogite) in rutile-saturated assemblages. This anomalous value could be due to: 1) crystal-chemical coupling between Ca substitution and Ti substitution (Crawford, 1974); 2) disequilibrium incorporation of Ti into the overgrowth (see Chapter III); or 3) metamorphism of the second stage garnet in 70-308 at high-pressure in the greenschist facies.

Crawford (1974) suggested a crystal chemical coupling between Ti substitution into garnet and Ca substitution. Grossular has a larger unit-cell than almandine/pyrope (Novack and Gibbs, 1971), which may facilitate Ti substitution. Dowty (1971) noted that high Ti garnets are frequently Ca-rich. Typical garnetiferous pelites, in which garnet is the most calcareous major-phase other than plagioclase, show an increase in Ca content with increased pressure (Ghent, 1976). In order to deconvolute the effects of Ca-Ti coupling, pressure and temperature, suites of garnets from interbedded units of differing bulk composition should be examined. The apparent Ti variability with pressure and temperature cannot be effectively quantified at this time. However, the decoupling of Ti and Ca at the rim of BF-9E suggests
that crystal chemistry does not dominate the incorporation of Ti into garnets.

Disequilibrium incorporation of Ti into garnet overgrowths during regional metamorphism is unlikely except at rapid growth rates (see chapter III). The results presented in chapter III suggest that in 70-308 high Ti as a result of disequilibrium partitioning would be expected in the early contact metamorphic almandine-rich core of garnet, rather than in the spessartine-rich overgrowths.

If crystal chemical effects and disequilibrium partitioning can be ruled out, then garnet growth in 70-308 probably occurred at higher pressure during second stage, biotite-zone growth than in the first stage garnet-zone growth.

Sodium activity in metamorphic fluids is buffered by equilibria such as: 2NaAlSi3O8 + 2H+ = 2Na+ + Al2SiO5 + 5SiO2 + H2O. The coupled-substitution mechanism of Na into garnets is enigmatic, although it is clear that Na is incorporated into the large, cubic, site in mantle garnets (Meagher, 1982). Na also shows a roughly decreasing solubility into garnet at lower pressures, and higher temperatures (Figure 4.8). This observation is potentially significant, but it is subject to larger vagaries than the titanium-P-T correlation. Two samples - 60-79 and 150 - do not contain plagioclase, with Na found
instead in omphacite and paragonite, respectively. Additionally, plagioclase compositions range from virtually pure albite (70-308) to andesine ($\approx$ An 35 in BF-9E).

4.9.1 Relative P's of metamorphism - Jamaica area

Karabinos' garnet experienced at least two (and probably three) prograde metamorphic events of approximately the same temperature. Each episode developed a similar AFM assemblage of garnet-chlorite-chloritoid. The relative pressures of metamorphism of the two events are unknown.

Figures 4.7 and 4.8 suggest that $P_1$ was at higher pressure than $P_2$. Both Na and Ti are much lower in abundance in the second growth zone than in the first. The presence of ilmenite and rutile as inclusions in the garnet core, and the ubiquity of ilmenite alone in the matrix are also indicative of early high-pressure metamorphism (Bohlen and Liotta, 1986). Early high-pressure metamorphism in Cambro-Ordovician units far to the north of the Jamaica area is documented by Laird and Albee (1981).

4.10 Conclusions

The trace element signatures in garnet zoning profiles of a number of important metamorphic processes have been investigated. Trace element zoning is complementary to major element zoning. Trace element
variability occurs at the same positions in garnet zoning profiles as does major element zoning, and can provide insight into the physico-chemical processes operating during garnet growth of zoned amphibolite facies garnets.

The zoning of buffered trace elements (Ti and Na) in garnets shows promise as a record of P-T conditions during garnet growth, provided disequilibrium and crystal-chemical effects are understood. An experimental study of Ti solubility into garnets is desirable.

Large trace elements such as Y are strongly partitioned into Ca-rich metamorphic phases such as amphibole. Zoning of these elements helps to fingerprint the nature of metamorphic reactions during garnet growth.

This preliminary study of trace element zoning in metamorphic garnets suggests that this technique may be a useful addition to the investigative arsenal of the metamorphic petrologist.
Table 4.1: Geologic and petrologic relations in rocks containing studied garnets

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>Reference</th>
<th>Assemblage</th>
<th>Grade</th>
<th>P-rim</th>
<th>T-rim</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PJ-9A</td>
<td>Selverstone &amp; Munoz, 1987</td>
<td>gar-ch-mu-qtz-ep-bi-pl-il-ru</td>
<td>kyanite</td>
<td>6.5 kbar</td>
<td>520° C</td>
</tr>
<tr>
<td>2</td>
<td>R229</td>
<td>Burton, 1986</td>
<td>gar-bi-qtz-pl-mu</td>
<td>kyanite</td>
<td>8</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
<td>Karabinos 1984, 1985</td>
<td>gar-ch-ctd-mu-par-qtz epi-ilm (rut)</td>
<td>garnet</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>4</td>
<td>70-308</td>
<td>Rumble &amp; Finnerty, 1974</td>
<td>gar-bi-mu-pl-mic-qtz-epi-sph-(ilm)</td>
<td>biotite</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>5</td>
<td>60-79</td>
<td>Cloos, 1986</td>
<td>gar-om-sph-rut (amp)</td>
<td>------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>6</td>
<td>BF-9E</td>
<td>Spear et. al. (in prep.)</td>
<td>gar-bi-mu-qtz-pl+ch +si+st+il (ksp)</td>
<td>garnet</td>
<td>5</td>
<td>500</td>
</tr>
</tbody>
</table>

Mineral abbreviations: garnet = gar, biotite = bi, chloritoid = ctd, chlorite = ch, staurolite = sta, kyanite = ky, sillimanite = si, muscovite =mu, paragonite = par, plagioclase = pl, epi = epidote, sph = sphene, omphacite =om, rutile =rut, ilmenite = ilm. Minerals in parentheses occur only as inclusions.
Figure 4.1: Element zoning in sample PJ-9A. Errors based on counting statistics are generally smaller than the symbol size. CU (the chemical unconformity) represents a break separating a region in which garnet existed with stable amphibole from a near rim region in which amphibole was breaking down.
Figure 4.2: Element zoning in R229 Errors based on counting statistics are generally smaller than the symbol size. Left half of profile is within garnet in a graphite-rich layer, rightmost three points are within garnet from a graphite-free layer. Note asymmetry of some profiles (Sc, Y) and the two cores, as defined by peaks in Mn, Sc and Y abundance.
The diagram shows the concentrations of various elements (Li/Si, Na/Si, Sc/Si, Co/Si, Y/Si) plotted against a gradient from rim to core, with a distinction between graphite-rich and graphite-free regions. The concentration values are on a scale from 0.00002 to 0.00005.
Figure 4.3: Zoning profile in sample 120. Errors based on counting statistics are generally smaller than the symbol size. TU represents a textural unconformity across which sigmoidal inclusions in garnet show a distinct break. CU represents a chemical unconformity where abrupt changes in major and trace element abundance occur.
Figure 4.4: Element zoning in 70-308. Errors based on counting statistics generally smaller than the symbol size. Leftmost two points within grossularite/spessartine-rich overgrowth, rest within almandine-rich core. Note that this garnet is extremely rich in inclusions, so some points show inclusion overlaps.
Figure 4.5 Element zoning in eclogite 60-79. Errors based on counting statistics generally smaller than the symbol size.
Figure 4.6: Element zoning in sample BF-9E. Errors based on counting statistics are generally smaller than the size of the symbols.
Figure 4.7 P-T diagram depicting Ti/Si contents of garnets as a function of calculated P-T conditions and/or facies series. Metamorphic facies from Ernst, 1976.
Figure 4.8. P-T diagram depicting Na/Si contents of garnets as a function of calculated P-T conditions and/or facies series. Facies series boundaries from Ernst, 1976.
Chapter V: Major and trace element zoning in garnets from calcareous pelites in the NW Shelburne Falls quadrangle, MA: Garnet growth histories in retrograded rocks
5.1 INTRODUCTION

Primary goals of metamorphic petrologists are: determination of P-T paths of metamorphism (Thompson and England, 1984; Spear and Selverstone, 1983; Spear et al., 1984), incorporation of P-T paths into thermo-tectonic models of orogenesis (Selverstone, 1985; Spear and Rumble, 1986) and understanding the composition and movement of fluids during metamorphism (Eugster, 1980; Ferry, 1986). Fundamental information needed to investigate any of these problems rigorously is the reaction histories of samples from metamorphic terrains; these can be related to P-T-fluid paths either semi-quantitatively using petrogenetic grids, or quantitatively through thermodynamic or mass-balance calculations.

Examination of the zoning of metamorphic porphyroblasts (Hollister, 1969; Tracy et al., 1976; Holland and Richardson, 1979; Laird and Albee, 1981; Tracy, 1982; Spear and Selverstone, 1983; Selverstone et al., 1984, Loomis, 1985), and study of inclusion suites in porphyroblasts (Thompson et al., 1977, Spear and Rumble, 1986; St. Onge, 1987) are two effective means of examining the reaction history of a metamorphic sample prior to equilibration of porphyroblast rims with
surrounding matrix assemblages. Zoned porphyroblasts, particularly garnets, are crucibles that preserve a record of the structural (Rosenfeld, 1968; 1970), chemical (Tracy, 1982; Spear and Selverstone, 1983; Loomis, 1983) and isotopic environments early in a metamorphic terrain's history, prior to the attainment of peak metamorphic conditions. However, similar major element zoning profiles can develop in different metamorphic environments; major element zoning cannot be interpreted uniquely in terms of metamorphic processes.

It is necessary to develop additional techniques that clarify interpretations of major element zoning and hence the reaction histories during the growth of porphyroblast cores. A particularly difficult problem is recognizing the former co-existence of a mineral that is no longer present in the stable matrix assemblage with a porphyroblast core. Mineral inclusions and pseudomorphic textures provide clues about mineral assemblages that were stable prior to matrix equilibration; however, preservation of these textures is unreliable and many metamorphic samples do not contain porphyroblasts with extensive inclusion suites or pseudomorphic textures. Trace element zoning has been shown to be another potentially useful monitor of processes occurring during garnet porphyroblast growth (Chapter II, Chapter III, Chapter IV).
In order to investigate the utility of trace element zoning as a probe of reaction histories it is necessary to study element zoning in samples that reveal their early reaction histories through major element zoning, pseudomorphic textures and mineral inclusions in porphyroblasts. This study examines the geochemistry and petrology of retrograded calc-pelites from two restricted areas in western Massachusetts and uses phase relations, mineral inclusions in garnets, major element zoning in garnets and trace element zoning in garnets to investigate reaction histories for the samples. This region was chosen for study for four reasons: 1) rocks from the region contain abundant garnet porphyroblasts over a wide range of pelitic bulk compositions, 2) the calcareous bulk compositions of rocks from the region stabilize high-Ca, trace element enriched minerals such as clinozoisite and amphibole, 3) inclusion relations and pseudomorphic textures provide clues into the early reaction histories of the samples, and 4) the metamorphic grade is low enough that garnet zoning profiles are not smoothed by diffusion. Trace element zoning is shown to be a useful monitor of processes occurring during garnet growth, particularly operation of reactions involving refractory minerals (Hollister, 1969). Trace element zoning studies should be a useful tool for the metamorphic petrologist, providing a window into the
history of metamorphic terrains unavailable through traditional petrologic techniques.

5.2 GEOLOGIC SETTING

The study area is located in the northwest corner of the Shelburne Falls Quadrangle, Massachusetts. Emerson (1898), Balk (1946), Segerstrom (1956) and Hall (unpub. work) all mapped in the area. Simpson (1974) completed a detailed gravity study of the region and Griscomb and Bromery (1968) presented a magnetic anomaly map of the area. The sampled outcrops are located on the east flank of the Shelburne Falls dome, one of a series of 'gneiss domes' underlying the metasediments of the Connecticut Valley-Gaspe Synclinorium (CVS) (Doll et al., 1961; Zen et al., 1983) (Figure 5.1). The CVS lies to the west of the Mesozoic sedimentary basin of central Massachusetts and the Bronson Hill anticlinorium (Thompson et al., 1968), and to the east of the Berkshire anticlinorium (Ratcliffe and Harwood, 1975; Norton, 1975).

5.2.1 Units and unconformities

The metasedimentary strata within the study area include well-bedded quartzites, gritty pelites and minor calc-silicates of the Goshen Formation (Hatch, 1975), and less well-bedded calcareous pelites, punky-weathering calc-silicates and amphibolites of the Waits River
Formation (Figure 5.2). These overlie the Collinsville Formation within the Shelburne Falls Dome, which consists of highly deformed felsic gneisses and associated amphibolites. A thin layer of amphibolitic Standing Pond Volcanics lies stratigraphically above the Waits River Fm. The contact between the Goshen and Waits River Formations is gradational whereas that between the Shelburne Falls Dome and the Siluro-Devonian rocks is abrupt.

The depositional and intrusive ages of the Connecticut Valley sequence are controversial. The Shelburne Falls Dome gneisses are considered to be Ordovician (Naylor, 1975; Zen et al., 1983). The Goshen Formation is classed as Silurian (Llandoveryan) based on correlations with fossil-bearing units near Shaw Mtn. Vermont (Boucot and Thompson, 1963). However, Bothner and Finney (1986) describe late Ordovician graptolites (zone 12-14) from the Gile Mountain Formation, which is supposedly up-section from the Goshen Fm. Hatch (personal communication) reports Devonian plant fossils in an outcrop 1.5 km on strike from the graptolite locality. Until this controversy is resolved, the metasedimentary sequence is classed as Siluro-Devonian. All the depositional ages postulated for the CVS sediments post-date the Taconic orogeny, so interpretations of the
metamorphism in terms of a single orogeny, the Acadian, are probably justified.

5.2.2 Deformation history

The Siluro-Devonian rocks of the Shelburne Falls Dome area experienced at least three, and possibly four, episodes of penetrative deformation (F₁ of Osberg, 1975; F₂, F₃, and F₄ of Hatch, 1975). F₁ produced overturned isoclinal folds manifest as inverted graded beds in the noses of upright F₂ isoclinal folds (Osberg, 1975; Simpson, 1974; Pferd, 1981; Hudec; 1983). F₂ produced the dominant foliation in the region. It is characterized by upright isoclinal folds with NE trending folds axes. F₂ foliation dips less steeply near the Shelburne Falls Dome. F₃ produced a crenulation-cleavage with axes that trend N-NE and plunge SSW; these features roughly parallel the strike of the belt of gneiss domes, and may be associated with the dome forming event (Simpson, 1974). Post F₃ cleavages are observed in the CVS to the south (Hatch, 1975), east (Hudec, 1983) and west (Osberg, 1975) of the Shelburne Falls dome.

5.2.3 Age of metamorphism and deformation

Metamorphism in the study area occurred during the Devonian Acadian orogeny. The Black Mountain granite, a New Hampshire Magma Series intrusive that cuts early
deformational fabrics of the Waits River Formation to the north of the Shelburne Falls Dome (Hepburn, 1975), yields 377 and 383 +/- 7 my Rb-Sr muscovite ages (Naylor, 1971). Sutter, Ratcliffe, and Mukassa (1985) obtained $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende plateau-dates in the Cambro-Ordovician rocks to the west and north of the study area, and claimed that a garnet-zone hornblende age from the Cambro-Ordovician Hoosac Formation of 376 +/- 5 my represents the age of peak Acadian metamorphism. Sutter and Hatch (1986) determined a peak metamorphic age of 387 +/- 2 my in the Cambro-Ordovician Rowe-Hawley zone to the west of the study area and suggested that the uplift rate between 388 and 360 my was approximately 0.12 mm/yr. The sole metamorphic age reported within Siluro-Devonian strata is a 368 +/- 4 my hornblende plateau-date from the Standing Pond Volcanics 40 km north of the study area (Sutter et al., 1985).

5.3 TECHNIQUES

Samples from two stratigraphic levels on the east flank of the Shelburne Falls Dome, one within the Goshen Formation up-section from the SFD-Goshen contact, the other three km to the east of that contact in the Waits River Formation and uppermost Goshen Formation, were selected for bulk major and trace element determinations, detailed electron microprobe study and ion microprobe
analysis (Figure 5.2). The samples were chosen on the basis of petrographic and preliminary electron probe study; maximum effort was focused on garnet-bearing, low-variance assemblages containing Ca-rich phase inclusion suites within garnet porphyroblasts or amphibole pseudomorphs.

5.3.1 Electron microprobe techniques

Electron microprobe analyses were made using two JEOL 733 superprobes, one at M.I.T., the other at R.P.I. Reported analyses are the average of 3-6 individual point analyses of unzoned matrix grains (micas, chlorite), and single representative analyses for zoned grains (clinozoisite, plagioclase) and small inclusions in garnet.

Standard operating conditions for the instrument were: a specimen current of 10-25 nanoamps, an accelerating potential of 15 kV, and a beam diameter of 1-2 microns. Analysis schedules measured Na x-rays first to minimize alkali volatilization. Standards were well-characterized natural and synthetic silicates and glasses. One-sigma counting statistics were generally better than +/- one-percent for stoichiometrically important components and +/- two to three percent for minor elements. Raw counts were corrected for absorbance
and fluorescence using the methodologies of Albee and Ray (1970) and Bence and Albee (1967). All iron is reported as FeO; in these graphite-bearing pelites Fe₂O₃ is presumed to be negligible in all phases except clinzoisite and magnetite.

5.3.2 Ion microprobe techniques

Ion microprobe analyses were made with a Cameca IMS-3F ion microprobe. Detailed analytical techniques and working curves for garnets are presented in Appendix I. Few standards are available for almandine-rich garnets; hence, absolute concentrations of trace elements are poorly constrained. However, relative variability, as shown by ion intensity ratios, provides significant petrogenetic information. Other minerals were scanned for ion intensities using standard ion probe techniques (Shimizu et al., 1978; Shimizu and Hart, 1982) in order to obtain rough constraints on element compatibilities relative to garnet. The lack of working curves for the other minerals relegates these data to a semi-quantitative level.

5.3.3 Whole-rock techniques

Whole-rock determinations of major and trace element abundances were made using X-ray fluorescence analysis at the University of Massachusetts, Amherst (Rhodes, 1983)
and neutron activation analysis at M.I.T. (Ila and Frey, 1984). The pelites were slabbed, cleaned with Al₂O₃ grit, washed ultrasonically in millipore water, crushed to pease size using a plastic coated hammer, examined to insure that clean unaltered chunks were analyzed (not always possible—see below), and ground to powder in an agate shatterbox.

5.3.3.1 XRF

Major element analyses are by XRF and represent the average of duplicate analyses (except for 84–48) of glass disks fused with a lithium tetraborate flux. Duplicate XRF values agreed to better than one percent for all the elements except Na₂O. Accuracy of the XRF data is evaluated by comparing the values determined for a standard rock run on the same three day period as the analysis of the unknowns (Table 5.1A). Errors based on duplicate determinations on the same pellet are significantly less than 1% for SiO₂, Al₂O₃, Fe₂O₃, MnO, CaO, and K₂O, and less than 2% for MgO and TiO₂.

The coarse-grained pelitic and semi-pelitic rocks of the Waits River and Goshen Formations are heterogeneous on thin-section to hand-sample scale; obtaining a representative whole-rock analysis is problematic. An additional complication is incipient alteration, manifest
as rusty layers near the surfaces of the hand-samples. To evaluate the effects of sample size and surficial weathering on major element chemistry one sample, 85-19B, was analyzed for major elements three times, once as a ten-gram rock chip split, once as a typical fifty-gram split, and once as a fifteen-gram split containing primarily rusty-looking chunks.

Table 5.1B demonstrates that there are compositional differences between the large split, the small split and the rusty-looking split. Na$_2$O, K$_2$O and MgO are slightly enriched in the larger split, whereas Fe$_2$O$_3$, CaO, and MnO are depleted. The rusty chips are higher in SiO$_2$, Na$_2$O and P$_2$O$_5$, and lower in the other elements than the non-rusty chips.

5.3.3.2 INAA

Na$_2$O, Sc, Cr, Co, Ba, Hf, Ta, Th, U and rare-earth-element (REE) concentrations were determined using neutron activation analysis. Flux corrections were not needed and U fission products did not affect the LREE analyses. Because only a single irradiation was done, no accuracy or precision data is reported; however, typical precisions of analyses based on repeat determinations of a granitic working standard in the M.I.T. N.A.A. lab are
< +/- 3% for La and Eu, +/- ≈ 5% for most other elements, and > +/- 10% for Th, U and Ta.

5.4 WHOLE-ROCK CHEMISTRY

5.4.1 Major element chemistry

Major element analyses are shown in Table 5.1C. Although the purpose of this paper is not an analysis of the sedimentary implications of the chemistry of these metasediments, a comparison of their major and trace element abundances with both New England sediments and typical pelitic sediments worldwide is instructive.

Calc-pelites from the Waits River Formation are characterized by low SiO₂ contents (40-50 wt%) compared to the Goshen Formation samples (59-72 wt%), and compared to the majority of pelite and shale analyses reported from New England (Shaw, 1956; Ferry, 1986) and worldwide (Taylor and McLennan, 1985). The Waits River sediments are also CaO- and Al₂O₃-rich relative to typical upper-crustal compositions such as the North American Shale Composite (Haskin et al., 1968). The Waits River samples are similar in bulk major element concentration to aluminous calc-pelites from the Alps studied by Frey (1978).
5.4.2 Trace element chemistry

Trace element analyses are presented in Table 5.2. The eight pelites and calc-pelites from the Goshen and Waits River Fms have unusual trace element signatures, such as low Th/Sc, La/Sc, and La/Th ratios, relative to the majority of upper-crustal metamorphic rocks and sediments described in the literature (see, for example, Taylor and McLennan, 1985 and references therein).

The REE display a wide range in element concentrations and ratios (Figure 5.3). For example, La concentrations range from 5.64 to 74 ppm; the highest La abundances occur in three of the low-silica, high-Ca samples from the Waits River Formation (84-48, 85-19B, 85-20A). There is a weak correlation between high LREE abundances and low SiO$_2$ contents. 84-45 is anomalous; it has a low La abundance at a low SiO$_2$ content. La/Yb (chondrite normalized) ranges from less than one (84-45) to over 10 (85-19B). The samples with the highest La/Yb are Waits River samples (84-48, 85-19B, 85-20A). The majority of the whole-rock analyses display negative Eu anomalies, with larger anomalies in the Waits River samples than in Goshen samples. However, the two units cannot be differentiated on the basis of REE systematics; 84-45, a Waits River sample, has a lower La/Yb ratio than two of the three Goshen samples, and 85-1B, a Goshen
sample, has a higher La/Yb ratio than two of the Waits River samples.

The other trace elements also vary significantly in abundance and element concentration ratios (Table 5.2). There is a rough correlation between virtually all the trace element abundances and SiO₂ content, and hence between high trace element abundances in the Waits River samples and lower abundances in the Goshen samples. Sample 84-45 is anomalously depleted in the elements Cr, Co, Ba and U (but not Th), as well as the REE, relative to other samples of similar SiO₂ contents.

The western Massachusetts suite has unusually low Th/Sc (0.366 to 0.747), La/Sc (0.202 - 1.885) and La/Th (0.467 to 3.815) ratios relative to the majority of Proterozoic and younger sediments. Th/Sc, La/Sc and La/Th ratios are quite homogeneous in post-Archean sediments (Taylor and McLennan, 1985); worldwide, Th/Sc ranges from ≈ 0.8 to ≈ 1.4, La/Sc from ≈ 2.0 to ≈ 3.5, and La/Th from ≈ 2.0 to ≈ 8.0 in sediments.

The anomalous ratios described above may reflect either selective removal of garnet-incompatible elements (La, Th) from the studied samples by metamorphic devolatilization reactions, or metasomatic enrichment of the more garnet-rich portions of the calcareous pelites in garnet compatible elements (Sc, HREE). The two studied units, particularly the Goshen Fm, exhibit graded bedding
in which garnet is enriched in the aluminous bed-tops; biased sampling of garnet-rich portions of graded beds probably occurred. The presence of garnet was required before a sample was studied in detail. The fractionation of garnet compatible elements relative to garnet incompatible elements into the studied, garnet-rich, beds is not surprising. However, this result suggests: 1) application of trace element discriminant diagrams to correlations of stratigraphic units in metamorphic terrains (Holland and Winchester, 1983) must consider the potential for redistribution of trace elements on an outcrop or bed scale during metamorphism, and sampling must be done accordingly, 2) differences in trace element ratios in sediments and metasediments observed between geologic epochs such as the Archean and Phanerozoic must be evaluated in terms of metamorphic and metasomatic processes, 3) trace elements may be useful for investigating the scale of equilibration during metamorphism, and 4) the 'immobility' of certain trace elements (Sc, the REE) during metamorphism is open to question, these element may be mobile during metamorphism at a finite scale larger than hand-sample size (Chapter II).
5.5 PETROGRAPHY AND MINERAL CHEMISTRY

Mineral assemblages in the pelites and calc-pelites of the Goshen and Waits River Formations are presented in Table 5.3. Point-count modes for the eight samples studied in detail are presented in Table 5.4. Only assemblages containing garnet, muscovite, and biotite are included; thus the K-poor amphibolites and calc-silicates of the Waits River Formation are not tabulated. Low-variance mineral assemblages are found as matrix associations and inclusion suites. Ignoring minor phases (apatite, tourmaline, etc.), low variance matrix assemblages include (roughly in order of increasing Mg/Fe): (1) garnet-biotite-staurolite-ilmenite-muscovite-plagioclase-quartz +/- rutile (85-7A), (2) garnet-biotite-staurolite-kyanite-ilmenite-muscovite-plagioclase-quartz +/- rutile (85-1B, 85-1C, 85-13A), (3) garnet-biotite-kyanite-rutile-muscovite-plagioclase+/-qtz +/- ilmenite (85-20A), (4) garnet-biotite-kyanite-rutile-ilmenite-muscovite-plagioclase-clinozoisite +/- qtz (85-19B). Chlorite is found as a retrograde product with assemblages 1-4. Amphibole (as represented by pseudomorphs) was an additional phase with assemblages (3) and (4). Graphite is plentiful in all samples. The polymetamorphic and retrograded nature of this epeirogenic terrain necessitates careful attention to the
existence and timing of mineral-mineral equilibria. Thus, detailed petrographic descriptions of the minerals are provided below. Mineral compositions are provided in Tables 5.5a-5.5f. Trace element ion intensity data are in Table 5.6.

5.5.1 Garnet

Garnets form large (up to 10 mm) irregular anhedral porphyroblasts that are often rich in inclusions. The garnets are differentially resorbed with their irregular habits due primarily to the late-stage metamorphism that affected the region. The inclusions are used to evaluate phase relations early in the history of the samples and the reactions involved in garnet growth. Inclusions encompass virtually all the other phases described here, except amphibole, staurolite, and aluminosilicate.

In keeping with the calcareous bulk compositions, the garnets are more Ca-enriched (X_{Gross} ranges up to 0.25) than garnets from typical pelites, resembling instead garnets from calcareous pelites in the Alps (Selverstone and Munoz, 1987) and the Sangabawa belt of Japan (Enami, 1983). Details of major and trace element zoning in the garnets are provided in later sections.

Garnet growth was largely synkinematic. Garnets nucleated prior to the development of the F₂ foliation; asymmetric pressure shadows associated with that
foliation are present in several samples. Many garnets display rotational fabrics in their cores (Figure 5.4A) but the rims are post-kinematic - in contrast to garnets described by Rosenfeld (1968). Overgrowths generally display features indicative of growth in a post-kinematic environment such as concentric graphite inclusion bands. Shear sense, as inferred from garnet rotational fabrics, is the opposite of that implied by the asymmetric pressure shadows in several samples. However, it is not obvious whether the asymmetric pressure shadows are coeval with $F_2$, the widespread penetrative deformation event, or with $F_3$, the late-stage deformation. The rotational fabrics are similarly ambiguous. They may be associated with $F_1$, the west-vergent overturned isoclinal folding, or with $F_2$, the upright isoclinal folding.

All garnets are retrograded to either muscovite + biotite + plagioclase + ilmenite or to chlorite. Samples from the near-dome area are most severely retrograded. Garnet retrogradation prevails throughout the CVS in western Massachusetts (Hatch, 1975; Abbott, 1979; Hudson, 1983; Goeldner, 1983). Abbott (1979) suggested that the muscovite + biotite retrogradation was due to a second prograde event in which early retrograde chlorite was remetamorphosed to biotite + muscovite concentric to the Connecticut Valley domes. More detailed studies (Dibble, 1981; Hudson, 1983; Goeldner, 1983) reveal that the
muscovite + biotite after garnet texture is not restricted to regions around the domes, but rather is an effect of regional significance, perhaps with its greatest intensity overlying the domes.

5.5.2 Biotite

Brown biotite occurs in two distinct habits: graphite microinclusion-rich and graphite microinclusion-poor (see Figure 5.4B). Graphitic biotites parallel the $F_2$ foliation and crosscut that foliation. Non-graphitic biotites appear as overgrowths on graphitic biotites, in strain-cracks in graphitic biotites, and in retrograded garnet rims and pressure shadows (Figure 5.4B).

The matrix biotites are all of intermediate $X_{Fe}$ (0.40-0.60) and moderate TiO$_2$ content (1.5-1.9 wt%). Waits River biotites contain slightly more TiO$_2$ than Goshen biotites. Chemically, graphitic and non-graphitic biotites are indistinguishable within a single thin section. Biotites in hornblende pseudomorphs are similar in composition to matrix biotites, whereas biotites adjacent to the retrograded rims of garnets are occasionally more Fe-rich and Ti-poor than matrix biotites. Biotite inclusions in garnet are more Fe-rich than matrix biotites. Generally, biotite inclusions in garnet contain approximately the same TiO$_2$ as matrix biotites. The TiO$_2$ contents are similar to those of
lowest sillimanite-grade biotites described by Guicotti and co-workers in western Maine (Guidotti, Cheney and Guggenheim, 1977). Biotite inclusions contain less Si\textsuperscript{iv} and concomitantly more Al\textsuperscript{iv} and Al\textsuperscript{vi} than matrix biotites. Surprisingly, there is no systematic difference in Si\textsuperscript{iv} between matrix biotites from quartz-rich and quartz-poor metasediments.

Biotite is strongly enriched in Li and moderately enriched in Co and V relative to garnet on the basis of secondary ion yields normalized to silica (see Table 5.6). This comparison rests heavily on the assumption that the ion yields of different silicate minerals are not radically different. Shimizu (personal communication) suggests that this assumption is reasonable. In all the discussions of relative ion yields, particularly for the oxides, it cannot be overemphasized that the results are qualitative and should not be directly applied to the formulation of K\textsubscript{d}'s or mass-balance expressions.

5.5.3 Chlorite

Chlorite is a minor modal constituent (< 1 volume %) found in four environments in these samples: (1) as Fe-rich inclusions in garnet, (2) as a retrograde reaction product of garnet breakdown, (3) as euhedral grains crosscutting F\textsubscript{2} schistosity, and (4) as lamellar intergrowths in biotite. No 'primary' matrix chlorite,
chlorite paralleling $F_2$ fabrics, is observed. Chlorite compositions vary markedly between locales within single samples.

Chlorite incorporates substantial Li, Sc, Co, V, and Cr relative to co-existing garnet (Table 5.6).

5.5.4 Staurolite

Staurolites are found in low-Ca, high-Fe pelites. Staurolite is a late-stage mineral invariably overgrowing both $F_2$ foliation and $F_3$ crenulations. Staurolite appears to nucleate preferentially perpendicular to $F_2$ foliations from garnet porphyroblasts. Staurolites are locally weakly retrograded to sericite, but in general are pristine and euhehdral. Staurolite growth preceded garnet retrogradation; frequently staurolites abut the ghostly outlines of pseudomorphic garnet rims. Staurolites are Zn- (up to 1.10 wt %) and Li-rich (see also Dutrow et al., 1986), but otherwise are poor in trace elements.

5.5.5 Kyanite and Sillimanite

Kyanite is found in two habits, correlating with the presence or absence of staurolite. Kyanite in staurolite-bearing pelites is euhehdral, overgrows $F_3$ crenulations and has well-developed cleavages. Kyanite in staurolite-free pelites is retrograded to white micas, does not exhibit prominent cleavages and appears to parallel $F_2$
fabrics. Kyanite contains no detectable trace impurities at high concentrations. Minor fibrolitic sillimanite occurs in sample 85-19B.

5.5.6 Clinozoisite

Clinozoisite is included in numerous garnets and is also found as a matrix phase in the most calcareous samples (i.e. 84-48, 85-19B). Unlike the most calcareous samples from the Waits River Fm (84-48, 85-19B, 85-20A) clinozoisite inclusions are restricted to the cores of garnet in sample 84-45 (Figure 5.4C); they do not exist rimward of a textural unconformity defined by a decrease in the abundance of inclusions (Appendix A). The small grain-size of these epidote group minerals precludes investigation of zoning in individual grains. Clinozoisites are weakly enriched in Sc and V and strongly enriched in Y and Zr, relative to co-existing garnet (Table 5.6).

5.5.7 White micas

Two white micas, muscovite and margarite, are found. Muscovite is ubiquitous whereas margarite is always included within garnet and kyanite and occurs only in the more magnesian samples (85-19B, 85-21A).

Muscovite is the predominant matrix phase in both the Waits River and Goshen Formations (see Table 5.4) and it occurs in four habits: (1) graphitic elongate
foliation-defining grains, (2) graphite-free reaction product after garnet, (3) fine-grained sercite after staurolite and kyanite, and (4) inclusions in garnet. Muscovite compositions are moderately phengite-rich (Si/(22 oxygen) = 6.16–6.5); these Si contents are significantly higher than low-pressure facies series micas of amphibolite grade (Guidotti, 1978; Miyashiro and Shido, 1984). Goshen rocks have lower Si/(22 oxygen) than Waits River samples, except for 85-19B. The other quartz-free Waits River samples (85-20A, 85-21A) all have high Si abundances. Muscovites become more Si-rich at higher pressures in K-buffered assemblages (Massone and Schreyer, 1987). X_Na (Na/Na+K) values are quite low (<0.15) compared to muscovite of similar grade from low-P facies series (Guidotti, 1978). Muscovites contain significant Na, Li and V compared to garnets (Table 5.6).

5.5.8 Amphibole pseudomorphs

Large (up to 7 mm) pseudomorphs after amphibole were observed in several Waits River samples, and are widely distributed (if not widely recognized) in the Waits River Formation in western Massachusetts (Goeldner, 1983; Hudson, 1983). The pseudomorphs consist of an approximately 3:1 (point-counted mode) mixture of graphitic biotite and distinctive blebby plagioclase (Figure 5.4D). These pseudomorphs are postulated to be
after hornblende for four reasons: (1) they frequently have a diamond-shaped outline, (2) the preponderance of calcic plagioclase and low-alumina biotite in the pseudomorphs precludes high-Al Ca-free diamond-shaped minerals such as staurolite, (3) the pseudomorphs are restricted to the most magnesian (85-19B, 85-20A, 85-21A) bulk-compositions (see Table 5.1), and (4) similar pseudomorphs containing relict hornblende are found in lower-grade calc-pelites of the western Tauern window, Austria (Selverstone and Munoz, 1987; Selverstone, personal communication). No amphibole remains in the western Massachusetts pseudomorphs, so regression analysis of the pseudomorphing reactions is difficult.

Selverstone and Munoz (1987) propose several hornblende breakdown reactions in rocks of similar bulk composition. A generalized reaction appropriate to the western Massachusetts samples is:

\[
(1) \text{hornblende} + \text{phengite} +/- \text{chlorite} = \text{biotite} + \text{plagioclase} +/- \text{garnet} +/- \text{quartz} + \text{H}_2\text{O}
\]

The exact stoichiometry of the reaction, and the status of garnet as product or reactant, depends on the Tschermak contents of the silicates and the availability of quartz. The amphibole pseudomorphs are confined to samples without abundant matrix quartz.
5.5.9 Plagioclase

Plagioclase is an abundant mineral in all of these samples (Table 5.4). It occurs primarily as isolated porphyroblasts (1-3 mm in size) in the Goshen samples, and as abundant graphite-rich elongate grains in the Waits River samples. Plagioclase recrystallized throughout the thermal history of the region; it is included in garnets, and yet is also a late mineral, overgrowing $F_3$ crenulations. Albite-rich plagioclase is locally present in late-stage fractures and as exsolution lamellae in more calcareous plagioclase.

Plagioclase zoning is pronounced. The majority of grains from the Waits River Formation have sodic cores and calcareous rims, whereas Goshen samples exhibit the opposite trend. Plagioclase inclusions are frequently more sodic than matrix grains in Waits River samples.

Plagioclase compositions overlap the Huttenlocher gap region ($A_{50}-A_{70}$) (Grove et al., 1983). Although no microstructural (TEM) investigations of the plagioclases were attempted, the extinction patterns are compatible with Huttenlocher exsolution (T.L. Grove, personal communication, 1987).

5.5.10 Quartz

The modal abundance of quartz is significantly higher in the Goshen than the Waits River samples (Table
5.4). Indeed, several Waits River samples appear to contain quartz solely as inclusions in garnet. Garnet cores in 84-48 contain quartz inclusions, but have inclusion poor overgrowths.

5.5.11 Oxides, sulfides and accessory minerals

Rutile is the predominant Ti-oxide in these rocks (Table 5.3 and 5.4). It occurs as inclusions in garnet, plagioclase, and staurolite, and in the matrix of virtually every sample. Ilmenite predominates over rutile in the more Fe-rich staurolite-bearing pelites of the Goshen Formation (85-1B, 85-10B). Ilmenite often overgrows early rutile. Magnetite is found only as inclusions in garnet in the most ferruginous sample (84-48).

Ilmenite is V-enriched, and magnetite is Co-enriched relative to garnet (Table 5.6). Comparison of ion yields between a silicate and an oxide is more problematic than between two silicates, because of potentially more severe matrix effects between silicates and oxides (e.g. Shimizu, 1986).

Pyrrhotite, tourmaline, zircon, apatite, xenotime, allanite, barite, and thorite are accessory minerals in these calc-pelites. The latter four minerals were found using back-scattered electron imaging on the JEOL superprobe. These minor minerals may contain a dominant
proportion of the trace element budgets of several elements (REE in allanite; Y, REE, P$_2$O$_5$ in xenotime or apatite; Zr, Hf, REE in zircon), just as in granitic systems (Gromet and Silver, 1983). Due to their small grain size, examination of trace element ion yields for these minerals was not attempted.

5.5.12 Graphite

Graphite is ubiquitous in these samples. It is laced throughout the early formed minerals, forming localized bands and patches in many of the garnets.

5.6 PHASE EQUILIBRIA

Phase relations in the Goshen and Waits River Formation pelites are described in the model system SiO$_2$-Al$_2$O$_3$-TiO$_2$-MgO-FeO-CaO-MnO-Na$_2$O-K$_2$O-C-O-H. P$_2$O$_5$, ZrO$_2$ and other minor and trace elements do not significantly modify the phase relations. MnO stabilizes low-grade garnet (Spear and Cheney, in press); however, Mn fractionation into garnet cores rapidly reduces the effective bulk composition of MnO in a rock system. Growth of modally abundant garnet occurs in the above model system without MnO (Loomis, 1982; Loomis, 1986). Fe$_2$O$_3$ is present primarily in the mineral clinozoisite, except in the most ferruginous sample, 84-48, which also contains magnetite. The remaining ten component system
can be depicted graphically in three and four component space by projection from ubiquitous phases.

Phase relations are presented for minerals considered to be in equilibrium with garnet during growth, because an understanding of garnet growth reactions is a principal goal of this chapter. In the discussion of phase relations late-stage sodic plagioclase, re-equilibrated garnet rims, and apparently retrograde biotites are excluded from consideration.

5.6.1 AFM

Phase relations projected from quartz, muscovite and H₂O into Al₂O₃-FeO-MgO (AFM) (Thompson, 1957) are shown in Figure 5.5 for each locale. The lack of matrix quartz in the Waits River samples invalidates the projection as a thermodynamically rigorous phase diagram in the least siliceous samples. A simple equilibrium AFM facies-type within this system cannot describe the phase relations of the samples from either the Waits River or Goshen Formations. Addition of either SiO₂ or H₂O as a plotting component does not lead to non-intersecting phase volumes. Similar results in AFM in limited geographic areas were presented by Rumble (1977), Hodges and Spear (1982), Silverstone and Spear, (1985), and many others.
5.6.2 ACFN

An additional projection from biotite (Annite 50) into \( \text{Al}_2\text{O}_3-\text{CaO}-\text{FeO}-\text{Na}_2\text{O} \) (ACFN) allows study of phase relations involving plagioclase, clinozoisite, and grossular component in garnet (Figure 5.6). This projection uncrosses the majority of the crossed tie-lines in AFM, particularly in the Waits River samples; the wide variations in whole rock Ca/Al ratio leads to differences in phase relations outside AFM. Garnet is stabilized by the presence of CaO (Spear and Cheney, in press). The lack of entirely systematic Fe/Mg partitioning, particularly in the Goshen samples, reflects the retrograde non-equilibrium processes that have affected the samples, and exemplifies the difficulties in interpretation of phase relations in polymetamorphic terrains.

5.6.3 AFMC

Chlorite inclusions in garnets and biotite+plagioclase pseudomorphs after amphibole suggest that magnesian minerals such as chlorite and hornblende were involved in phase-relations early in the histories of these samples. Thus, a projection from biotite yields plotting points for modally important phases that project through infinity; this situation complicates visualization of phase relations. Hence, an ad-hoc
projection from quartz-muscovite-intermediate plagioclase (anorthite 35) - H₂O - rutile into Al₂O₃-FeO-CaO-MgO (AFCM) is used to investigate garnet-growth reactions (Figure 5.7). Plagioclase compositions vary widely in this suite of samples (Table 5.5) and quartz is not present in some Waits River rocks, so this projection is not strictly appropriate for quartz-free rocks; however, it allows schematic representation of phase volumes for garnet growth reactions.

In a thermodynamically valid projection into a four-component phase diagram, a four-phase coexistence is divariant. The composition of a phase in such an assemblage is uniquely defined at a given temperature and pressure. Such an assemblage is called a limiting assemblage using the terminology of Albee (1965),

In the projected AFMC system, observed four-mineral divariant limiting phase volumes for matrix assemblages are: garnet-biotite-staurolite-kyanite (85-1B; 84-45), garnet-biotite-staurolite-ilmenite (85-7A), garnet-biotite-kyanite-clinozoisite (85-19B), and garnet-biotite-ilmenite-clinozoisite (84-48).

Four-mineral assemblages compatible with observed inclusion suites in garnet and the assumption that biotite preceded garnet in all samples are: garnet-biotite-chlorite-ilmenite (85-1B); garnet-biotite-chlorite-margarite (85-19B; 85-21A), garnet-biotite-
chlorite-clinozoisite (84-45; 85-19B; 85-20A; 85-21A), and garnet-biotite-margarite-clinozoisite (85-19B, 85-21A). Five and six phase inclusion assemblages (i.e. garnet-biotite-chlorite-margarite-clinozoisite-ilmenite) may either be stabilized by components outside the system of interest, particularly Fe$^{+3}$ in clinozoisite and amphibole or MnO in garnet, or may have an additional phase at equilibrium due to the absence of quartz or water as a phase. They also may represent a series of phase volumes that were stable during the histories of the rocks (Thompson et al., 1977). If garnet and hornblende stably co-existed other likely four-phase volumes are: garnet-hornblende-biotite-chlorite, garnet-biotite-hornblende-margarite and garnet-biotite-hornblende-clinozoisite. The hornblende-free divariant assemblages described above will be investigated algebraically in a subsequent section of this paper.

5.7 INTENSIVE VARIABLES OF METAMORPHISM

5.7.1 Geothermometry and geobarometry

The CVS metasediments are not well-suited to geothermometric and geobarometric analysis. Although the samples contain appropriate assemblages (garnet-biotite-muscovite-kyanite-qtz-plagioclase-ilmenite-rutile), the compositions of the minerals are outside accepted ranges
for mineral solution models; it is also difficult to determine equilibrium mineral co-existences due to the extensive mineral retrogradation. Plagioclase compositions range above An$_{40}$, into the I1 structural regime. Solution models applied to andesine and oligoclase (Newton et al., 1980; Hodges and Crowley, 1985) may be inappropriate. Garnet solution models (Hodges and Spear, 1982; Ganguly and Saxena, 1984) are also hard-pressed to deal with compositions more calcareous than about $X_{\text{Gross}}=0.20$. The scale of equilibration during retrogradation of minerals with small diffusion coefficients is difficult to evaluate - in a later section of this chapter this problem is considered in more detail. Nonetheless, we cautiously proceed with a thermobarometric analysis.

Experimental and empirical fluid-independent geothermometers and geobarometers that apply to these samples are: garnet-biotite (Thompson, 1976; Ferry and Spear, 1978), garnet-plagioclase-qtz-kyanite (Ghent, 1976), garnet-plagioclase-muscovite-biotite (Ghent and Stout 1979), and garnet-rutile-ilmenite-plagioclase-quartz (GRIPS) (Bohlen and Liotta, 1987).

Solution models are similar to those described by Hodges and Crowley (1985) for garnet, muscovite and biotite, except for the GRIPS barometer in which the garnet solution model of Ganguly and Saxena without
ternary interaction terms (see Perkins and Chipera, 1985) was used. The anorthite activity coefficients empirically calculated by Hodges and Crowley range from 1.5 at 500°C to 1.2 at 700°C (consistent with Orville's hydrothermal experiments); these values are clearly inadequate for high-Ca plagioclase (Grove et al., 1983; Carpenter and Ferry, 1985). We have adopted a simple constant plagioclase activity coefficient of 1.8 for $X_{An}$ less than 0.50, and allowed $a$(An) to vary between 0.9 and 1.0 for all plagioclase in the range An(50) to An(90). Carpenter and Ferry (1985), and Grove et al. (1983) suggest that this is a valid approximation for II plagioclase at the temperatures of metamorphism in the Shelburne Falls region.

5.7.2 Garnet-biotite geothermometry

Temperatures calculated from the garnet-biotite geothermometer range between 600-670°C for the Waits River samples, and 500-575°C for the Goshen samples (Figure 5.8). A range of garnet rim analyses were matched with a range of matrix biotite compositions; the large $T$-scatter (+/- 70°C) is due to the variable retrogradation of both garnet rims and matrix biotites in the samples. The extremely large $T$ variation in 84-45 reflects (Fe/Fe+Mg) values ranging from 0.82-0.88 for nominal rim points.
5.7.3 Garnet-plagioclase geobarometry

Garnet-plagioclase-kyanite-quartz and garnet-plagioclase-muscovite-biotite-quartz equilibrium constant lines suggest pressures of 5-8 kbar for the Goshen samples, and 7-10 kbar for the Waits River samples (Figure 5.8), except sample 84-45, which plots at higher pressures. The pressures for the Waits River samples are minimum pressure estimates, valid only if quartz existed in equilibrium with growing garnet in these samples. (Garnet)-(plagioclase inclusion) ln K lines overlap the P-T conditions calculated for matrix assemblages.

5.7.4 GRIPS

Four out of the five minerals involved in the geobarometric association garnet-rutile-ilmenite-anorthite-quartz occur in samples from the study area. Bohlen and Liotta (1987) experimentally bracketed the equilibrium:

$$\text{Fe}_2\text{CaAl}_2\text{Si}_3\text{O}_{12} + 2\text{TiO}_2 = 2\text{FeTiO}_3 + \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{SiO}_2$$

(the GRIPS barometer) and its shallow dP/dT slope and widely spaced ln(K) lines suggest it is an excellent geobarometer. GRIPS ln K's range from 4.7-7.4 for matrix assemblages in the Waits River samples (84-45, 84-48, 85-19B, 85-20A, 85-21A) corresponding to minimum pressures of 6-8 kbars at the calculated temperatures of 500° to 650° C. These pressures are minima because in each sample
(save 84-45) one of the low-pressure phases (ilmenite-anorthite-qtz) is not present in the matrix. Highest ln K's, and lowest minimum pressures, are calculated for 85-19B. Goshen samples containing four of the five phases yield similar minimum pressures. Samples containing three of the four phases involved in the GRIPS equilibrium as associated inclusions in garnet yield similar ln K's, and similar minimum pressures, to matrix assemblages.

5.7.5 Fluid compositions

Maxima in \( f(O_2) \) are calculated based on the absence of carbonate and the presence of graphite + Ca-silicates in the pelites (Ohimoto and Kerrick, 1977). Ca silicate-calcite-graphite assemblages buffer \( f(O_2) \). In the western Massachusetts pelites \( f(O_2) \) is lower than oxygen fugacities defined by equilibria such as:

\[
(2) \quad \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{garnet}) + 3 \, \text{C}(\text{graphite}) + O_2(\text{fluid})
\]
\[
= 3 \, \text{CaCO}_3(\text{calcite}) + \text{Al}_2\text{Si}_5\text{O}_{10}(\text{kyanite}) + 2 \, \text{SiO}_2(\text{quartz})
\]

Values of \( f(O_2) \) calculated for this equilibrium assuming a grossular activity of 0.1-0.2 and using thermodynamic data summarized in Appendix (II), are presented in Figure 5.9. Non-ideal mixing in the fluid is accounted for using a Redlich-Kwong equation of state (Holloway, 1977; Flowers, 1979). The \( f(O_2) \) based on this equilibrium is slightly lower than QFM. These calculations are directly applicable to the alumino-
silicate bearing matrix assemblages of 84-45, 85-20\(\lambda\), 85-19B, and 85-1B.

Based on T-X(CO\(_2\)) diagrams calculated by Bucher et al. (1983), fluid compositions in these samples were water-rich. Clinozoisite stability is limited to values of \(X(H_2O)\) greater than 0.50 in the simple system SiO\(_2\)-Al\(_2\)O\(_3\)-CaO-Na\(_2\)O-H\(_2\)O (Bucher et al., 1983) at these P-T conditions, although Fe\(_2\)O\(_3\) solubility into clinozoisite enlarges its T-X stability.

5.8 GARNET GROWTH REACTIONS - MAJOR ELEMENT CONSTRAINTS

Garnet growth reactions can be roughly constrained based on major element zoning and matrix and inclusion phase relations. In this section, major element zoning in garnets is presented, theoretical zoning profiles in a range of assemblages are calculated using the Gibbs method (Spear et al., 1982, Spear and Selverstone, 1983, Spear and Cheney, in press) and the measured zoning profiles are compared to the calculated ones. Major element relations provide first order constraints on reaction histories. Trace element zoning is used to refine the reaction histories in the next section.

5.8.1 Garnet zoning - major elements

Major element zoning is presented in Appendix A. The largest garnet in each ion-probe mount (1" diameter) was
chosen for study to ensure that a crystal with a near center-cut was investigated. Nonetheless, variability in (core composition)/(bulk-rock composition) for major and trace elements may reflect non-center cuts. Garnet zoning is usually concentric in interiors (an exception is 85-1B); the differential retrogradation of garnet rims leads to non-concentric near-rim zoning. This phenomenon is pronounced in the Goshen samples. Compositions are especially patchy and irregular within 10 microns of garnet rims.

An axiom of the following discussion is that an inflection or break in major and trace element zoning represents a change in the physicochemical environment during garnet growth: either a change in P and/or T, a change in the garnet growth reaction, a change in growth rate, or a change in fluid composition. It is important to emphasize that both major and trace element zoning are affected by different geologic processes in similar ways.

Typically, Mn is zoned toward lower values outward from garnet cores. All of the Goshen samples (85-1B, 85-2A, and 85-10B) and four out of the five Waits River samples (84-45, 85-19B, 85-20A, and 85-21A) exhibit such 'bell-shaped' Mn patterns. 'Bell-shaped' Mn profiles are typical of garnets from amphibolite facies pelitic schists (Hollister, 1969; Tracy, 1982; Loomis, 1986, Spear, in press). 84-48 is anomalous; Mn increases
consistently towards its rim. It is somewhat surprising that 84-48 is also the sample with the highest bulk MnO content.

All of the samples exhibit minor near-rim Mn enrichment, often below the level of the contour intervals depicted. Samples 85-2A and 84-45 display particularly irregular near-rim abundances. Mn concentrations vary by up to a factor of two within ten microns of garnet rims. This extreme variation may reflect patchy rim retrogradation and the difficulty in analyzing representative rim compositions in retrograde garnets (see discussion below). Similar near-rim Mn enrichments are common in amphibolite to granulite facies environments (Hollister, 1969; DeBethune et al., 1975; Tracy, 1982).

\(X_{\text{Pyrope}}\) contents of the garnets generally rise from core to rim except in the retrograded near-rim zones. 85-19B exhibits a wide outer zone of decreased \(X_{\text{Pyrope}}\). 84-48 shows the smallest variation in pyrope component. \(X_{\text{Almandine}}\) of garnets behaves roughly antithetically to CaO; coupled with the rimward MgO increases, \(\text{Fe}/(\text{Fe+Mg})\) generally decreases from core to rim, except in the outermost reaches of the garnets.

Ca zoning is variable from sample to sample. The high and variable bulk CaO contents of these samples and their variable Ca/Na and Ca/Al ratios combine to produce
a variety of Ca zoning profiles. Ca growth zoning patterns are divided into five types: Type I - unzoned core with decreasing Ca near the rim (85-1B, 85-10B); Type II - weakly increasing then steeply decreasing Ca with a low-Ca overgrowth (85-2A); Type III - continuously increasing Ca (84-48); Type IV - weakly decreasing then weakly increasing Ca (84-45, 85-19B, 85-20A); and Type V - essentially unzoned Ca (85-21A). Figure 5.10 schematically depicts the five types of Ca zoning. Types I and II are confined to Goshen rocks, and Types III through V are restricted to Waits River rocks. The five types of Ca zoning serve as a reference point for the discussions of reactions histories that follow. Retrograde near-rim low Ca re-equilibration is locally superimposed on the above growth zoning in Waits River Rocks.

The two Type I Goshen samples (85-1B, 85-10B) each maintain high (> 0.20) $X_{\text{Gross}}$ values in their cores, then $X_{\text{Gross}}$ falls to values less than 0.10 at garnet rims. 85-2A, the Type II garnet, exhibits a graphite-free core ($X_{\text{Gross}}=0.17-0.18$), an increase in $X_{\text{Gross}}$ to 0.20, then a decrease in $X_{\text{Gross}}$ to < 0.13 in its partially resorbed, graphite-rich exterior.

The Waits River garnets all have high CaO contents ($X_{\text{Gross}}$ mostly > 0.20). In the Type III garnet, 84-48, $X_{\text{Gross}}$ rises from core to rim, in some traverses
abruptly. The Type IV garnets, 84-45, 85-19B, and 85-20A, each show rimward declines in $X_{\text{Gross}}$ (delta $X_{\text{Gross}} = 0.02-0.04$), then an increase in $X_{\text{Gross}}$ out towards the rims. 84-45 shows patchy near-rim re-equilibration to low $X_{\text{Ca}}$; this dropoff is confined to near rim points and is not contoured in Appendix A. Type V garnet 85-21A exhibits no systematic Ca zoning.

5.8.2 Gibbs method calculations

The variable major element zoning presented in the last section is due to the differences in bulk composition, reaction history and perhaps P-T path, between different samples from the two units. Theoretical garnet zoning profiles in a variety of assemblages over different P-T paths can be calculated using the Gibbs method (Spear et al., 1982). The theoretical profiles can then be compared to the observed profiles to place constraints on P-T paths and/or reaction histories.

To first order, garnet growth reactions can be described within the systems $\text{Al}_2\text{O}_3$-$\text{FeO}$-$\text{MgO}$-$\text{K}_2\text{O}$-$\text{SiO}_2$-$\text{H}_2\text{O}$ projected from quartz, muscovite and water (AFM) (Thompson, 1957) and $\text{Al}_2\text{O}_3$-$\text{CaO}$-$\text{Na}_2\text{O}$-$\text{SiO}_2$-$\text{H}_2\text{O}$ projected from quartz and water (ANC). The former system contains the garnet end members almandine and pyrope, the latter contains grossular. Reactions within AFM are similar to those described by other workers (Thompson and Nortor, 1968; Thompson et al., 1977). These reactions can be
conveniently written as a combination of an almandine-producing end-member reaction and an MgFe$_2$O$_4$ exchange. Similarly, reactions in AMI are grossular-producing in the Ca-end-member system and can be coupled with an Na$_2$Si$_3$Al$_2$O$_8$ exchange. Although reactions are discussed in the following sections of this thesis in terms of grossular-producing and almandine-producing end-member reactions the actual garnet growth reactions experienced by a rock are linear combinations (weighted by mineral stoichiometry) of the end member reactions. Because all the garnets studied are primarily almandine (X$_{\text{almandine}} > 0.50$) the Fe-end member mass transfer reactions always predominate over the Ca end-member reactions.

The Gibbs method (Spear et al., 1982; Spear and Silverstone, 1983; Spear and Cheney, in press; Spear, in press) is used to investigate numerically the movement of low-variance phase volumes as a function of pressure and temperature. The Gibbs method begins with a mineral assemblage at an initial P and T (frequently this is determined using geothermometry and geobarometry) and calculates changes in intensive variables (P, T and mineral composition) away from the reference conditions as a function of changes in n independent variables (where n is equal to the variance) (Spear and Silverstone, 1983). A principal advantage of the Gibbs method over more conventional thermodynamic approaches
that use $\Delta G = -RT \ln K$ is that it uses entropies and volumes of minerals in solving for changes in intensive parameters rather than enthalpies (which are often the least constrained thermodynamic data for a mineral). Extensive parameters (modes) can be incorporated into Gibbs method calculations via addition of differential mass balance equations (Spear, in press). Calculations follow the methodology of Spear and Silverstone (1983), with the following improvements in technique (see also Spear, in press; Spear and Cheney, in press): 1) changes in entropies with temperature are explicitly calculated using a Maier-Kelley heat capacity expression (Helgeson et al., 1978); 2) the entropy of water of Burnham et al. (1969) is accessed at each pressure and temperature rather than utilizing a constant value of $S_{H2O}^{298}$ at all temperatures and pressures. Thermodynamic data utilized are presented in Appendix B.

Pressure and temperature enter into the calculations through heat-capacity effects on entropies for minerals, through the expression for $RT \ln K$ used to relate chemical potential and mineral composition, and through the temperature and pressure effects on the thermodynamic parameters for water. Solution models of minerals only affect the calculations of the curvatures of the Gibbs free energy surface in the equations relating chemical potential and composition. Hence, consideration of
complicated solution models is generally unnecessary for small changes from the reference conditions (Spear and Selverstone, 1983).

The system investigated is SiO$_2$-Al$_2$O$_3$-FeO-MgO-TiO$_2$-CaO-K$_2$O-Na$_2$O-H$_2$O. The mineral compositions of sample 85-20A were chosen as a starting point for the calculations. Prograde chlorite composition was calculated based on Fe/Mg K$_d$ values presented by Albee (1965). An initial rim P and T of 7 kbar and 550$^\circ$ C were chosen as a starting point for the calculations and P and T were incremented over small changes in P and T ($\Delta T = 10^\circ$, $\Delta P = 1$ kbar).

Garnet composition is a function of pressure and temperature in a divariant assemblage. If garnet growth occurs in the presence of plagioclase, muscovite, biotite, quartz, H$_2$O and rutile, then any two of the following phases define a divariant four-phase volume in A-C-F-M: clinozoisite, margarite, ilmenite, and chlorite. These phases occur as inclusions in garnet in the studied samples, and therefore are likely reactants in garnet growth reactions. Quartz absent reactions are considered because of the dearth of quartz in the Waits River samples. Quartz absent assemblages require three of the aforementioned phases to define a divariant phase volume.

Carbonate and amphibole are additional calcareous phases that may have been important during garnet growth; their role is difficult to evaluate because neither is
preserved in the studied samples either as inclusions or matrix phases. Staurolite and kyanite do not occur as inclusions in garnet and overgrow late-stage foliation; they are not likely to have been present during garnet growth. Additionally, involvement of modally abundant staurolite in garnet growth reactions would deplete the garnets in Li (Dutrow et al., 1986), and no aberrant near-rim Li behavior is observed in the staurolite-bearing samples. Neither staurolite nor kyanite are considered in the garnet growth models.

The movement of phase volumes calculated for plausible garnet growth assemblages are presented in Figure 5.11 and discussed below.

5.8.2.1 Reactions in AFM

Garnet growth is traditionally considered in terms of prograde reactions in AFM +/- Mn (Hollister, 1969; Thompson et al., 1977)). Reactions producing the grossular component of garnet are less widely studied (however, see Crawford, 1974). A modified AFM subsystem is first considered that includes rutile as a projection point, thus allowing ilmenite to be considered to be an AFM phase.

Low-variance continuous net transfer reactions in this system are represented by three phase triangles on
AFM and four-phase volumes in the quartz-free system. In this section, the net-transfer reactions responsible for phase volume movement in bulk compositions appropriate to the western Massachusetts calc-pelites are delineated. The movement of three phase triangles in this simplified system as subassemblages of the more complicated chemical system described above is examined.

Low-variance AFM garnet growth reactions compatible with the observed inclusion suites and assemblages at lower metamorphic grades are the AFM continuous reactions:

(3) \[3 \text{chlorite} + \text{muscovite} + 3 \text{quartz} = 4 \text{garnet} + \text{biotite} + 12 \text{H}_2\text{O}\] (Hollister, 1969; Thompson and Norton, 1968; Loomis, 1985)

for the three phase co-existence garnet + biotite + chlorite, and:

(4) \[6 \text{ilmenite} + 3 \text{quartz} + \text{muscovite} = \text{garnet} + \text{biotite} + 6 \text{rutile}\]

for the three-phase co-existence ilmenite+garnet+biotite. Note that equilibrium (4) is water-absent; it is analogous to the GRAIL barometer (Bohlen et al., 1983) in the same fashion the pressure-sensitive equilibrium grossular-plagioclase-alumino-silicate-quartz (Ghent,
1976) is analogous to the equilibrium grossular-
plagioclase-muscovite-biotite-quartz (Ghent and Stout,
1979). The former three-phase triangle moves toward more
magnesian garnet compositions with increased temperature
in all the assemblages investigated (Figure 5.11A, a &
b)(see also Loomis, 1985; Spear, in press, a, b, c). The
AFM three phase triangle defined by reaction (4) is not
strongly temperature sensitive. It moves to slightly
lower (Fe/(Fe+Mg)) with margarite (11A, d) and higher
(Fe/(Fe+Mg)) with clinozoisite (11A, e). Iron/magnesium
in garnet is not a sensitive function of pressure at
constant temperature in these assemblages. However,
garnet moves to slightly higher (Fe/(Fe+Mg)) with
decreasing pressure at constant T in all the assemblages
investigated.

The AFM discontinuous reaction:

\[(5) \text{ilmenite + chlorite + muscovite + quartz} = \text{garnet + biotite + rutile + H}_2\text{O}\]

also defines a divariant phase volume in the model system
(the exact stoichiometry of the AFM reaction depends
explicitly on the Fe/Mg ratios of the silicates). This
phase volume moves toward higher (Fe/(Fe+Mg)) with
increased temperature (at constant P) and deceased
pressure (at constant T) (Figure 5.11A, c).
A linear combination of AFM reactions (3) and (4) yields a low-variance quartz-free reaction:

\[(6) \text{chlorite} + 2 \text{rutile} = 2 \text{ilmenite} + \text{almandine} + 2 \text{H}_2\text{O}\]

Garnet composition is a strong function of temperature in the quartz absent assemblage (11B, b & d) in both margarite and clinzoisite Ca-limited assemblages. Garnet becomes more ferruginous with increased temperature (at constant P) and decreased pressure (at constant T).

Reaction (1), the generalized hornblende breakdown reaction, also provides a source for Fe and Mg during garnet growth. This potentially important reaction was not investigated numerically because: 1) its stoichiometry is sensitive to amphibole composition, 2) the amphibole composition in equilibrium with garnet is unknown, and 3) the thermodynamic data for amphibole end members are not well-constrained.

5.8.2.2 Reactions in ANC

Grossular-producing reactions are important in the calcareous samples of the CVS. \(X_{\text{Gross}}\) is generally higher than \(X_{\text{Pyrope}}\) and \(X_{\text{Spess}}\) in samples from both locales. Thus, prime consideration must be given to the grossular-forming reactions. It is also important to understand the
reactions in the calcareous system because the partition of Ca between phases provides useful constraints on pressure during metamorphism (Ghent, 1976; Bohlen and Liotta, 1987).

Reactions in the simple system $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{CaO-Na}_2\text{O-}$ $\text{H}_2\text{O}$ projected from quartz and $\text{H}_2\text{O}$ (ANC) are considered, although modeling is done in the system $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{FeO-}$ $\text{MgO-K}_2\text{O-}\text{CaO-Na}_2\text{O-}\text{H}_2\text{O-}\text{TiO}_2$ projected from quartz, rutile, muscovite, biotite, and water +/- chlorite +/- ilmenite. Garnet and plagioclase are ubiquitous in the studied western MA rocks, thus we consider two likely Ca-saturating phases (margarite and clinozoisite) co-existing with these two minerals as defining three phase triangles in ACN.

In high-alumina samples characterized by the three-phase ACN assemblage garnet-plagioclase-margarite, grossular-rich garnet growth occurs by the ACN continuous reaction:

$$(7) \ 5 \ \text{anorthite} + 2 \ \text{H}_2\text{O} = \ \text{grossular} + 2 \ \text{margarite} + 3 \ \text{quartz}$$

In this assemblage with chlorite, the Ca content of garnet falls with rising temperature at constant pressure and with decreased pressure at constant temperature, whereas with ilmenite Ca increases with rising
temperature (Figure 5.11A, a & d).

At lower Al the three-phase triangle clinozoisite-garnet plagioclase in ACN defines the continuous reaction:

(8) 20 clinozoisite + 5 qtz = 5 grossular + 25 anorthite + 10 H₂O

Garnet in this phase volume (with either ilmenite or chlorite) shows a slight shift to higher \( X_{\text{Gross}} \) with temperature (Figure 5.11A, b & e). \( X_{\text{Gross}} \) increases with decreasing pressure in both a chlorite-limited assemblage and an ilmenite-limited assemblage.

The ANC discontinuous reaction that is divariant in the modeled system is:

(9) clinozoisite + plagioclase + H₂O = grossular + margarite + quartz.

This phase volume moves to higher \( X_{\text{Ca}} \) with increased temperature and decreased pressure (Figure 5.11A, f).

Other reactions of interest can be generated by linear combination of these reactions. For example, a quartz absent reaction is a linear combination of reactions (7) and (8):
(10) 12 clinozoisite = 2 margarite + 10 plagioclase + 4 grossular + 4 H₂O

Ca content of garnet in this assemblage (with chlorite) is relatively insensitive to changes in P and T (11B, a), whereas with ilmenite it moves to higher X_Ca with increased temperature and decreased pressure (11B, c).

5.8.2.3 Other reactions

The AFM reactions delineated above are specific to the particular phyllosilicate compositions chosen. The actual stoichiometry of such reactions depends on the Tschermak contents (extent of FeSiAl₂ exchange) of the minerals (Thompson, 1979). Additionally, higher variance reactions in which the Tschermak content of the sheet silicates varies, such as:

(11) 2 biotite + 6 quartz = 2 muscovite + almandine + 3 FeSiAl₂ (muscovite) (Thompson, 1979),

are possible AFM garnet growth reactions, but are not likely to have contributed a large volume of garnet.

Reactions involving magnetite occurred in sample 84-48. For example, a generalized oxidation-reduction reaction producing almandine in western Massachusetts assemblages is:
(12) muscovite + 2 magnetite + 3 quartz = almandine + biotite + O₂

Hornblende, like garnet, contains significant amounts of Fe, Mg, and Ca, and thus must be considered as a possible reactant in both subsystems described above. Generalized consideration of hornblende breakdown is provided through reaction (1).

Addition of C to the model system adds graphite as a projection component and allows carbonate to be considered as a reactant in the presence of a C-O-H fluid. At lowest Al, in the presence of calcite + graphite, a generalized grossular producing reaction is:

(13) quartz + 2 calcite + anorthite = grossular + 2 CO₂.

The low-Ca Goshen samples may undergo Ca-rich garnet growth in an assemblage in which garnet is the Ca-saturating phase.

(14) 3 anorthite + biotite = grossular + almandine + muscovite

This assemblage is not limiting with respect to Ca in garnet; metamorphic fractional crystallization can lead to strong decreases in garnet Ca content (Hollister, 1969; Spear, in press). This assemblage defines the Ghent
and Stout geobarometer, and moves to higher $X_{\text{Ca}}$ in garnet with increased pressure (at constant $T$) or decreased temperature (at constant $P$), at constant plagioclase activity.

Continuous exchange reactions such as FeMn$_{-1}$ occur in these samples; they change the variance, but not the nature of the net-transfer reactions.

5.8.2.4 Summary - Gibbs method modeling

The most important result derived from the Gibbs method modeling is that changes in garnet composition during growth are extremely sensitive to the phases co-existing with garnet. As emphasized by Spear (in press) misidentification of the assemblage during growth is by far the largest source of errors in P-T path determinations using the techniques of Spear and Selverstone (1983). Identical garnet zoning profiles can be produced along widely varying P-T paths in different assemblages, and conversely variable garnet zoning profiles may be generated in rocks of different bulk composition (assemblage) along the same P-T path.

5.8.3 Garnet Growth Reactions (I)

The theoretical profiles calculated above are compared with the observed profiles and inclusion suites to place limits on garnet growth reactions. Whenever
possible, reactions occurring with increased temperature are favored over reactions occurring with decreased temperature. A given compositional change, such as an increase in \((\text{Fe}/(\text{Fe+Mg}))\) can be produced through garnet growth over a range of P-T vectors. For example, in Figure 5.11A (a) increased \((\text{Fe}/(\text{Fe+Mg}))\) can be produced along any P-T path within a rosette spanned by roughly \((\Delta T \approx -10, \Delta P \approx 1000)\) to \((\Delta T \approx 10, \Delta P \approx -1000)\). In the following discussion we do not discuss the full rosette over which a given compositional change may occur, but rather roughly describe the assemblages that can produce a given change in a compositional parameter with either an isobaric change in T or isothermal change in P. The full rosette over which a given change in a compositional parameter may occur may be roughly derived by the reader from Figure 5.11.

5.8.3.1 Mg-Fe zoning

The quartz bearing samples (85-1B, 85-2A, 85-10B, 84-45, and 84-48) all: 1) are zoned toward lower \((\text{Fe}/(\text{Fe+Mg}))\) at their rims, 2) contain inclusions of ferruginous chlorite (85-1B, 84-45, 84-48) and/or biotite (85-1B, 84-45, 84-48), and 3) contain ilmenite primarily as overgrowths on matrix rutile. These data and Figure 5.11A suggest that reaction (3) with increased temperature contributed to the formation of almandine-
pyrope rich garnet components in these samples. 84-48 contains magnetite inclusions so reactions such as (12) also contributed Fe to the formation of almandine component in this garnet.

The quartz-poor samples: 1) are also zoned primarily towards lower (Fe/(Fe+Mg)) at their rims (although the outer part of 85-19B shows the opposite trend), 2) contain inclusions of both ferruginous chlorite (85-19B, 85-20A) and ilmenite (85-19B, 85-20A, 85-21A), 3) have high Mg/Fe bulk compositions. These phase relations and the directions of phase volume movement calculated in Figure 5.11B are not compatible with isobaric increased T or isothermal decreased P metamorphism in either ilmenite + chlorite bearing assemblage. Four possibilities are: 1) quartz existed during garnet growth and reaction (3) occurred early in the history of these samples with increased T; 2) garnet growth occurred by reaction (5) along an unusual P-T path; 3) growth of the ferromagnesian component of garnet in the quartz-poor rocks occurred by a non-modeled reactions (i.e. 1, 11, or 14); or 4) an ignored component (MnO) changes the movement directions of the low variance phase volumes

5.8.3.2 Ca zoning

The Ca zoning in the Type I garnets (85-1B, 85-10B) is not well understood. It is observed that Ca values are
high in garnet cores \( (X_{\text{Gross}} > 0.20) \) and drop to low rim values \( (X_{\text{Gross}} < 0.10) \), and that most plagioclase grains are zoned towards more sodic rims. The high core Ca suggest garnet growth in an assemblage in which Ca content was buffered to a high level. The phase relations described above demonstrate that \( X_{\text{Gross}} \) in garnet remains high \( (> 0.20) \) in the presence of Ca rich minerals such as clinozoisite. However, Ca-rich inclusions besides plagioclase are not present in the Type I garnets.

A likely scenario for the formation of grossularite component in garnet is by reaction (14). Growth in this assemblage with decreased P or increased T produce \( X_{\text{Ca}} \) decreases at constant anorthite activity (Ghent, 1976). However, it is difficult to rule out the presence of clinozoisite or carbonate during the early growth histories of the garnets, despite the absence of inclusions of these minerals in garnet cores.

The Type II garnet (85-2A) experienced a more complicated growth history in the ACN system than did Type I garnets. The outer portions of 85-2A's Ca profile are roughly similar to the Type I profiles, and probably formed by similar reactions, although graphite inclusions are restricted to the outer low-Ca zones of this garnet. However, what reaction produced the initial increase in Ca? The early episode of growth is compatible with growth
by reaction (8) in a chlorite bearing assemblage (Figure 5.11) with increased T; however, there are no clinozoisite inclusions in the core of the garnet that support this reaction history. Margarite is an unlikely reactant in this sample, because margarite is confined to magnesian bulk compositions. Quartz is abundant in 85-2A, so quartz absent reactions are unlikely.

The type III garnet, 84-48, is: 1) zoned toward higher Ca ($X_{\text{Gross}} > 0.24$) at its rims, 2) contains inclusions of sodic plagioclase and matrix plagioclase zoned to higher $X_{\text{anorthite}}$, and 3) contains clinozoisite inclusions throughout. This evidence and the calculations of Figure 5.11A are roughly compatible with formation of grossular component by reaction (8) with increased temperature in the quartz-rich core of this garnet. A potentially complicating factor is the presence of magnetite inclusions in the garnet.

Although the Type IV (84-45, 85-19B, 85-20A) zoning profiles are similar (decrease to point A then increase) the samples have radically different phase relations in the ACN system, and differing bulk compositions. Thus, 84-45 is discussed separately from 85-19B and 85-20A.

84-45 contains: 1) quartz as both inclusions and a matrix phase, 2) clinozoisite inclusions restricted to
its inner core (inside marker A), 3) plagioclase zoned to higher $X_{Na}$, and 4) late-stage ferruginous phases (ilmenite, staurolite). The small initial decrease in $X_{Gross}$ in 84-45 is compatible with garnet growth by reaction (8) with increased temperature (Figure 5.11A). Phase equilibria presented earlier suggest that margarite is an unlikely mineral in ferruginous samples. The increased $X_{Gross}$ zoning near the rim is difficult to reconcile with increased T metamorphism and the phase relations, which suggest that plagioclase was the only Ca-rich phase other than garnet during the final growth interval.

The Mg-rich Type IV garnets (85-19B, 85-20A): 1) are quartz-free, 2) contain clinzoisite inclusions throughout, 3) coexist with plagioclase zoned toward high-Ca rims, 4) contain margarite inclusions, and 5) coexist with amphibole pseudomorphs. Reaction (10) with chlorite (Figure 5.11) could produce the initial Ca decrease in these samples with increased T and increased P. The increased Ca zoning at the garnet rims can be rationalized by prograde metamorphism in several quartz-free assemblages.

The high Ca, ubiquity of clinzoisite, and lack of Ca zoning in the Type V garnet suggest that it produced grossular component by reaction (8), (9) or (10).
The major element results and inclusion relations do not provide unambiguous answers to what the garnet growth reactions were, particularly in the calcareous subsystem. There is not a single smooth P-T path which can generate all the observed zoning profiles and phase relations in the modeled assemblages. The following problems remain: 1) were any high-Ca phases (clinozoisite, carbonate) present during the early metamorphism of the Type I and II garnets? 2) What reaction produced grossular component in the outer portions of the Type III garnets? 3) When did magnetite breakdown begin in the Type III garnet? 4) How was the increased $X_{Ca}$ zoning at the rims of Type IV garnets produced? 5) When did the amphibole pseudomorph producing reaction occur in the Type IV garnets?

5.9 GARNET GROWTH REACTIONS - TRACE ELEMENT CONSTRAINTS

This section attempts to: 1) review the effects of different metamorphic processes on major and trace element zoning in garnets, 2) predict trace element signatures of reactions 1 through 14, and 3) discuss the relation between element zoning and the reaction histories for the western Massachusetts samples.

The trace element results are referenced to the five types of Ca zoning profiles. Because garnet Types I and II are restricted to Goshen samples and Type III through V are found in the Waits River samples, this distinction
is essentially equivalent to dividing the samples on the basis of stratigraphic unit.

Trace element zoning in garnets from eight samples is presented in Figure 5.12 (a-h). The locations of these traverses are depicted in Appendix A. A representative traverse from each sample is shown; several samples (85-1B, 84-45, 85-19B, 85-21A) were traversed more than once and the overall details of multiple traverses from the same sample are similar. Rare earth element (REE) patterns from core to rim for five samples are presented in Figure 5.13 and locations of REE points are shown in Appendix A. REE were examined in at least one garnet from each Ca zoning type (except Type V) in order to constrain reaction histories within the calcareous subsystem.

Trace elements are divided into four categories: 1) buffered elements (Ti, Na), 2) manganophile elements (Sc), 3) calciphile elements (Y, Zr, REE), and 4) other elements (Li, V, Co, Cr). These rough divisions are not meant to suggest that these trace elements substitute for particular major elements; rather, they exemplify the strong connections between processes affecting major elements and those affecting trace elements. However, trace element abundances may more strongly respond to changes in both intensive and extensive variables than do
major elements, and may simplify differentiation between processes that identically affect major element zoning.

5.9.1 Processes controlling trace element zoning

Prior to examining the trace element zoning features of these garnets the effects of different metamorphic processes on element zoning are reviewed. Examples from the literature (particularly the other chapters of this thesis) and theoretical calculations are combined to highlight the first-order effects of a variety of metamorphic processes on trace element incorporation into metamorphic garnets.

Trace element abundances in a growing garnet are controlled in large part by partition equilibrium. The concentration of an element in a garnet's rim is given by $C_s = D^*(C_o)$, where $C_o$ is the effective bulk composition (EBC) in equilibrium with the garnet rim, and $D^* = \Sigma X_i D_i$ is the bulk partition coefficient (McIntyre, 1963). $X_i$ is the weight mode of phase $I$ in equilibrium with garnet, and $D_i$ is the mineral-mineral partition coefficient. Both the $X_i$ and the EBC are not easily defined in metamorphic rocks for kinetic reasons (see Chapter II). The bulk partition coefficient is a function of pressure, temperature, garnet composition, and the nature and abundance of minerals co-existing with garnet. Processes that control trace elemental composition during garnet
growth are similar to those proposed by many authors to explain major element zoning in garnet. These include: 1) simple Rayleigh-type fractionation (Harte and Henley, 1966; Hollister, 1966), 2) growth involving an assemblage-change, particularly if the assemblage change involves refractory minerals (Hollister, 1969; Kretz, 1973; Chapters II & III), 3) variation in garnet/mineral distribution coefficients caused by changes in pressure and temperature during metamorphism. (Cygan and Lasaga, 1982; Spear and Selverstone, 1983; Loomis, 1986), 4) disequilibrium partitioning (Loomis, 1982; Chapter III), 5) open system behavior due to influx of a fluid out of equilibrium with the mineral assemblage of the rock (Ferry, 1983; Ferry, 1987; Chapter II), 6) changes in trace element substitution mechanisms with P, T and composition (Chapter IV), 7) diffusional re-equilibration of garnet rims subsequent to peak metamorphic conditions (Dempster, 1985), and 8) polymetamorphism (Rumble and Finnerty, 1973; Karabinos, 1984). These processes are not independent of each other; several may operate together, or in different samples from the same metamorphic terrain.

5.9.1.1 Rayleigh fractionation

Closed system isothermal isobaric Rayleigh-type fractionation yields continuously decreasing core-to-rim
profiles for compatible trace elements, flat profiles for trace elements with bulk distribution coefficients near unity, and slightly increasing profiles for incompatible trace elements. Hollister (1966, 1969) argued that 'bell-shaped' Mn profiles were produced by Rayleigh fractionation. Rayleigh-type fractionation is an important control on trace element zoning in environments in which refractory minerals grow. As garnet itself is a refractory mineral, and several other minerals present in the western Massachusetts samples are refractory minerals, Rayleigh processes probably were important in the Shelburne Falls samples.

5.9.1.2 Assemblage change

An assemblage change in which a mineral that strongly accepts a trace element is produced or breaks down both affects the bulk distribution coefficient and can change the metamorphic EBC. If the assemblage change involves a refractory mineral, a mineral not in equilibrium with its surroundings due to sluggish intraminal diffusion kinetics, then internal metasomatism can occur and effects on trace element abundances in co-existing growing minerals are particularly significant (Chapter II). Breakdown or growth of a refractory mineral enriches or depletes the EBC in trace elements compatible in the refractory
mineral; the effect can be complex particularly if the refractory mineral is itself zoned in trace elements (Hollister, 1969; Kretz, 1973; Hickmott et al., 1987). Garnet, plagioclase, amphibole, clinozoisite, ilmenite, staurolite, phengite and minor phases such as zircon are all refractory minerals at mid-amphibolite temperatures. Their breakdown or growth will provide distinctive trace element signatures to growing garnets. This process was probably quite important in the western Massachusetts calc-pelites because of the ubiquity of refractory minerals in the rocks.

5.9.1.3 Disequilibrium behavior

Matrix-diffusion-controlled disequilibrium partitioning (Albarede and Bottinga, 1972) produces drop-offs in compatible elements in a growing porphyroblast due to near-rim solute depletion, and enrichments in those porphyroblasts in incompatible elements due to solute rejection, relative to simple Rayleigh fractionation (see Chapter III). Interface-controlled disequilibrium leads to enrichment of small highly-charged cations in growing porphyroblasts (Chapter III). Ti and Zr are the elements most strongly affected by interface controlled disequilibrium partitioning. Consideration of non-dimensional numbers arising during consideration of these effects suggest that these
phenomena are unlikely in a slowly heated regional metamorphic terrain such as western Massachusetts (Chapter III).

5.9.1.4 Open system behavior (External metasomatism)

External metasomatism of a fluid out of trace element equilibrium with the mineral assemblage of a rock produces enrichment or depletion in trace elements in growing porphyroblasts (see Chapter II). Such open-system behavior may most strongly affect trace element zoning for alkali metals. These are elements that probably have high solubilities in high temperature fluids (Eugster, 1981; Langmuir, 1982). No unequivocal examples of external metasomatism dominated garnet zoning profiles are reported in the literature. A more detailed discussion of this process is provided in Chapter II.

A change in fluid composition from a water-rich fluid to a CO₂-rich fluid could significantly change the solubility, and hence the transportability, of either a major or a trace element (Walther and Orville, 1983). Results presented in Chapter IV showed differences between trace element abundances in garnet in equilibrium with H₂O-rich fluid dominated regimes and CO₂-rich fluid dominated regimes. This process is difficult to identify in the western Massachusetts samples a priori; if unusual Na and Li humps are observed in the western Massachusetts
garnet zoning profiles external metasomatism may be considered likely.

5.9.1.5 Coupled substitution

Coupled substitution mechanisms may lead to complementary variations in trace elements that charge-balance each other's entry into a mineral's structure. For example, if Na+Ti=Ca+Al (the Ti-plagioclase substitution) is the primary Ti-substitution in garnet (Ringwood and Major, 1971), then concomitant increases and decreases in Na and Ti abundance may be expected (Dowty, 1971).

5.9.1.6 Variations in P and T

Mineral-mineral distribution coefficients, and therefore bulk D, vary as a function of pressure and temperature for all trace elements, but are most easily interpreted for elements (such as Ti and Na) that are essential structural constituents of phases co-existing with garnet (see Chapter IV). The activities of these two elements are buffered in metamorphic systems by equilibria with rutile or ilmenite+Fe-silicate, and plagioclase, respectively; the contents of Ti and Na in garnets may be strong functions of P and T but weaker functions of whole-rock bulk composition (see Chapter IV).
Previous studies of trace element zoning in garnet (Hickmott et al., 1987; Chapters II and IV) suggest that Ti-solubility in garnet decreases with both decreasing temperature and pressure in Ti-oxide bearing assemblages. Na appears to diminish in abundance in garnet with both decreasing pressure and increasing temperature (Chapter II and Chapter IV) in plagioclase-bearing pelitic assemblages. The apparent pressure and temperature dependence of Na content of garnet is problematic for two reasons: 1) in the presence of garnet of constant grossular activity, quartz, and an Al\textsubscript{2}O\textsubscript{3} buffer assemblage, the albite content of plagioclase increases with pressure, and 2) Na substitution may charge balance the entry of Ti or other highly charged cations into the garnet structure. The apparent increase in Na in garnet with pressure may represent a combination of effects: 1) an intrinsic rise in mineral-mineral distribution coefficient with pressure, 2) a change in Na-activity in a whole-rock system due to a change in plagioclase composition, and 3) Na-Ti coupled substitution.

The incorporation of other elements into garnet will show temperature and pressure dependences; however, these will vary markedly from assemblage to assemblage. It is difficult to differentiate between mineralogic and bulk-compositional effects in interpreting the P-T dependence of non-buffered trace element solubility in garnet.
Variations in Ti and Na in the western Massachusetts samples must be evaluated in terms of changes in pressure, temperature, and sodic-phase composition.

5.9.1.7 Polymetamorphism

Polymetamorphism involving multiple episodes of garnet growth in distinct P-T environments may impart abrupt breaks to garnet zoning profiles under mid-amphibolite facies conditions (Rosenfeld, 1968; Thompson et al., 1977; Karabinos, 1984; Rumble and Finnerty, 1974; Chapter IV). If resorption follows initial garnet growth then characteristic humps in garnet compatible elements (Mn, Y) are observed (Chapter IV). The textural and major element breaks in the western Massachusetts samples (84-48) suggest that polymetamorphism may have to be called on in interpreting trace element zoning profiles.

5.9.1.8 Retrograde reequilibration

Prior to a discussion of the relation between zoning patterns and prograde metamorphism it is necessary to evaluate the likelihood of modification of prograde zoning profiles by retrograde metamorphic processes. Such modification may be especially severe near the rims of garnets from polymetamorphic terrains, where garnet-compatible elements reincorporate themselves back into mineral surfaces exposed to the sample matrix by retrograde processes (Karabinos, 1984). Rule of thumb
(ROT) calculations and observations of natural materials are used to address the likelihood of modification of zoning profiles by retrograde processes at the pressures and temperatures of metamorphism in the Connecticut Valley Synclinorium.

The homogenization of garnet zoning at high metamorphic grade by diffusive processes is widely recognized (Tracy et al., 1976; Woodsworth, 1977). Partial re-equilibration of garnet zoning profiles near rims during cooling also occurs (deBethune et al., 1975; Dempster, 1984); however, the extent of such rim effects is not well-understood. In this section we evaluate the potential for modification of the near-rim portions of the western Massachusetts samples using ROT approximations and experimental Mg self-diffusion coefficients.

Diffusion equations for garnet reequilibration that include provision for temperature effects on both diffusion coefficients and partition coefficients as well as moving grain boundaries are not analytically tractable. Because of the complexity of the diffusion problem involved in re-equilibration of a retrograded garnet we utilize the simplest possible model that may provide insights into the diffusional re-equilibration of cooling garnets, the rule of thumb $x = \sqrt{Dt}$ (Crank, 1975;
Freer, 1981), to estimate characteristic diffusion penetration time scales in retrograding environments.

D is calculated at each temperature and the ROT is solved at penetration distances of 10 and 100 microns. The diffusion coefficient at a given temperature is described using an Arrhenius relation: \( D = D_0 \exp(-E/RT) \), where \( D_0 \) is the diffusion coefficient at infinite temperature, and \( E \) is the activation energy of the diffusive process. Calculations presented use values of \( D_0 \) (9.8x10^{-9} m^2/sec) and \( E \) (239 kJ/mole) from Cygan and Lasaga (1985). Use of coefficients presented by Lasaga et al. (1977) or Elphick et al. (1985) do not significantly modify the results presented below.

Temperature-time-transformation (T-T-T) diagrams (Putnis and McConnell, 1980; Dempster, 1984) are often used to evaluate whether a kinetically-limited transformation proceeds to completion during a specific time interval at a given temperature. Figure 5.13 displays ROT characteristic penetration times on a T-T-T diagram.

The T-T-T diagram in Figure 5.13 suggests that: 1) measurable near-rim (10 micron) compositional change is predicted at mid-amphibolite temperatures over reasonable cooling/retrogradation time-scales (0.1-10 million years,
and 2) significant re-equilibration over length scales of 100 microns is not likely at mid-amphibolite conditions.

Previously investigated natural examples also demonstrate that small-scale re-equilibration of amphibolite facies garnets is common. Dempster (1984) documents minor (Fe/(Fe+Mg)) retrogradation of garnet rims to depths of 50 microns from garnet surfaces at upper-staurolite grade whereas Spear and Rumble (1986) postulate shortening of calculated P-T paths due to smoothing of garnet zoning profiles in staurolite grade samples from western New Hampshire.

Many mid- to upper-amphibolite grade garnets (Tracy et al., 1976; Spear and Rumble, 1986; Tracy, 1982) do not show extensive near-rim re-equilibration or are re-equilibrated solely adjacent to ferromagnesian minerals. This observation is problematic in light of the calculations; these suggest that near-rim retrogradation should be ubiquitous at mid- to upper-amphibolite temperatures. The extent of re-equilibration is strongly dependent on kinetic factors affecting the matrix around garnets, particularly the availability of fluids to drive retrograde net-transfer reactions and flux ion movement during retrogradation.
Kinetic models of retrograde exchange that do not take the chemical driving force of diffusion into account are of limited utility. Neither the ROT nor the Dodson equation (Spear and Hodges, in prep.) explicitly take the partial molar enthalpy, volume and entropy of retrograde exchange reactions into account, and hence are only applicable to natural cooling systems over restricted cooling paths. The driving force for a retrograde exchange is dependent on retrograde P-T path; in a worst case, a cooling path corresponds to a compositional isopleth for an element, and no diffusion occurs.

5.9.1.9 Minor phase involvement

Trace element enriched minor phases (allanite, xenotime) are present in the western Massachusetts calc-peoples (see Table 5.3). The trace element budgets of crustal igneous systems are dominated by trace element enriched minor phases (Gromet and Silver, 1983; Sawka and Chappell, 1985; Rapp and Watson, 1986). Do interpretations of trace element variations in crustal rocks solely reflect breakdown and growth of minor minerals?

As one end-member, if thermodynamic equilibrium applies in a metamorphic system the co-existence of zircon + quartz, xenotime + apatite + silicates, and allanite + silicates buffer the activities of Zr, Y and
Ce in fluid-bearing metamorphic systems (at constant P, T and fluid composition) by hydrolysis reactions such as:

\[(15) \text{ZrSiO}_4 + 4\text{H}^+ = \text{SiO}_2 + \text{Zr}^{4+}_{\text{aq}} + 2\text{H}_2\text{O} \]

Trace elements that are not essential structural constituents of minor phases (i.e. HREE in xenotime) are not buffered in a thermodynamic sense, but rather by the strong element compatibility in the minor phase leading to "pseudo-buffering" by a domination of the bulk distribution coefficient by the minor phase.

As the other end-member, the minor minerals are inert. They do not interact with a reacting metamorphic system due to sluggish intra-mineral, surface kinetic, or intergranular kinetic effects.

The following criteria suggest that zoning for most trace elements does not solely reflect equilibrium with trace element saturating phases (Figure 5.12 and 5.13):
1) major elements and trace elements vary simultaneously and the trace elements respond to petrogenetic events that also affect major element concentrations (changes in P, T, and composition), 2) variation of abundances of Y and Zr are often extremely large, as at point A of 34-48. Such major variations are unlikely to be due to P-T effects on the equilibrium constant for reactions such as reaction (15), and 3) garnet core compositions of Y and Zr vary roughly sympathetically with whole-rock Yb and Hf. If Zr and Y compositions were buffered, a smaller
range of core abundances would be expected.

However, some buffering of LREE and Y may occur in certain samples. LREE variations are significantly smaller than HREE variations despite involvement of LREE enriched minerals such as clinozoisite and hornblende in garnet growth reactions. Elements of similar size and charge are decoupled; for example, Y and Yb variations are not always parallel. In xenotime bearing sample 84-45, Yb varies by a factor of over two orders of magnitude and Y varies by a mere factor of ten.

This evidence suggests that the minor phases influence, but probably do not dominate, trace element behavior in the western Massachusetts samples. Geologic reality lies between the two end members delineated above.

5.9.2 Predictions of effects of reactions on garnet zoning

Reactions 1 through 14 each impart a trace element signature on garnet. These signatures are predicted on the basis of garnet-mineral partition data and an understanding of the identity of refractory minerals in this suite of samples. Trace element signatures are most strongly recorded in garnets when refractory minerals that have characteristic trace element compatibilities are involved in garnet growth reactions (Chapter II, Chapter IV). Refractory minerals found in these calc-
pelites include amphibole, clinozoisite, ilmenite, plagioclase and garnet. These are all minerals that are frequently zoned at amphibolite facies P-T conditions (Tracy, 1982).

Trace element compatibilities in metamorphic minerals relative to garnet were reviewed for each mineral earlier in this paper on the basis of ion yields and in Appendix II on the basis of trace element determinations of mineral separates. Mineral-mineral REE partition coefficients are also presented in Table 5.7. Generalizations about the trace element in refractory minerals in these samples are: 1) hornblende is MREE enriched compared to co-existing garnet (see also chapter II); 2) clinozoisite contains slightly more Sc and V and significantly more of all the REE than co-existing garnet (factor of more than 10 for Yb); 3) ilmenite is V enriched compared to coexisting garnet; 4) magnetite is Co enriched compared to garnet; 5) plagioclase develops strong positive Eu anomalies relative to co-existing garnet, and 6) garnet takes in more Sc, Mn, Y, and HREE than any of the major minerals in these calc-pelites, except for clinozoisite. The elements listed above for each refractory mineral are referred to as characteristic elements.
Table 5.8 summarizes the garnet growth reactions of an earlier section. Each reaction will impart a different signature on garnet's trace element zoning profiles. The predicted trace element effects are also summarized in Table 5.8. A refractory mineral growing coevally with garnet depletes the EBC in equilibrium with garnet in its characteristic elements, and leads to 'bell-shaped' zoning in the characteristic element in all growing refractory minerals. A refractory mineral breaking down during garnet growth enriches the EBC in its characteristic elements, and leads to internal metasomatism induced humps in growing refractory minerals (Chapter II). The extent of these effects depends on mass balance constraints: plagioclase is strongly Eu enriched, relative to the other REE, but its low bulk REE abundance suggests its involvement in a metamorphic reaction will minimally effect the EBC. In contrast, involvement of small modal amounts of clinzoisite in garnet growth reaction has profound effects on Y and REE abundances in garnet, because of its trace element enriched nature.

Reaction (1) releases MREE from amphibole, reactions (4) and (5) release a small amount of V from ilmenite, reactions (7), (13) and (14) may enrich the EBC in Eu relative to the other REE, and reactions (8), (9) and (10) each release Y and the REE. Garnet growth by all of
the tabulated reactions fractionates Mn, Sc, and the HREE (except in the presence of clinohumite). Plagioclase growth with garnet, by reactions (1), (8), and (9), may reduce Eu anomalies in growing garnet.

5.9.3 Trace element zoning

Trace element zoning can provide information on a wide variety of metamorphic processes (Chapter II, Chapter III, Chapter IV). On the basis of the review of processes controlling trace element zoning presented above, Rayleigh fractionation, assemblage change/internal metasomatism, polymetamorphic effects and pressure-temperature effects on trace element partitioning are likely to be important in the western Massachusetts samples.

The two goals of the exposition of trace element zoning are: 1) to identify periods of change in pressure and temperature during garnet growth, and 2) to constrain more accurately the mineralogy during each episode of garnet growth. Thus, buffered trace elements are first used to identify locales where P-T variations may have occurred, and then calciphile trace elements are used to investigate garnet growth in the calcareous subsystem.

Quantitative modeling of the trace element features described below is complicated by: 1) a lack of accurate partition coefficient data for metamorphic minerals at
any pressures and temperatures, and 2) difficulties in determining the size of the system in equilibrium with growing garnet. How much of a zoned mineral will chemically communicate with the growing exterior of garnet? This problem is particularly acute for trace element enriched minor minerals, such as zircon.

As a first approximation, mass balance constraints on proposed reactions can be obtained using a closed-system Rayleigh fractionation expression:

\[ C = D \times C_0 (1 - W_g)^{D-1} \]

(Hollister, 1969) where \( C \) is the weight fraction of an element in a growing mineral, \( C_0 \) is the weight fraction of an element in the growth system (however it is defined) at the initiation of a mineral growth event, \( W_g \) is the weight-fraction of the mineral grown, and \( D \) is the bulk distribution coefficient, defined previously as \( \Sigma X_i D_i \). \( D_i \) is a mineral-mineral distribution coefficient, and \( X_i \) is the weight fraction of mineral i that is effectively in equilibrium with the growing refractory mineral. \( X_i \) does not necessarily correspond to a weight mode, as is assumed for igneous systems, for a zoned mineral. Chapters II and III demonstrate that simple Rayleigh fractionation is not a valid model for trace element zoning in most metamorphic mineral growth environments; however, it provides the best approximation available for modeling short periods of mineral growth in
which equilibrium assemblages do not change, the size of an equilibrating system remains constant, and bulk partition coefficient does not change.

5.9.3.1 Buffered elements

Titanium and sodium are major elements in the minerals rutile and ilmenite or white mica and plagioclase, respectively. The chemical potential of Ti and Na components in garnet are therefore buffered by phase relations with these minerals in a rock (see chapter IV). Thus, at equilibrium, their zoning may reveal changes in pressure, temperature, and phase relations of sodic and Ti-rich minerals during garnet growth.

Titanium zoning shows a rough decrease from core to rim in virtually all samples (84-48 is an exception). The precision of Ti/Si ratios is roughly +/- 10%, so interpretation of fine-scale structures superimposed on the overall core to rim Ti decreases is difficult. However, several samples clearly show departures from continuous core-rim Ti zoning. Na/Si exhibits both core to rim decreasing profiles, and profiles characterized by minimal zoning.

Type I garnets (85-1B, 85-10B) exhibit strongly Ti-decreasing profiles near their rims. The two Type I samples from the Goshen Formation also show a core to rim
decrease in Na/Si (0.0006-0.0003 and 0.0007-0.0003 respectively), with the drop-off concentrated primarily in the outer few dozen microns. This Ti/Si and Na/Si dropoff correlates with the Ca dropoff described earlier.

85-2A, a Type II garnet, displays a Ti and Ca trough midway through its profile. Its Na profile roughly mimics Ti and Ca. Na/Si in the graphite-free core of this sample is at a moderate level (0.0005), drops somewhat, then increases slightly before a final rimward dropoff. Ti, Na and Ca all dip in abundance at a break between graphite-rich garnet and graphite-poor garnet (point A).

The coupling of Na and Ti with the Ca decrease at points A in both the Type I and Type II garnets either represents a change in P-T conditions, or a coupled change in Na\(^+\)\(_{aq}\) and Ti\(^+4\)\(_{aq}\) activity. This zoning suggests a change in intensive parameters (P, T or fluid composition) during garnet growth. The overgrowths of ilmenite on rutile in the matrices of these samples suggests that an isothermal isobaric decrease in Ti\(^+4\)\(_{aq}\) activity due to replacement of rutile by ilmenite could explain the Ti dropoff in garnet. However, in an isothermal/isobaric metamorphic environment, a parallel variation in the activities of Na\(^+\)\(_{aq}\) and Ca\(^+2\)\(_{aq}\), leading to parallel Ca and Na zoning, is unlikely in a plagioclase bearing rock. An increase in the albite content of plagioclase should lead to antithetic changes
in the activities of Na\(^+\) and Ca\(^{2+}\) in a metamorphic environment. In Chapter IV a correlation between decreased pressure and decreased Ti and Na in garnet was noted; thus the Type I and II near-rim zoning suggests that these Goshen garnets grew in response to a decrease in pressure.

The Waits River samples have variable Ti/Si and Na/Si behavior. Type III garnet, 84-48, shows flat Ti/Si except at the rim, where Ti/Si drops, and a flattish Na/Si profile (≈ 0.0008) from core to point A, then a slight decrease in Na/Si to 0.0007. The break in major and buffered trace element zoning at point A suggests a hiatus in garnet growth during which intensive variables changed. However, unlike at the Type I and Type II garnet rims, Na and Ca variabilities are antithetic. Thus, an isothermal, isobaric change in plagioclase composition could conceivably explain the Na/Ca variability. A change in P-T conditions across break A can neither be ruled out nor substantiated.

Type IV sample 84-45 exhibits a decrease in Ti to the same points where Ca content is a minimum (Point A). The Na/Si in garnet 84-45 increases from 0.0007 to 0.0009 at point A, drops to 0.0005 at point A, then maintains a fairly flat profile to the rim.

Ti abundance in other Type IV and V garnets decreases from core to rim. With the exception of 84-45,
Type IV and the Type V garnets display fairly constant Na/Si between 0.0005-0.0006. 85-19B displays the most irregular Na profile, and may contain many Na-rich microinclusions.

5.9.3.2 Mn sensitive elements

Sc profiles roughly mimic Mn profiles except near sample rims. Each of these two garnet compatible elements initially decrease from cores outwards in virtually all of the samples. Type I samples 85-1B and 85-10B show Mn increases decoupled from Sc at the rim; the increase in 85-1B is larger than that in 85-10B. Type II sample 85-2A exhibits a small Sc dip at the Mn hump. Each of these locales showing decoupling of Mn and Sc occur where Ca, Na and Ti all decrease.

Once again, the three Goshen garnets display similar element behavior in portions of the zoning profiles in which the buffered elements decrease. Sc and Mn, both highly compatible elements in garnet, are decoupled at the buffered element decrease. This information further supports the interpretation of the Type I and II garnets' zoning profiles in terms of a variation in intensive parameters rather than effective bulk composition and suggests that over the P-T path of these samples, Sc has the same sense of P-T variability as Na and Ti and Mn has the opposite sense of variability.
Sc in Type III through V garnets drops from core to rim. Generally, this Sc decrease parallels Mn, an exception being at the rim of 85-19B, where Sc and Mn are decoupled. Because Mg/Fe also reverses in this interval it too probably represents a change in P-T path.

5.9.3.3 Ca sensitive elements

Y, Zr and the REE may be particularly useful for monitoring reactions involving calcareous minerals such as clinozoisite, plagioclase, and amphibole. These mineral are enriched in large radius trace elements, and Y, Zr, and REE discontinuities often occur at points in the garnet zoning profile where Ca profiles display inflections or discontinuities. An important problem is determining when these Ca breaks and associated trace element breaks represent a change in assemblage, when they represent a change in P-T conditions, and when they represent both. In order to distinguish between these processes the Type I and II garnet profiles that probably developed during changing P-T conditions are considered first.

In the Type I garnets an increase in Y near the rims correlates with a decrease in Ca and buffered element abundance. 85-1B has simple continuously decreasing REE zoning (Figure 5.13) up until the point where the buffered trace element decrease begins. Throughout this
interval no negative Eu anomaly is present in garnet. However, the near rim point (point 1) in the low Ca-Na-Ti zone has higher abundances of all the REE than any of the interior points, and has a small but distinct negative Eu anomaly.

The enrichment of both compatible (HREE) and incompatible (LREE) elements in the near-rim low Na-Ti-Ca zone of 85-1B suggests antithetic Na-Ca-Ti and REE P-T variability over the P-T path of these samples. The larger magnitude of this enrichment for the HREE than the LREE suggests either a component of compatible element re-incorporation in 85-1B during formation of the buffered element declines, or a greater dependence of HREE than LREE partition coefficients on the intensive variables that changed during this interval. The presence of a negative Eu anomaly solely in the outermost rim point suggests: 1) that a large amount of Eu-rich plagioclase grew during or preceding the final episode of garnet growth, or 2) that f(O₂) decreased during the second episode of garnet growth, leading to an increase in Eu⁺²/Eu⁺³ in the metamorphic environment or 3) that large amounts of Eu⁺²-rich fluid were devolatilized out of the system prior to the final episode of garnet growth. Debye-Huckel theory predicts that Eu⁺² should be more soluble in metamorphic fluids that Eu⁺³. A study of
REE zoning in the plagioclase coexisting with garnet could perhaps resolve this question.

Table 5.8 suggests likely garnet growth reactions in the ACN subsystem. Variations in the calciphile elements that correlate with Ca, Na and Ti variability are not interpreted in terms of changes in mineral assemblage, because these portions of the zoning profiles appear to have formed during changes in intensive parameters (P, T and fluid composition). The initial formation of grossular component of garnet in 85-1B was probably by reactions (7), (13) or (14). Each of these reactions should produce the observed decreases in Mn, Sc, Y and the HREE. The Y zoning does not decrease strongly from core to rim. As suggested earlier xenotime may partially buffer the Y abundance in metamorphic garnets and is present in 85-1B. Reaction (7) is less likely because there are no margarite inclusions in garnet. Because each of these reactions has anorthite as a reactant, one might expect to see Eu enrichment accompanying HREE depletion.

Type II garnet 85-2A exhibits a hump in the abundance of the calciphile elements Y and the REE (85-2A, REE point 5) at the point where Ca and the buffered trace elements decline. The REE behavior in the core of this garnet differs from that in the Type I garnet in that there is no continuous decrease in HREE abundances. Rather, points 2 and 3 exhibit higher HREE abundances
than the core (point 1); this HREE increase is not
coupled with a strong Y increase. No negative Eu anomaly
is present in 85-2A, in fact the outermost rim points (6
and 7) have a slight positive Eu anomaly. The Type II
garnet (85-2A) exhibits increased HREE abundances from
points 1 to 3, accompanied by Sc and Mn depletion. Point
4 shows universal REE depletion. At point 5, the Y, Mn
and Sc hump, all of the MREE and HREE rise by over a
factor of two. In the outer, graphite-rich portion of
the garnet (points 6 and 7) Yb and Er are fractionated
relative to Dy, and Sm and Nd abundances are higher than
in the core.

Table 5.8 suggests the core's trace element
signature is compatible with garnet growth by reaction
(8). Further growth may be by reactions (13) or (14) for
similar reasons to those outlined for the Type I garnets.
The outer portion of 85-2A's profile is graphite-rich and
its core is graphite free, thus reaction (13) is likely
to have operated in the outer portion of the garnet.

Type III garnet 84-48 displays no Na, Ti or Ca
zoning that is compatible with significant changes in
intensive variables. Its calciphile elements are
interpreted in terms of metamorphic reactions. 84-48 is
the most REE-enriched bulk composition and has the most Y
and HREE-enriched core (points 1-2) (Figure 5.12) of any
of the studied samples. Nd abundances in the core are low
and no Eu anomaly is apparent, despite the whole-rock Eu anomaly and the Eu anomaly at the rim. Y and the HREE plummet in 84-48 at point A, accompanying the increase in Ca and V and the drops in Li, Na, Sc, Fe, and Zr. Moving rimward, the Y depleted region is characterized by lower HREE abundances (point 3-7) and an obvious negative Eu anomaly. Point 4 shows a Yb enrichment relative to Point 3, and Point 5 shows a general LREE enrichment. Towards the rim (points 6-7) further decreases in all the HREE are visible.

Initial garnet growth in the Type III garnet was followed by an interval during which refractory minerals enriched in Zr, Y, Eu, and the HREE must have grown. The magnitude of the decrease in Y, Zr, and the HREE and the formation of a Eu anomaly during this interval cannot be solely due to P-T effects. Y, Zr and the HREE drop by a factor of greater than five, which is more than twice the size of the Y decrease seen over a 200° interval in a Bellows Falls sample (see Chapter IV). One or more refractory phases grew during the garnet growth hiatus. These minerals were probably clinzoisite and/or plagioclase; clinzoisite is strongly enriched in Y and Zr compared to garnet (based on ion yields), and plagioclase preferentially incorporates Eu$^{+2}$ relative to the other REE at low f(O$_2$) (Drake and Weill, 1975). In 84-48, as in several of these rocks, the Sm and Nd
variations do not support involvement of refractory clinozoisite in garnet growth reactions. Yb/Sm ratios drop from 83 to 22 between points two and three, Sm falls slightly in abundance from 0.67 to 0.49 ppm, and Nd actually increases in abundance. Both Nd and Sm are much more compatible than Yb in clinozoisite compared to co-existing garnet (over two orders of magnitude difference). Growth of refractory clinozoisite accompanied by simple fractionation should yield an increase in Yb/Sm ratio in garnet. Yet, the data suggest that the bulk partition coefficient for Sm was near one. None of the major minerals in this rock (plagiocline, micas, chlorite, oxides) partition LREE strongly enough to yield a low equilibrium bulk distribution coefficient. Allanite is present in the rock, and may buffer the LREE abundances in garnet (Gromet and Silver, 1983). The development of a negative Eu anomaly between points 2 and 3 immediately suggests growth of refractory plagioclase during this growth interval; however, if the LREE are buffered by a minor phase, the dropoff in Eu/Sm could possibly be ascribed to clinozoisite fractionation. Mass balance constraints require a bulk D (plag/EBC) of 12 to deplete Eu sufficiently across interval 2 to 3 by Rayleigh fractionation, even allowing all the presently observed modal plagioclase to grow during this interval. Epidote/plagioclase Eu distribution coefficients are
large (>250; (Gromet and Silver, 1983) so a much smaller amount (< 1%) of clinozoisite could deplete Eu and the heavy REE to the required degree. A reaction history compatible with the observed trace element zoning is: 1) initial garnet growth prior to clinozoisite nucleation, perhaps by a reaction such as (13), 2) a period of clinozoisite +/- plagioclase growth during which garnet did not grow or was resorbed, 3) garnet growth by a reaction such as (8) that leads to Y and HREE enrichment of garnet and final garnet growth by a reaction such as reaction (13) or (14).

Type IV garnets (84-45, 85-19B, 85-20A) have similar Ca zoning profiles to each other but different calciphile element zoning and phase relations. Thus, although 84-45 and 85-20A have similar Ca profiles, they have different reaction histories. 85-20A and 85-19B are of similar bulk composition, and have similar trace element zoning, thus calciphile elements in 84-45 and 85-20A are compared. The primary difference between these samples is in Y and REE zoning.

84-45 has a strongly HREE enriched core (Points 1 and 2) with a minor negative Eu anomaly (Figure 5.13). Points 3 and 4 are strongly Yb depleted relative to the core (factor of over 50), moderately Dy depleted, and Eu and LREE enriched relative to the core points. Continued growth was accompanied by Dy, Er, and Yb enrichment
(through point 6), whereas the LREE maintain fairly constant abundance levels. The outer portions of 84-45, rimward of the break in inclusions, are further depleted in all the REE.

The humps in Y, Zr the HREE are due to a change in garnet growth reaction from one in which clinzoisite was a reactant to one characterized by a different Ca-bearing phase as a reactant. Clinzoisite provides Y, Zr and REE to the EBC during its breakdown, particularly if it had an allanite core. This locale corresponds with the textural break in the garnet rimward of which no clinzoisite inclusions are found (Appendix A). Garnet growth in 84-45 just prior to this textural break was by reaction (8), and growth in the core may have been by reaction (13). Later growth was probably by (13) or (14). The increased magnitude of the Eu anomaly in this outer interval suggests that plagioclase was also a product mineral.

85-20A has a flat Y abundance in its core and exhibits an increase prior to point A, whereas 84-45 displays a more pronounced Y spike at its Point A. A pronounced negative Eu anomaly is present in points 1 through 5 in 85-20A. The Eu anomaly deepens throughout this interval (Sm/Eu ranges from 3.6 at point 1 to 4.2 at point 5) suggesting concomitant growth of garnet and
plagioclase. HREE patterns fluctuate within these five points, whereas the LREE continuously diminish in abundance from the core (point 1) to point 6. Points 7 and 8 display no significant Eu anomaly; Eu, Dy, and to a lesser extent Er and Yb concomitantly rise from point 6 to points 7 and 8.

The combined fractionation of Mn and Sc, and the continued growth of the Eu anomaly suggest initial garnet growth (up to point A) by either reaction (8) or (10). The absence of quartz and presence of margarite inclusions in this sample suggests reaction (10) is more likely. The lack of a Eu anomaly and increase in Dy abundance at the rim of garnet suggests that the second episode of garnet growth in 85-20A (REE points 6-8) was by amphibole breakdown (reaction 1). In an Alpine garnet (Chapter II) in which epidote and garnet were co-products in an amphibole breakdown reaction, an Y increase is seen in garnet during hornblende breakdown. Hornblende is a refractory mineral, so its breakdown releases elements into the system in equilibrium with garnet. An amphibole in this Alpine sample was strongly MREE (including Eu) enriched. 85-20A also contains distinctive amphibole pseudomorphs. Similar explanations may hold for 85-19B and 85-21A, based on similarities to 85-20A in major and
abundant trace elements, and the ubiquity of amphibole pseudomorphs.

5.9.3.4 Insensitive elements

Li drops slightly in abundance or remains flat from core to rim in most of the calc-pelites, except 84-48 in which a decrease in Li abundance occurs at point A. V decreases in abundance or remains flat in all the samples save 84-48, where a small drop occurs at point A. Cr roughly declines in abundance in all the samples except 84-45 and 84-48, where a Cr enrichment occurs at point A in the former, and Cr increases continuously towards the rim in the latter. Co increases in abundance from core to rim in all the samples. Note that sample 84-48, which contain Co-rich magnetite inclusions in garnet, exhibits the largest Co-increases near garnet rims.

The insensitive elements are contained primarily in AFM silicates and oxides. The two refractory minerals that accept large amounts of these elements are ilmenite, which accepts significant V, and staurolite which accepts significant Li. The lack of humps and radical depletions of Li and V in the garnet zoning profile suggests minimal involvement of these phases in garnet growth reactions.
5.9.4 Summary of Observations and Processes

Garnets from the two structural levels have distinct major and trace element characteristics. The Goshen samples (Type I and Type II) all exhibit an interval in which buffered major and trace elements (Ca, Na, Ti) drop in abundance. 85-2A, the most calcareous Goshen sample, underwent a second episode of garnet growth after this dropoff. In contrast, none of the Waits River samples (Types III through V) exhibits large decreases in the buffered trace elements. However, they do display complex zoning patterns in the calciphile elements (Y, Zr, and the REE) suggesting varied reaction histories, including assemblage changes involving plagioclase, clinzoisite, and amphibole.

5.10 REACTION HISTORIES

The trace element zoning, inclusion relations, and consideration of directions of phase volume movement in theoretical assemblages can be combined to place limits on garnet growth reactions in the subsystems AFM and ACN.

5.10.1 AFM

5.10.1.1 Goshen Fm

All of the garnets are zoned toward lower (Fe/(Fe+Mg)) at their rims, and none exhibit enrichments in ilmenite-compatible elements (V). Thus, the
ferromagnesian component of garnet probably formed by reaction (3) in all of the Goshen assemblages. Quartz is present in all of the Goshen samples so reaction (6) is not likely. Ilmenite is a matrix phase in these samples, but overgrows early rutile and appears to have developed after garnet growth in the Goshen samples.

5.10.1.2 Waits River Fm

The Waits River samples have experienced more complicated AFM reactions than the Goshen samples. 84-45 contains chlorite inclusions, matrix quartz, and uninflected V and Co zoning; thus it provides no evidence for garnet growth by reactions other than reaction (3). 84-48 has experienced both reaction (3), in its quartz and chlorite-rich core, and reaction (12) based on magnetite inclusions and the increase in the Fe-oxide-compatible element Co. 85-19B, 85-20A, and 85-21A initially produced ferromagnesian component through reaction (5) or a non-modeled reaction containing amphibole. Secondary garnet growth was probably by a combination of reactions (1) and (4). These samples contain no quartz, either as a matrix phase, or as inclusions in garnet, and exhibit rimward decreasing ($\text{Fe}/(\text{Fe}+\text{Mg})$) values.
5.10.2 ACN

Reactions in ACN are also determined based on inclusion relations, trace element zoning, and major element zoning. Although clues to the nature of the calcareous phases providing Ca for growth of the grossular component of garnet are provided by the trace element zoning, accurate determinations of when margarite, carbonate, clinzoisite, plagioclase and amphibole participated in the garnet growth reactions are not possible.

5.10.2.1 Goshen Fm

The relatively unzoned, high $X_{\text{Gross}}$ garnet cores, lack of clinzoisite inclusions, and lack of REE enrichment or depletion preclude involvement of clinzoisite in early garnet growth in 85-1B and 85-10B. Thus, the Goshen samples may have initially grown grossular component by reaction (13) or (14), although 85-2A may have experienced growth by reaction (8). The absence of a pronounced Eu anomaly, either positive or negative, in plagioclase-bearing rocks suggest that plagioclase was not growing in significant amounts during garnet growth. Later garnet growth/equilibration in 85-1B and 85-10B was probably by reaction (14); in this assemblage $X_{\text{Gross}}$ in garnet decreases along with an increase in albite content of plagioclase.
5.10.2.2 Waits River Fm

The Waits River samples display complicated Ca zoning profiles and inclusion relations.

No Eu anomaly is visible in the garnet core of 84-48, and Y and HREE abundance are high. 84-48 (Type III) probably developed earliest garnet by reactions with carbonate (reaction 13). After an interval in which clinzoisite and plagioclase grew, garnet growth began by a reaction such as (8) or (10). 85-19B and 85-20A (Type IV) have similar major and trace element zoning. Initial grossular component was probably produced by reaction (8) or (10). The slight decease in Ca, gradual increase in Y, decreasing LREE abundances, and presence of a deepening Eu anomaly in garnet, suggest that plagioclase grew at the same time as garnet. Growth by this reaction is hypothesized to have ended at point A (the Ca trough) in both samples. The second episode of garnet growth is probably by reaction (1). Margarite is a possible product because it is found as inclusions in these low (Fe/(Fe+Mg)) samples.

84-45 (Type IV) may have produced grossular component initially by reaction (13), as deduced from the absence of a Eu anomaly and the high HREE content in the core. An episode of growth involving clinzoisite followed (reaction (8)). Clinzoisite inclusions are
confined to the interior of the garnet and the Y, Zr, and REE plateau is in accord with breakdown of refractory clinozoisite; the increasing Eu anomaly suggests continuous plagioclase growth throughout this interval. The final grossular-producing reaction may be (13) or (14); plagioclase becomes more Na-rich, however, the negative Eu anomaly increases in magnitude rather than decreasing.

5.11 IMPLICATIONS FOR P-T PATHS

The P-T-deformation history of these samples during garnet growth is roughly constrained by the inclusion relations, trace element zoning, and phase relations of the samples. Earliest garnet growth accompanied $F_2$, and occurred at high pressure. Evidence for early high pressure is provided by: the coexistence of rutile, Ca-Fe-rich garnet and plagioclase in garnet cores, the presence of phengite-rich micas in garnet cores, the high Ti in garnet cores, and the ubiquity of rutile rather than ilmenite as primary Ti-oxide inclusions. Static growth subsequent to $F_2$ was apparently accompanied by minor decompression, based on the Ti zoning. $F_3$ deformation (doming) led to strong decompression in the near-dome Goshen rocks, manifest in the near-rim Na, Ca and Ti decrease and the ilmenite overgrowths on rutile. The dips in the Ca and Ti profiles of 84-45 suggests
minor decompression during garnet growth in the Waits River samples. A final episode of garnet growth with increased temperature and pressure may be indicated by the Ti and Ca increased profiles in 84-45 and 85-2A.

5.12 CONCLUSIONS

Phase equilibria, major element zoning in garnets and trace element zoning in garnets have been investigated in calc-pelites of varying Fe/Mg ratio from Goshen and Waits River Fms in the NW Shelburne Falls quadrangle, MA. In several Waits River samples trace element zoning appears to be genetically related to mineralogical changes (reaction histories) determined through major element investigations, whereas in other samples (particularly from the Goshen Fm) trace element variability appears to reflect changing intensive variables during garnet growth.

Trace element zoning suggests involvement of trace element enriched phases in garnet growth reactions that is in accord with phase equilibria, major element zoning and textural constraints on garnet growth reactions:
1) Y, Zr and heavy REE increases appear to accompany clinzoisite involvement as a reactant in garnet growth (i.e. 84-45).
2) Middle REE increases may correlate with amphibole breakdown during garnet growth (85-20A).
3) Co increases accompany magnetite involvement in garnet growth (84-48).

4) Y, Zr and heavy REE decreases in garnet may be caused by clinozoisite growth (84-48).

The zoning of the buffered trace elements, Na and Ti, often parallels Ca zoning, particularly in the Goshen samples (85-1B, 85-2A, 85-10B). This parallel zoning requires a change in intensive parameters during garnet growth. Y, Mn and the REE appear to have the opposite P-T dependence from Na, Ca and Ti over the P-T-fluid path of the Goshen samples.

Trace element zoning appears to be capable of providing additional information on both P-T paths and reaction histories during garnet growth. In a complex metamorphic terrain such as western Massachusetts, trace element zoning aids in interpretation of major element zoning that could be interpreted in terms of either P-T variability, or assemblage changes during metamorphism. At present mineral-mineral partition coefficients and their temperature dependence are not constrained sufficiently to allow quantification of the processes suggested by the trace element zoning. Nonetheless, this example demonstrates the power of trace element zoning to reveal the dynamics of metamorphism during garnet growth in a complicated metamorphic terrain.
Table 5.1A: Analyses of standard rock GSP-1 measured during analyses of western Massachusetts calc-pelites. T. Furman XRF operator. One-sigma in parentheses. Consensus values from Gianniny and Burns (1983).

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<tr>
<th></th>
<th>this (avg. of 5)</th>
<th>consensus values</th>
</tr>
</thead>
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<tr>
<td>SiO₂</td>
<td>67.25 (0.03)</td>
<td>67.37</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.67 (0.01)</td>
<td>0.66</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>15.10 (0.01)</td>
<td>15.16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.26 (0.02)</td>
<td>4.32</td>
</tr>
<tr>
<td>MnO</td>
<td>0.04 (0.00)</td>
<td>0.04</td>
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<tr>
<td>MgO</td>
<td>1.07 (0.02)</td>
<td>0.99</td>
</tr>
<tr>
<td>CaO</td>
<td>2.02 (0.00)</td>
<td>2.04</td>
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<tr>
<td>Na₂O</td>
<td>3.26 (0.05)</td>
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<tr>
<td>K₂O</td>
<td>5.51 (0.01)</td>
<td>5.50</td>
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<tr>
<td>P₂O₅</td>
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<tr>
<td>Total</td>
<td>99.46 (0.05)</td>
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Table 5.1B: Multiple analyses of splits of 85-19B; (Waits River). T. Furman XRF operator.

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<th>large 50 gm</th>
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<th>rusty 15 gm</th>
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<tr>
<td>SiO₂</td>
<td>45.33</td>
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<td>TiO₂</td>
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<td>26.95</td>
<td>26.35</td>
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<td>Fe₂O₃</td>
<td>9.56</td>
<td>10.56</td>
<td>8.60</td>
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<td>MnO</td>
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<tr>
<td>MgO</td>
<td>4.43</td>
<td>4.21</td>
<td>4.40</td>
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<tr>
<td>CaO</td>
<td>6.30</td>
<td>6.78</td>
<td>5.80</td>
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<tr>
<td>Na₂O</td>
<td>1.65</td>
<td>1.37</td>
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<tr>
<td>K₂O</td>
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<td>3.83</td>
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<tr>
<td>P₂O₅</td>
<td>0.081</td>
<td>0.072</td>
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<tr>
<td>Total</td>
<td>99.93</td>
<td>100.55</td>
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Table 5.1C: Whole rock analyses of pelites from the East flank of the Sheburne Falls dome
Waits River samples (WR), Goshen samples (G). T. Furman XRF operator.

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<tr>
<th></th>
<th>WR 84-48</th>
<th>WR 84-45</th>
<th>WR 85-10B</th>
<th>WR 85-20A</th>
<th>WR 85-21A</th>
<th>WR 85-2A</th>
<th>G 85-10B</th>
<th>G 85-1B</th>
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<tr>
<td>SiO₂</td>
<td>40.49</td>
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<td>TiO₂</td>
<td>2.64</td>
<td>1.25</td>
<td>1.31</td>
<td>1.69</td>
<td>1.40</td>
<td>0.94</td>
<td>0.93</td>
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<tr>
<td>Al₂O₃</td>
<td>25.87</td>
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<td>Fe₂O₃</td>
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<tr>
<td>CaO</td>
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<td>P₂O₅</td>
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<tr>
<td>Total</td>
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<td>99.48</td>
<td>99.93</td>
<td>99.74</td>
<td>99.22</td>
<td>100.10</td>
<td>100.46</td>
<td>99.39</td>
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<tr>
<td>Fe/Mg</td>
<td>5.643</td>
<td>5.197</td>
<td>2.156</td>
<td>2.820</td>
<td>2.731</td>
<td>3.926</td>
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<td>Si/Al</td>
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<td>0.0094</td>
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<td>0.0039</td>
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<td>Ti/Al</td>
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<td>0.049</td>
<td>0.053</td>
<td>0.047</td>
<td>0.048</td>
<td>0.046</td>
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</table>
Table 5.2: Trace element data for metapelites from Shelburne Falls, MA. Data in ppm.

Waits River Fm (WR), Goshen Fm (G)

<table>
<thead>
<tr>
<th>Element</th>
<th>WR 84-46</th>
<th>WR 84-45</th>
<th>WR 85-10B</th>
<th>WR 85-20A</th>
<th>WR 85-21A</th>
<th>G 85-2A</th>
<th>G 85-10B</th>
<th>G 85-1B</th>
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<tbody>
<tr>
<td>La</td>
<td>74.0</td>
<td>7.52</td>
<td>57.0</td>
<td>39.2</td>
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<td>5.64</td>
<td>5.64</td>
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<td>123.9</td>
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<td>26.7</td>
<td>11.9</td>
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<tr>
<td>Nd</td>
<td>81.0</td>
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<td>54.6</td>
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Table 5.3: Mineral assemblages of garnet bearing pelites; Shelburne Falls Area, MA

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* = sample studied in detail; ** minor phases examined.

x = present in matrix; x' = present in matrix and as inclusions in garnet; I = inclusions only
P= only as pseudomorphs; s = minor fibrolite. Tourmaline, zircon, apatite are common. Allanite is present in 84-45, 84-48, 85-19B, xenotime in 84-45, 85-1B, barite in 84-45, 85-19B, thorite in 84-45. Minor phases probably present in many samples.
Table 5.4: Point-count modes of Shelburne Falls quadrangle samples examined in detail

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Area percent modes based on counts of at least 1500 points/thin section.
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### Table 5.5C: Representative analyses of plagioclase

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Table 5.5E: Representative analyses of clinzoisite

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<td>38.52</td>
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<td>TiO₂</td>
<td>0.14</td>
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<tr>
<td>MgO</td>
<td>0.08</td>
<td>0.11</td>
<td>0.05</td>
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<tr>
<td>FeO</td>
<td>6.08</td>
<td>3.76</td>
<td>6.45</td>
<td>5.50</td>
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<td>MnO</td>
<td>0.10</td>
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<tr>
<td>CaO</td>
<td>22.06</td>
<td>23.58</td>
<td>22.47</td>
<td>23.08</td>
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<tr>
<td>Total</td>
<td>95.59</td>
<td>95.90</td>
<td>95.93</td>
<td>95.74</td>
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Si  6.059  6.072  6.041  6.067  6.041
Al 5.237  5.367  5.212  5.377  5.211
Ti 0.017  0.040  0.013  0.039  0.013
Mg 0.019  0.026  0.012  0.025  0.013
Fe³⁺ 0.798  0.492  0.846  0.491  0.845
Mn 0.014  0.013  0.018  0.013  0.018
Ca 3.708  3.951  3.776  3.948  3.776
Table 5.6: Secondary ion intensities of metamorphic minerals relative to co-existing garnet. Values are ion intensity \( \frac{\text{el}^+(\text{gar})}{\text{Si}^+(\text{gar})} \) or \( \frac{\text{el}^+(\text{min})}{\text{Si}^+(\text{min})} \), except for the oxides where raw ion counts are used.

<table>
<thead>
<tr>
<th></th>
<th>biot</th>
<th>biot</th>
<th>musc</th>
<th>musc</th>
<th>plag</th>
<th>czoil</th>
<th>ilm</th>
<th>mag</th>
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<tr>
<td></td>
<td>WR</td>
<td>G</td>
<td>WR</td>
<td>G</td>
<td>WR</td>
<td>WR</td>
<td>WR</td>
<td>WR</td>
<td>WR</td>
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<tr>
<td>Li</td>
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<td>0.05</td>
<td>0.6</td>
<td>0.5</td>
<td>55.</td>
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<td>0.5</td>
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<td>Sc</td>
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<td>5.</td>
<td>7.</td>
<td>5.</td>
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<td>Ti</td>
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<td>0.2</td>
<td>0.08</td>
<td>22.</td>
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<td>V</td>
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<td>0.2</td>
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<td>1.1</td>
<td>---</td>
<td>1.8</td>
<td>---</td>
<td>1.7</td>
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<tr>
<td>Co</td>
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<td>5.1</td>
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<td>2.</td>
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<tr>
<td>Y</td>
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<td>90.</td>
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<tr>
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<td>---</td>
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<td>3.</td>
<td>---</td>
<td>0.03</td>
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Table 5.7: Garnet-mineral partition coefficients for REE from the literature.

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<th>plag$^1$</th>
<th>hbde$^{1,3,4}$</th>
<th>biot$^{2}$</th>
<th>czoil$^5$</th>
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<tr>
<td>Ce</td>
<td>0.5-1.4</td>
<td>0.086</td>
<td>0.5</td>
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<tr>
<td>Nd</td>
<td>---</td>
<td>---</td>
<td>12.0</td>
<td>---</td>
</tr>
<tr>
<td>Sm</td>
<td>3.1-8.0</td>
<td>0.21-0.27</td>
<td>43</td>
<td>0.0004</td>
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<tr>
<td>Eu</td>
<td>0.9-1.9</td>
<td>0.41-0.44</td>
<td>10.</td>
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<tr>
<td>Tb</td>
<td>16-22</td>
<td>1.482</td>
<td>294</td>
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</tr>
<tr>
<td>Dy</td>
<td>---</td>
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<tr>
<td>Er</td>
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<td>---</td>
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<tr>
<td>Yb</td>
<td>120-320</td>
<td>8.7</td>
<td>223</td>
<td>0.066</td>
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</table>

1) Pride and Mueke, 1981
2) Schnetzler and Philpotts, 1970
3) Mason and Allen, 1971
4) Irving and Frey, 1978, 1984
Table 5.8: Predicted trace element signatures of garnet growth reactions;

<table>
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<tr>
<th>#</th>
<th>Reaction</th>
<th>Predicted trace element effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>hb+mut/-ch = bi+an+gr+qz+H_2O</td>
<td>HREE↑, Eu*↑, (Sc, Mn, HREE)*↓</td>
</tr>
<tr>
<td>3</td>
<td>ch+mut+qz = gr+bi+H_2O</td>
<td>(Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>4</td>
<td>il+qz+mut = gr+bi+ru</td>
<td>V↑, (Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>5</td>
<td>il+ch+mut+qz = gr+bi+ru+H_2O</td>
<td>V↑, (Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>6</td>
<td>ch+ru = il+gr+H_2O</td>
<td>V↓, (Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>7</td>
<td>an+H_2O = gr+mr+qz</td>
<td>Eu*↑, (Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>8</td>
<td>cz+qz = gr+an+H_2O</td>
<td>Y, Zr, REET↑, Eu*↓, (Sc, Mn)*↓</td>
</tr>
<tr>
<td>9</td>
<td>cz+an+H_2O = gr+mr+qz</td>
<td>Y, Zr, REET↑, Eu*↑, (Sc, Mn)*↓</td>
</tr>
<tr>
<td>10</td>
<td>cz = mr+an+gr+H_2O</td>
<td>Y, Zr, REET↑, Eu*↓, (Sc, Mn)*↓</td>
</tr>
<tr>
<td>11</td>
<td>bi+qz = mu+gr+TK</td>
<td>(Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>12</td>
<td>mut+mg+qz = gr+bi+O_2</td>
<td>Co↑, (Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>13</td>
<td>qz+cc+an = gr+CO_2</td>
<td>Eu*↑, (Sc, Mn, Y, HREE)*↓</td>
</tr>
<tr>
<td>14</td>
<td>an+bi = gr+mu</td>
<td>Eu*↑, (Sc, Mn, Y, HREE)*↓</td>
</tr>
</tbody>
</table>

Mineral abbreviations: gr=garnet (both grossular and almandine), bi=biotite, mu=muscovite, ch=chlorite, qz=quartz, hb=hornblende, an=anorthite, cz=clinozoisite, mr=margarite, cc=calcite, mg=magnetite, il=ilmenite, ru=rutile, TK = tscharmk component, H_2O=water, CO_2=carbon dioxide. 

↑ means element rises in garnet  ↓ means it declines. Eu* is Eu relative to the adjacent REE (size of Eu anomaly).
Figure 5.1: Sketch map of the Connecticut Valley Synclinorium and associated tectonostratigraphic units. Fine dots = Cambro-Ordovician strata; unpatterned = Siluro-Devonian strata of the CVS; dots = New Hampshire sequence metasediments (Littleton, Erving, Clough Fms); bars = Devonian intrusives; bimodal pattern = Mesozoic sediments. Geology after Zen et al., 1983.
Figure 5.2: Geologic map of the study area showing sample localities and lithologies. Ocr = Collinsville Fm in the Shelburne Falls Dome; Dgq = Quartzritic subunit of the Goshen Fm; Dg =Goshen Fm; Dwr = Waits River Fm; Dsp = Standing Pond volcanics. Geology after Segerstrom (1956) and Zen et al., 1983.
Figure 5.3: Rare earth element (REE) patterns for the CVS metasediments. Chondrite normalizing values from Evensen et al., 1978.
Figure 5.4: Photomicrographs showing textures of CVS metasediments. A: 85-22 (through xed nichols) showing rotated garnet core overgrown by unrotated overgrowth. Garnet is also differentially resorbed (garnet ≈ 4 mm in widest diameter). B: 85-2A showing two generations of biotite, graphitic and non-graphitic, two generations of garnet graphitic and non-graphitic and differential resorption of garnet rim (garnet 3 mm in widest diameter). C: 84-45 garnet (through xed nichols) showing inclusion-ridden core and inclusion-poor overgrowth (garnet ≈ 2.5 mm in widest diameter). Core inclusions include quartz, clinozoisite, chlorite and Ti oxides. D: Amphibole pseudomorph in 85-20A. Note diamond-shaped biotite+plagioclase aggregate (pseudomorph ≈ 2 mm across).
Figure 5.5: AFM projection from quartz, muscovite, and \(H_2O\) of pelitic matrix assemblages from the Goshe\(n\) and Waits River Fms.
Figure 5.6: Stretched AFCN projection from quartz, muscovite, biotite (Annite 50) and H₂O of the Goshen and Waits River Fm matrix assemblages.
Figure 5.7: ACFM projected from quartz + muscovite + $\text{H}_2\text{O}$ + rutile + plagioclase (Anorthite 35) for Waits River matrix assemblages. Ilmenite plots at the Fe axis in the presence of rutile. Amphibole plots on the Mg-rich side of the kyanite-clinozoisite-biotite plane.
Figure 5.8: Diagram showing P-T conditions for samples from the east flank of the Shelburne Falls dome calculated using the garnet-biotite geothermometer and garnet-plagioclase-quartz-kyanite or garnet-plagioclase-quartz-muscovite-biotite geobarometer. Dotted lines represent range of garnet-plagioclase inclusion $K_d$ lines. Alumino-silicate triple point after Holdaway (1971).
Figure 5.9: Isobaric T-f(O₂) (P=7 kbar) diagram for the
decarbonation equilibria calcite + quartz + kyanite =
grossularite + graphite + O₂. Absence of carbonate
provides maximum f(O₂) values. Activity of grossular
allowed to vary between 0.1 and 0.2. Thermodynamic data
utilized is summarized in Appendix B. QFM is the quartz-
fayalite-magnetite buffer and HM is the hematite-
magnetite buffer.
T-f(O2)
P 7 kbars

log f(O2)

400 500 600 700 800

Temp C

HM calcite-qtz-kyanite gross-graph-O2 QFM
Figure 5.10: Schematic Ca zoning profiles for western Massachusetts samples. Type I (85-1B, 85-10B) [Goshen]; Type II (85-2A) [Goshen]; Type III (84-48) [Waits River]; Type IV (84-45, 85-19B, 85-20A) [Waits River], and Type V (85-21A) [Waits River].
Schematic Ca zoning profiles
Figure 5.11: Theoretical calculations of changes in garnet compositions with changes in pressure and temperature in assemblages that are divariant in the model system SiO$_2$-Al$_2$O$_3$-TiO$_2$-FeO-MgO-CaO-Na$_2$O-K$_2$O-H$_2$O. Assemblages are garnet - biotite - muscovite - plagioclase - rutile +/- quartz + H$_2$O + the two phases or three phases listed in the upper-right of each panel. A: assemblages in quartz-bearing rocks. B: assemblages in quartz-free rocks. Solid lines are changes with pressure ($\Delta P = +/- 1$ kbar), dotted lines are changes with temperature ($\Delta T = +/- 10^\circ$ C). Squares at low-P end and high-T end. Initial conditions of 550 $^\circ$C, 7 kbars. Fine dotted lines roughly show location of endpoints of calculated vectors. These lines are not calculated, they were sketched in to aid in visualizing the relations presented in the figure.
Figure 5.12: Trace element zoning profiles from the CVS samples. Location of traverses depicted in Appendix A. Left ordinate, ion intensity/Si ion intensity. Features described in the text designated by letters. Errors based on counting statistics are generally smaller than the size of the symbols. Anomalous points (particularly for Na/Si and Ti/Si) may reflect overlap of microinclusions.
Figure 5.13: REE abundances in select points across western Massachusetts garnets. Locations of points depicted in Appendix A. Errors based on counting statistics generally smaller than symbol size, except for Nd. Concentrations estimated from working curves for pyrope-rich garnets.
Figure 5.14: Temperature-time-transformation (T-T-T) diagram showing regimes in which measurable compositional changes in concentration would be expected for re-equilibration of garnet rims based on ROT considerations. Other details of calculation presented in the text.
Appendix A: Garnet maps for calcareous pelites from the NW Shelburne Falls quadrangle. Ion probe traverses depicted by heavy lines. Numbers represents locations of REE points. Dotted lines represent loci of interest; these zones are referred to in the text.
Appendix B: Thermodynamic data and mineral compositions

<table>
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<tr>
<th>Mineral</th>
<th>Formula</th>
<th>$G^0_{298}$</th>
<th>$H^0_{298}$</th>
<th>$S^0_{298}$</th>
<th>$V^0_{298}$</th>
<th>a</th>
<th>bx10^{-3}</th>
<th>cx10^{5}</th>
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</thead>
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<tr>
<td>Almandine</td>
<td>Fe$_3$Al$_2$Si$<em>3$O$</em>{12}$</td>
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Appendix I: Analytical techniques and working curves for garnets
AI.1 Introduction

Trace element analyses for garnets were made using a Cameca IMS-3f ion microprobe. Operation of this machine for trace element analysis is described in detail elsewhere (Shimizu and Hart, 1982; Shimizu and Lerouex, 1986). Nonetheless, the specific machine conditions and trace element working curves for pyrope-rich garnets are outlined below.

AI.2 Operating conditions

The Cameca IMS-3f is a doubly focusing ion microprobe. Negatively charged oxygen ions are produced at a Ni-rich cathode, accelerated to 12.5-12.7 keV, and focussed on an aluminum plate using primary beam deflectors and apertures to a spot size of either ≈ 5 or ≈ 20 microns. Beam currents for the former (used for abundant trace elements) were generally 0.2-0.3 nanoamps, and for the latter (used for rare earth elements) were usually about 4-5 nanoamps. An image field of 25 microns was utilized, in this way beam drift could be monitored easily as a function of Si count-rate.

Primary high-energy oxygen ions bombard the sample and produce a collision cascade that excites secondary ions, molecular ions and neutral ions, some of which acquire sufficient excess energy to be sputtered away from the surface of the sample. The sputtered secondary ions are then accelerated to a nominal secondary high
voltage of 4500 volts and refocused through an immersion lens, a transfer lens (25 μ), a contrast aperture (generally number 3), a field aperture (750 microns), stigmators, up to three secondary beam deflectors, and analyzed with a 90° electrostatic sector and a 90° magnetic sector. Secondary ion intensities were measured by a 17 dynode Allen-type electron multiplier in pulse-counting mode.

Mass calibration and analysis were controlled by a Hewlett-Packard 9835A computer using software written at M.I.T.. Five cycles of data were taken in ascending mass order, with backgrounds measured 0.5 mass units below the lightest isotope in a group of elements. For each abundant trace element analysis four sets of doubly time interpolated ratios were calculated, corrected for elemental abundances, backgrounds and deadtimes (∼43 ns), and normalized to the ion intensity of a reference isotope (28Si). The rare earth analysis technique differed slightly: seven REE (Ce, Nd, Sm, Eu, Dy, Er, Yb) were measured five times in ascending mass order, doubly time interpolated ratios were calculated, and corrected for backgrounds, deadtimes, and element abundances; however, 30Si measurement and normalization occurred after the REE analysis to minimize problems with hysteresis. Counting times in each block were generally: background - 10 seconds, 7Li - 20 seconds, 23Na - 20
seconds, $^{24}\text{Mg} - 2$ seconds, $^{28}\text{Si} - 2$ seconds, $^{40}\text{Ca} - 2$ seconds, $^{45}\text{Sc} - 20$ seconds. $^{47}\text{Ti} - 20$ seconds, $^{51}\text{Y} - 20$ seconds, $^{52}\text{Cr} - 20$ seconds, $^{55}\text{Mn} - 4$ seconds, $^{56}\text{Fe} - 2$ seconds, $^{59}\text{Co} - 20$ seconds, $^{89}\text{Y} - 20$ seconds, $^{90}\text{Zr} - 20$ seconds, and REE - 20 seconds. $^{28}\text{Si}$ ion intensities on pyrope-rich garnet at 0.2-0.3 nanoamps were usually between 80,000 to 120,000 counts/second.

Samples were mounted in 1" aluminum rings, polished with 0.3 micron Al$_2$O$_3$ grit and gold coated (300 Å thick). For each point, the primary beam was allowed to drill into the sample for twenty minutes to reach a steady state of ion formation (Shimizu and Hart, 1982; Ray, 1982) prior to commencing taking data.

**AI.3 Molecular ion interferences**

The primary obstacle to quantitative ion microprobe analysis of geologic materials is that the secondary ion mass spectrum contains strong signals for molecular ion species (dimers, oxides, hydrides, multiply charged ions), as well as for the monoatomic ions.

Molecular ion interferences are minimized by the use of energy-filtering (Herzog et al., 1973; Shimizu et al, 1978; Shimizu and Hart, 1982). Shimizu (Shimizu et al., 1978; Shimizu and Hart, 1982) has shown that monoatomic secondary ions have a significantly larger high energy ion components than do complex molecular ions. Thus, by measuring only high energy ions the vast majority of
molecular ion interferences can be eliminated from the mass spectrum. High energy ions are selected by adjusting the bandpass of the energy slit to a narrow window (+-10 V), and decreasing the secondary accelerating voltage from its nominal value of 4.5 kV. Energy filtering results in a loss of secondary ion intensity, but an increase in stability and a decrease in matrix effects (Shimizu, 1986) The degree of energy filtering utilized depended on the elements being analyzed, -90 eV (secondary accelerating voltage of 4410) for the abundant trace elements (Li, Sc, Ti, V, Cr, Co, Y, Zr) and -35 to 50 eV for the REE (secondary accelerating voltage of 4465-4450). Investigation of pyrope-rich garnets of known trace element abundance reveals that these amounts of energy filtering eliminate the vast majority of molecular ion interferences, and allow working curves to be constructed for some elements. The HREE mass range also contains signals for the LREE oxides at these high voltage offsets; however, because garnets encountered in this study are invariably HREE enriched, and oxide ion-yields are significantly smaller than those for monoatomic species at large high voltage offsets; the HREE ion abundances are not significantly distorted by LREE oxide overlaps, except for GdO on Yb.
AI.4 Working curves

In order to verify that element/Si ratios can be used as petrogenetic indicators and to provide rough working curves, a series of garnets that were analyzed by other analytical methods were studied using the ion microprobe techniques described above. Description of working standards are provided in Table A-1. Suitable, unzoned, pyrope-rich working standards are available but few 'unzoned' almandines were found. Further work on almandines from granulite xenoliths is in needed to evaluate the nature and extent of matrix effects between almandine and pyrope.

Linear relations exist between ion intensity and element concentrations for several trace elements. As can be seen in Fig. A-1 and A-2, good linear relations exist between I(Sc/Si), I(Cr/Si), I(Ti/Si), I(Y/Si), I(REE) and trace element abundances (the REE working curve was constructed by N. Shimizu). York regressions of these working curves are provided in Table 5. Other elements (Na/Si, V/Si, Co/Si, Zr/Si) display more scattered 'working curves'.

Inaccuracies in working curves are produced by three factors: 1) Inaccurate analyses, or mineral heterogeneity, of the working standards, 2) Ion probe-induced matrix effects, and 3) unfiltered molecular ion interferences.
The first factor, inadequate working standards, is probably the cause of the low quality of the Na, V, Y and Zr 'working curves'. Few garnets analyzed for these elements were available to the author. The Y and Zr data for Kakanui pyrope (Mason and Allen, 1973) is by spark-source mass spectrometry. No evaluation of the accuracy of the spark-source data is provided by Mason and Allen; however, based on the agreement (sic) between isotope dilution and spark source values for REE (ie. Sm (ID) = 1.15, Sm (SS)=1.9; Eu (ID) = 0.645, Eu (SS) = 0.9) the data is probably extremely poor. The V data for Kakanui is by neutron activation, V is not done by INAA at M.I.T. so the values presented must be considered dubious. The Na data (by INAA) is also probably not of high quality.

The Co data (by INAA) is probably of fairly high quality. The three aberrant points (Kiglapait, Tumut and Binge Binge) are the three almandine-rich garnets. Two explanations consistent with this observation are: 1) the $^{59}$Co mass spectra is interfered by $^{58}$Fe hyrides or 2) there is a matrix effect for Co due to enhanced Co ionization in the presence of iron (see Shimizu et al., 1978). Shimizu (pers. comm. 1988) reports that he was unable to develop adequate Co working curves for clinopyroxenes.
AI.5 Precision and accuracy of data

The precision of the ion probe data can be evaluated by repeated analyses of a working standard. Means and standard deviations of over 40 analyses of Monastery garnet (Irving and Frey, 1978) or MNAG (Shimizu, unpub. data) are presented in Table AI.4. Reproducibility of the element/Si or element/Dy analyses is better than +/- 10% for all the trace elements studied except for Co/Si. This difference is outside counting statistics for most elements and may be due to: 1) minor element heterogeneity on a grain scale, or 2) minor fluctuations in focusing or machine conditions over the two years of operation. Relative variability from point to point on a zoning profile is limited primarily by counting statistics.

The accuracy of the trace element analyses depends on both the accuracy of the analyses of the working standards and the inherent accuracy of the ion probe microanalysis. Accuracy is hence a difficult parameter to evaluate. For the elements with good 1σ errors on slopes in the compositional range bracketed by working standards accuracy of analyses is estimated to be in the 10-20% range.

AI.6 Summary

For the purposes of this study relative variations in element abundance from garnet core to rim are of
primary petrogenetic interest. Absolute abundances are not required unless one attempts to formulate partition coefficients or engage in detailed mass balance calculations. Hence although adequate working curves for trace elements in garnet are available for a few element (Sc, Ti, Cr, Y, REE) the relative variability of the element/silicon ratios can be interpreted with some confidence in terms of metamorphic processes.
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(a) wt. %, (b) ppm, (c) major elements by electron microprobe, (d) wet chemical analysis (Jun Ito analyst), (e) trace elements by neutron activation analysis, (f) wet chemical analysis, (g) trace elements by various techniques (INAA, spark-source), (h) trace element by wet chemistry, (i) trace element by electron microprobe.
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Table A1.4: Reproducibility of ion microprobe analyses.

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<td>Zr/Si</td>
<td>4.08e-4</td>
<td>3.44e-5</td>
<td>39</td>
</tr>
<tr>
<td>146/R-Nd</td>
<td>0.319</td>
<td>0.019</td>
<td>6</td>
</tr>
<tr>
<td>147/R-Sm</td>
<td>0.309</td>
<td>0.027</td>
<td>6</td>
</tr>
<tr>
<td>151/R-Eu</td>
<td>0.150</td>
<td>0.009</td>
<td>6</td>
</tr>
<tr>
<td>167/R-Er</td>
<td>0.677</td>
<td>0.021</td>
<td>6</td>
</tr>
<tr>
<td>174/R-Yb</td>
<td>0.772</td>
<td>0.023</td>
<td>6</td>
</tr>
</tbody>
</table>

ppm    | 1 sigma | I.D. value (N. Shimizu unpub. data) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>2.138</td>
<td>0.133  2.48</td>
</tr>
<tr>
<td>Sm</td>
<td>1.913</td>
<td>0.166  1.96</td>
</tr>
<tr>
<td>Eu</td>
<td>0.998</td>
<td>0.081  1.09</td>
</tr>
<tr>
<td>Dy</td>
<td>6.720</td>
<td>0.642  7.37</td>
</tr>
<tr>
<td>Er</td>
<td>5.161</td>
<td>0.454  5.20</td>
</tr>
<tr>
<td>Yb</td>
<td>4.949</td>
<td>0.455  5.55</td>
</tr>
</tbody>
</table>
Table A1.5 York regression parameters for working curves. 5% one-sigma errors used.

<table>
<thead>
<tr>
<th>Element</th>
<th>slope</th>
<th>sigma on slope</th>
<th>intercept</th>
<th>sigma on intercept</th>
<th>Quality of working curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2.17e5</td>
<td>3.3e4</td>
<td>71</td>
<td>25</td>
<td>poor</td>
</tr>
<tr>
<td>Sc</td>
<td>7.62e4</td>
<td>4.6e3</td>
<td>-2</td>
<td>5</td>
<td>good</td>
</tr>
<tr>
<td>TiO₂</td>
<td>24.92</td>
<td>1.4</td>
<td>-0.12</td>
<td>0.098</td>
<td>good at high wt %</td>
</tr>
<tr>
<td>Cr*</td>
<td>2.87e5</td>
<td>9.8e3</td>
<td>-23</td>
<td>1.85</td>
<td>good at high conc.</td>
</tr>
<tr>
<td>Co</td>
<td>4.04e5</td>
<td>8.6e5</td>
<td>13</td>
<td>9</td>
<td>fair</td>
</tr>
<tr>
<td>Y</td>
<td>1.20e5</td>
<td>9.5e3</td>
<td>10</td>
<td>2</td>
<td>fair</td>
</tr>
</tbody>
</table>

Working curves of the form: ppm = slope*El/Si + intercept, except TiO which is in weight percent.

V and Zr were not regressed because only two standards (each of questionable quality) were available.

*Only pyrope-rich garnets regressed.
Figure A.1: Element ion intensity/silicon ion intensity vs. element concentration (ppm, except for TiO₂). Errors in element/silicon are 1 sigma analytical errors, errors in concentration are the quoted +/- 5% errors on the neutron activation data (Irving and Frey, 1978). Large element/silicon errors may represent both analytical errors and grain heterogeneity; the three almandine-rich garnets are all slightly zoned.
SC/SPM * 10E-3
CR/SI * 10E-3
Y/SI * 10E-2
ZR PPm

ZR/SI * 10E-4
Figure A.2 REE working curves (determined and plotted by N. Shimizu). All REE show similar ion yields except for Ce.
Appendix II: Evaluation of garnet-mineral partition coefficients
AII.1 Introduction

Quantitative modeling of trace element zoning in metamorphic garnets requires a knowledge of garnet/mineral partition coefficients. Unfortunately, there is a dearth of partitioning data for trace elements at metamorphic temperatures and pressures; trace element modeling is fraught with uncertainties in metamorphic environments. In this Appendix I: 1) review the available garnet-mineral trace element partitioning data from the literature, 2) briefly discuss the data, and 3) divide the trace elements into three categories (compatible, incompatible, and intermediate). The overall goal of the Appendix is to provide a framework for interpreting the trace element zoning data presented in Chapters II-V.

Detailed reviews of trace element partition coefficient theory are presented by McIntire (1958, 1962). The mineral-mineral partition coefficient is defined as: \( C_{\text{mineral 1}} / C_{\text{mineral 2}} \), where \( C_i \) is the concentration (in ppm) of element I in a mineral. Mineral-mineral partition coefficients are functions of temperature, pressure and major element composition of the minerals, but are not a function of trace element abundance (Henry's Law is obeyed).
AII.2 Metamorphic partition coefficients: Literature review

Mineral-mineral trace element distribution studies in metamorphic rocks were widely undertaken in the late 1950's through late 1960's (DeVore, 1955a, 1955b; Kretz, 1959; Engel and Engel, 1960; Turekian and Phinney, 1962; Albee, 1965; Hunziker, 1967; Hietenan, 1969). These studies were initiated in hopes of showing partition equilibria between phases with a goal of using the pressure and temperature dependence of partition coefficients as geologic thermometers and barometers. The former goal was occasionally realized: Kretz (1959) and Engel and Engel (1960) demonstrated partition equilibria for certain elements between minerals (i.e. V and Ti between hornblende and biotite (Kretz, 1959)). The latter goal tantalized (see Engel and Engel, 1960), but remained a pipe dream. Geothermometric and barometric applications in geology were usurped by electron probe based major element studies.

More often (DeVore, 1955a, 1955b; Turekian and Phinney, 1962)) irregular mineral-mineral partitioning was found and ascribed to: 1) adsorption of trace elements into mineral structures rather than attainment of thermodynamic equilibrium (DeVore, 1955a), 2) hand sample scale disequilibrium (Turekian and Phinney, 1962),
3) unclean mineral separates (McIntire, 1963), or 4) low data quality (Engel and Engel, 1960).

An unrecognized factor that probably contributed to the irregular mineral-mineral distributions is trace element zoning of metamorphic porphyroblasts (Hickmott et al., 1987). This hypothesis is supported by: 1) the fairly systematic mineral-mineral partitioning observed in upper-amphibolite to granulite facies terrains (Engel and Engel, 1960; Kretz, 1959) where homogeneous minerals predominate as a result of rapid intracrystalline diffusion at high temperatures, 2) the frequently unsystematic partitioning observed in lower- to mid-amphibolite facies rocks (DeVore, 1955; Albee, 1965; Hietenan, 1969) where zoned phases are common, 3) the involvement of garnet in mineral pairs showing the least systematic partitioning (Albee, 1965) (garnet is the frequently studied mineral with the slowest diffusion rates at low temperatures (Freer, 1980) and the mineral most strongly zoned in metamorphic environments (Tracy, 1982)).

The ubiquity of mineral zoning, low-data quality, and minor phase inclusions in mineral separates all degrade the quality of mineral-mineral partition data; however, if we eliminated data on suspicion of zoning, impurities and low-quality then we would have virtually no mineral pairs for consideration. Thus, we consider
virtually all the available partitioning data and broadly
categorize elements into garnet compatible, garnet
incompatible and intermediate. An element is placed in
the first category if all (or almost all) measured
garnet/mineral partition coefficients are greater than
one, in the second category if all (or almost all)
are less than one, and in the third category if partition
coefficients widely overlap one.

Partition coefficients (ppm element in garnet vs ppm
element in other mineral) are presented in Figure AII.1-6
for the trace elements widely used in this thesis (Sc, V,
Cr, Co, Y, Zr). Na and Ti are not considered because
their chemical potentials are defined by equilibria
between Na- and Ti- bearing silicates and oxides, and
hence are not amenable to treatment by using a partition
coefficient approach. Data sources, analytical
techniques, locales, and trace elements considered are
listed in Table AII.1.

Li

Li analyses of garnet and co-existing metamorphic
minerals are presented by Dutrow et al. (1986). Only two
garnet Li analyses are reported, so a garnet-mineral
distribution plot for Li is not included. Li is an
incompatible element in garnet relative to co-existing
staurolite (D ranges from 0.04-0.05), biotite (0.19), and
muscovite (0.76-0.96). Based on Dutrow's data and her considerations of the literature the following order of Li incorporation into minerals appears to exist:

staurolite > cordierite > biotite > muscovite > garnet >
≈ tourmaline ≈ chloritoid.

Sc

Scandium in garnet vs Sc in co-existing minerals are presented in Figure AII.1. Scandium is classed as a compatible element in garnet compared to all co-existing minerals, except hornblende, in which it is classed as an intermediate element. Figure AII.1, and detailed consideration of the references suggest the following order of Sc enrichments: garnet ≈ hornblende > muscovite > biotite ≈ chloritoid > chlorite ≈ staurolite > plagioclase. Krylova et al. (1970) suggest that $D_{Sc}^{(gar/biot)}$ roughly increases from the epidote-amphibolite facies to the granulite facies. Comparison of the data of Engel and Engel (1960) with amphibolite facies garnet-biotite pairs supports this hypothesis.

V

Vanadium garnet/mineral partitioning is in Figure AII.2. V is an incompatible element in garnet relative to most metamorphic silicates. The order of enrichment of V in these minerals is roughly: biotite > muscovite > staurolite > chloritoid ≈ amphibole > chlorite > garnet.
V has not been measured in metamorphic plagioclase, but presumably occurs at low levels. Comparison of the Engel's V (garnet/biotite) partitioning data with other lower temperature data sets suggests that $D_V$ (garnet/biotite) decreases with increased temperature. Kretz (1959) noted a distinct correlation between increased Ca in garnet and increased $D_V$ (garnet/biotite) (from $\approx 0.1$ to $\approx 0.5$ as Ca/Ca+Fe+Mg+Mn rises from 0.02 to 0.22).

Cr

Cr partitioning between garnet and other minerals is shown in Figure AII.3. Consideration of Figure AII.3 suggests that Cr is incorporated into metamorphic minerals in approximately the following order: biotite > chloritoid $\approx$ staurolite > chlorite $\approx$ muscovite $\approx$ garnet $\approx$ amphibole $>>$ plagioclase. Thus Cr is a garnet incompatible element relative to most metamorphic minerals.

Co

Figure AII.4 shows Co garnet:mineral partition coefficients. Relative Co partitioning is apparently: chlorite > staurolite $\approx$ chloritoid > biotite > amphibole > garnet > muscovite. Thus Co is classed as a garnet incompatible element.
Y
garnet-mineral distributions are shown in Figure AII.5. There are fewer points shown for Y than any other element because Y occurs at such low levels in many metamorphic minerals other than garnet that it was below the detection limit (20 ppm for most of the emission spectrometry based studies) in the majority of minerals. Clearly Y is a strongly compatible element in garnet relative to the other common metamorphic silicates. The enrichment order for Y appears to be: garnet >> amphibole > chlorite ≈ biotite ≈ muscovite > chloritoid ≈ staurolite. Y analyses of co-existing silicates (without garnet) are rare, so the order of compatibility between micas, staurolite and chloritoid is not determinable. Y has not been measured in metamorphic plagioclase, but presumably is very low; heavy REE, which are geochemically similar to Y, in are low in igneous plagioclase (Gromet and Silver, 1983).

Zr
Zirconium partitioning between garnet and other silicates is shown in Figure AII.6. Zr fields for biotite, chlorite, muscovite, amphibole, staurolite, and chlorite all overlap the D = 1 line, thus Zr is classed as an intermediate element. Zr partitioning is extremely irregular so an order of enrichment is not attempted.
Table 1: Sources for data presented in Figures 1 through 6.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Analytical method</th>
<th>Co-existing</th>
<th>Elements</th>
<th>Facies</th>
</tr>
</thead>
<tbody>
<tr>
<td>DeVore (1955a, 1955b)</td>
<td>Spectrographic</td>
<td>ch, bi, am, mu</td>
<td>Sc, Ti, V, Cr, Co, Y, Zr</td>
<td>Mostly Amphibolite</td>
</tr>
<tr>
<td>Kretz (1959)</td>
<td>Spectrographic</td>
<td>am, bi</td>
<td>Sc, Ti, V, Cr, Co, Y, Zr</td>
<td>Granulite</td>
</tr>
<tr>
<td>Engel &amp; Engel (1960)</td>
<td>Emission Spec.</td>
<td>bi, pl</td>
<td>Sc, Ti, V, Cr, Co, Y, Zr, Yb</td>
<td>Amphibolite to granulite</td>
</tr>
<tr>
<td>Turekian &amp; Phinney (1962)</td>
<td>Spectrographic</td>
<td>bi</td>
<td>Cr, Co</td>
<td>Amphibolite</td>
</tr>
<tr>
<td>Albee (1965)</td>
<td>Emission Spec.</td>
<td>bi, mu, ch, ct, il</td>
<td>Sc, Ti, V, Cr, Co, Y, Zr, Y</td>
<td>Mid-amphibolite</td>
</tr>
<tr>
<td>Hunziker (1967)</td>
<td>Spectrographic (?)</td>
<td>bi, mu, am</td>
<td>Ti, V, Cr, Co</td>
<td>Amphibolite</td>
</tr>
<tr>
<td>Hiettenan (1969)</td>
<td>Spectrographic</td>
<td>bi, mu, sta</td>
<td>Sc, Ti, V, Cr, Co, Y, Zr, REE</td>
<td>Mid-amphibolite</td>
</tr>
<tr>
<td>Krylova et al. (1970)</td>
<td>Spectrographic</td>
<td>bi</td>
<td>Sc</td>
<td>Amphibolite to granulite</td>
</tr>
<tr>
<td>Bollinberg &amp; Bryhni (1972)</td>
<td>Spectrographic</td>
<td>am</td>
<td>Sc, Ti, V, Cr</td>
<td>Eclogite</td>
</tr>
</tbody>
</table>

Mineral abbreviations: biotite=bi, chlorite=ch, chloritoid=ct, staurolite=st, amphibole=am, ilmenite=il, muscovite=mu, plagioclase=pl.
Figure AII.1: Sc (ppm weight) in garnet vs. Sc (ppm weight) in other coexisting minerals. Square=biotite, circle=chlorite, triangle=chloritoid, cross=ilmenite, diamond=staurolite, triangle-on-post=muscovite, star=amphibole, bow-tie on side=plagioclase. Fields for minerals circled. Dotted line represents locus of partition coefficients equal to one. Incompatible elements plot above the line, compatible below the line. Data sources listed in Table 1.
Figure AII.2: V (ppm weight) in garnet vs. V (ppm weight) in other coexisting minerals. Symbols, fields and data sources same as in figure 1.
Figure AII.3: Cr (ppm weight) in garnet vs. Cr (ppm weight) in other coexisting minerals. Symbols, fields and data sources same as in figure 1.
Figure AII.4: Co (ppm weight) in garnet vs. Co (ppm weight) in other coexisting minerals. Symbols, fields and data sources same as in figure 1.
Figure AII.5: Y (ppm weight) in garnet vs. Y (ppm weight) in other coexisting minerals. Symbols, fields and data sources same as in figure 1.
Figure AII.6: Zr (ppm weight) in garnet vs. Zr (ppm weight) in other coexisting minerals. Symbols, fields and data sources same as in figure 1.