Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts

ROBERT J. TRACY,1 PETER ROBINSON,
Department of Geology, University of Massachusetts
Amherst, Massachusetts 01002

AND ALAN B. THOMPSON
Department of Geological Sciences, Harvard University
Cambridge, Massachusetts 02138

Abstract

The distribution of Fe, Mg, Ca, and Mn within individual zoned garnets of medium- to high-grade metamorphosed pelitic rocks from west-central Massachusetts has been studied in detail with an automated electron microprobe, and is consistent with variations predicted for the Fe-Mg-Mn continuous reactions taking place at each metamorphic grade. This regular behavior allows use of compositions of garnet and coexisting phases for geothermometry and geobarometry if P-T-X relations of appropriate continuous reactions can be calibrated. Preliminary calibrations of garnet-biotite and garnet-cordierite Fe-Mg exchange reactions and several Fe-Mg-Mn continuous reactions have been used to evaluate P-T conditions of metamorphism in central Massachusetts. Results indicate pressure in the range of 5 to 7 kbar and a west to east temperature gradient from about 580-605°C for kyanite-staurolite grade to 650-700°C for sillimanite-orthoclase-cordierite grade. Pressure and temperature estimates are consistent with regional tectonic reconstructions indicating synmetamorphic uplift in the Bronson Hill anticlinorium and downbuckling in the Merrimack synclinorium.

Introduction

The Bronson Hill anticlinorium and Merrimack synclinorium in west-central Massachusetts, east of the Mesozoic border fault, are composed of late Precambrian and/or Cambro-Ordovician basement gneisses mantled by metamorphosed Middle Ordovician, Silurian, and Lower Devonian sedimentary and volcanic rocks, and various syntectonic plutons (Robinson, 1967a, 1967b; J. B. Thompson et al., 1968; Field, 1975). Zones of Acadian (Devonian) regional metamorphism have been mapped in pelitic schists of the Partridge, Littleton, and Erving Formations (Robinson, 1963, 1967a, b; Hess, 1969; Hall, 1970; Field, 1975) which indicate increasing metamorphic grade from west to east over a distance of about 50 km (Fig. 1). Assemblages characterizing the zones and the probable reactions separating them are summarized in Table 1. Locations and estimated modes of specimens studied in detail are listed in Table 2.

Various continuous (multivariant) reactions characterizing these zones have been studied in detail (Robinson, 1963; Hall, 1970; Tracy, 1975). Recent attempts to calibrate continuous reactions in terms of pressure (P), temperature (T), and activity of H2O (aH2O) (A. B. Thompson, 1976a, b) use experimentally determined and calculated pure-Fe and pure-Mg end-member reactions and Fe-Mg exchange potentials calculated from distribution coefficient (K_D) data. These calibrations are here applied to detailed petrographic and microprobe information on pelitic rocks, in an attempt to understand the pressure-temperature history of this portion of the Appalachian mountain belt.

The near ubiquity of garnet in assemblages in pelitic rocks over a wide range of metamorphic grade and bulk compositions makes it a useful mineral for continuous geothermometry and geobarometry. The nature and origin of the complex chemical zoning of

1 Present address: Department of Geological Sciences, Harvard University, Cambridge, Massachusetts 02138.
Assemblages, continuous reactions, and garnet zoning

During microprobe investigation of the samples, it was noted that garnets from different metamorphic zones exhibit a variety of element zoning patterns. It appears that slow homogeneous diffusion rates within garnet, unlike other phases, permit preservation of growth zoning at medium grades of metamorphism. This means that element distribution patterns within garnets may yield information on the nature of prograde and retrograde continuous reactions involving garnet. Differing styles of garnet zoning may be discussed conveniently in a framework of increasing metamorphic grade, as reflected by the various metamorphic zones observed in central Massachusetts.

Zones I and II

Metamorphic Zone I is characterized by assemblages of Kya-Mus-Sta-Gar-Bio with Qtz + Gph + Ilm ± Pla ± Pyh (Table 1), though kyanite is restricted to rocks with magnesian bulk compositions (Robinson, 1963; Hall, 1970). Zone II differs from Zone I only in the presence of sillimanite in place of kyanite. Sillimanite is much more abundant in this zone than kyanite in Zone I. Garnets from both zones are usually euhedral and generally contain inclusions of quartz and ilmenite, in some cases showing evidence of rotation during growth. These garnets exhibit “normal” chemical zoning (Hollister, 1966) characterized by Ca- and Mn-richer cores and Fe- and Mg-richer rims. Single garnets from these zones have been examined in great detail with an automated electron microprobe, and chemical contour maps of a typical garnet in sample 908 from Zone I are presented in Figure 2. These represent the two-dimensional distribution of end-member components in a section cut approximately through the center of a grain.

Zone I samples 908 and 4F5 show a roughly concentric and regular zoning with the notable exception of a ridge of higher pyrope content near the edge, caused by a considerable drop in Mg/Fe at the edge. Representative analyses of Zone I (908, 4F5) and Zone II (36Y, Q67) garnets have been plotted in terms of atomic percent Fe, Mg, and Mn in Figures 3a and 3b. In Zone I samples (Fig. 3a) initial outward zoning shows a decrease in Mn accompanied by a slight increase in Mg/Fe, consistent with the predicted trend of garnet compositions involved in the continuous Fe-Mg-Mn reaction

\[
\text{Sta + Bio + Qtz} \rightarrow \text{Mus + Gar + H}_2\text{O} \quad (1)
\]
with increasing temperature (A. B. Thompson, 1976a). From element distribution in the limiting binary systems it is predicted that $T_{Mg} > T_{Fe} > T_{Mn}$, where $T_{Mg}$ represents the temperature of the reaction in the pure-Mg system at constant $P$ and $aH_{2}O$. The Zone II garnets show a similar trend toward lower Mn, but have very little, if any, change in Mg/Fe from core to rim. This cannot be explained by a continuous Fe-Mg reaction, but may represent the effect of Mn on the discontinuous Fe-Mg reaction

$$Sta + Mus + Qtz = Sil + Gar + Bio + H_{2}O$$

which can be thought of as a continuous Fe-Mg-Mn reaction with $T_{Fe} \geq T_{Mg} > T_{Mn}$.

The abrupt change in zoning toward lower Mg/Fe observed near the margins of Zone I garnets (Figs. 2 and 3a) cannot be easily related to prograde continuous Fe-Mg-Mn reactions, and may be related to continuous reactions involving other types of cation exchange or to retrograde reactions, on the basis of features observed in higher-grade garnets (see below).

**Zones III, IV, and V**

Garnets from Zone III (Mus-Sil), Zone IV (Mus-Sil-Ksp), and Zone V (Sil-Ksp) are distinct from those of Zones I and II in that they are rarely euhedral and contain few inclusions. As indicated in Table 1, Zones II and III are separated by reaction
Fig. 2. Contours of atomic percent Fe, Mg, Ca, and Mn in a garnet from specimen 908, Zone I. Dots indicate microprobe analysis spots, and triangles indicate analyses of ilmenite inclusions, keyed by letter to Table 4. Probe section was specially prepared to pass as close as possible to the center of a subhedral crystal.

(2), which marks the upper stability of staurolite in these pelitic rocks. Figure 3b illustrates the zoning trend for a Zone III garnet, 892U. The rim has lower Mn than the core, but also has considerably lower Mg/Fe. The only prograde continuous Fe-Mg-Mn reaction which can operate in Zone III,

\[ \text{Mus} + \text{Gar} \rightarrow \text{Sil} + \text{Bio} + \text{Qtz}, \]  

(3)

cannot be used to explain garnet growth in this zone, since garnet is consumed by this reaction, for which \( T_{\text{Mn}} > T_{\text{Fe}} > T_{\text{Mg}} \). An alternative reaction producing garnet involves ilmenite,
TRACY, ROBINSON AND THOMPSON

Mus + Ilm + Qtz → Gar + Ti-Bio

or ilmenite and rutile.

Mus + Ilm + Qtz → Gar + Bio + Rutile

The limiting binary systems predict that $T_{Fe} > T_{Mn} > T_{Mg}$ for these reactions, which is consistent with the zoning in sample 892U (Fig. 3b).

The contours of composition for sample 933B in Zone IV (Fig. 4) show that the compositional variation is greatest in the marginal region of the garnet, in contrast to the more regular zoning across the lower-grade garnets. With regard to the distribution of Mn and Mg, the garnets from Zone IV may be considered to have reverse zoning from those in Zone I. The core to rim zoning trends for 933B and sample T12 from Zone V are shown in Figure 3c. Zoning from Mg-richer cores to Fe- and Mn-richer rims is strikingly different from zoning in inner parts of lower-grade garnets, though apparently similar to trends in outer parts of Zone I garnets. It is also similar to the garnet zoning observed by Grant and Weiblen (1971).

Garnet probably originated in Zones IV and V through operation of lower-grade continuous Fe-Mg-Mn reactions, as well as the continuous Fe-Mg-Mn dehydration reaction

Bio + Sil + Qtz → Gar + Ksp + H$_2$O

For reaction (5), the predicted relative end-member temperatures are $T_{Mg} > T_{Fe} > T_{Mn}$. Consequently, the three-phase triangle Gar-Bio-Sil in the AKFM projection from KAlSi$_3$O$_8$, SiO$_2$, and H$_2$O (J. B. Thompson, 1957) moves toward more Mg-rich compositions with increasing temperature. For Zone IV and V garnets, chemical zoning is strongest near the rims (Fig. 4), but is in the reverse sense from the trend predicted by this reaction. One explanation for this marginal zoning behavior, consistent with the shape of the garnets and zoning profiles (Fig. 3c), would involve late-stage operation of continuous reaction (5) in a retrograde sense:

Gar + Ksp + H$_2$O → Bio + Sil + Qtz.

For this case, reacting garnet rims are depleted in Mg relative to Fe and Mn.

The differences in element distribution in cores of garnets from Zones III, IV, and V compared to those from Zones I and II might be explained in a variety of ways. A first possibility is that the garnet in the higher-grade zones was not formed in these rocks at lower grade, either because of systematic bulk composition differences from the rocks now found in Zones I and II, or because they followed a different $P$-$T$ path during metamorphism. The bulk composition argument can be ruled out, however, because bulk compositions in all zones, deduced from amounts of analyzed phases, overlap extensively. If the $P$-$T$ path were the same and relict portions of lower-grade garnets remained within garnets of Zones III, IV, and V, then some internal mechanism, such as increased self-diffusion rates, could have caused elimination of the remnant internal-element distribution. The observation that zoning patterns...
are consistent with continuous reactions operating wholly within each zone may indicate that the higher-grade assemblages did not pass through the whole prograde sequence, but followed independent P-T trajectories.

Table I shows that Zones III, IV, and V contain the same AKFM assemblage (Gar–Bio–Sil) but are distinguished through the operation of continuous reactions involving Mus–Pla–Ksp–Sil–Qtz–H₂O (Evans and Guidotti, 1966; Tracy, 1975). While assemblages imply existence of the discontinuous reaction in a Ca-free system

\[
\text{Mus + Pla + Qtz} = \text{Ksp + Sil + H₂O} \quad (6)
\]

(A. B. Thompson, 1974a), the assemblage Mus–Pla–Ksp–Sil–Qtz is stabilized through continuous reactions involving Ca-exchange. In addition to continuous reactions due to Ca–Na–K exchange between Mus–Pla–Ksp, calcium is involved in a continuous reaction between plagioclase and garnet:

\[
\text{Ca–Pla} \rightarrow \text{Ca–Gar + Sil (or Kya) + Qtz} \quad (7)
\]

Data of Tracy (1975) suggest an equilibrium distribution of calcium between coexisting garnet and plagioclase in quartz-sillimanite bearing rocks, probably through operation of a continuous reaction such as (7) (see Appendix 2).

**Zone VI**

This zone is characterized by the occurrence of cordierite in pelitic rocks, possibly appearing by the discontinuous Fe–Mg–Mn reaction

\[
\text{Bio + Sil + Qtz} = \text{Gar + Crd + Ksp + H₂O} \quad (8)
\]

In general, garnets from Zone VI are similar in appearance to those of Zones IV and V but are commonly larger, up to 3 cm or more in diameter. They are nearly homogeneous except where in contact with a more magnesian phase, biotite or cordierite, where a substantial decrease in Mg/Fe occurs. Similar observations have been made for garnets at equivalent grade in northern Connecticut and central Massachusetts by Hess (1971) and Richardson (1975). Zone IV, V, and VI garnets are significantly more pyrope-rich than those from lower grades, probably as a result of significant progress of reaction (5), one of two continuous Fe–Mg reactions which intersect to form the discontinuous reaction (8). Because \( T_\text{Fe} \) is only modestly lower than \( T_\text{Mg} \) for reaction (5), small temperature increases (or dehydrations) result in relatively large increases in pyrope content of garnet.

Figure 5 illustrates the compositional variation in a Zone VI garnet from sample FW407. In sample FW407, the biotite immediately adjacent to the garnet shows a slight increase in Mg/Fe. Richardson (1975) has suggested that this phenomenon may be due to a local cation-exchange process occurring in the first 100–200°C of cooling from the maximum metamorphic temperature. The Fe–Mg–Mn trends for these garnets (Fig. 3d) resemble those for Zone IV and V garnets and the near-rim trends for Zone I, and it is therefore tempting to ascribe all these effects to retrograde processes. Local retrograde cation exchange can only be demonstrated convincingly for
Zone VI garnets, while it is possible to explain the other trends by continuous reactions, either prograde or retrograde, involving participation of most of the phases in the rock with the exception of garnet cores. It is important, therefore, not only to document the compositional variations in garnets, but to attempt to relate the variations to the appropriate continuous or exchange equilibria.

**Mineral composition and the estimation of temperature and pressure**

*Temperature estimates from $K_D(\text{Fe-Mg})$ data*

Temperatures may be estimated using two-phase Fe-Mg cation thermometry if the distribution coefficient, $K_D(\text{Fe-Mg})$, shows a definite temperature dependence or, alternatively, from the compositions of phases involved in continuous reactions, if they can be calibrated. Values of $\ln K_D(\text{Fe-Mg})$ obtained from analyzed coexisting Gar-Bio and Gar-Crd pairs have been crudely calibrated as functions of $T$ (A. B. Thompson, 1976b). The formulation necessarily assumes ideal solution of all components in the crystalline solution [$K_D(\text{Fe-Mg})$ is independent of composition] and that $\Delta C_p$ for the exchange reaction is zero.

Temperatures estimated from the $\ln K_D(\text{Fe-Mg})$ values obtained from microprobe analyses in this study, using the calibration of A. B. Thompson, are presented in Table 3. In contrast to the garnets, where core, intermediate, and rim compositions are available for $K_D$ calculations, biotite was found to be essentially homogeneous within individual specimens, except in Zone VI where biotite immediately adjacent to garnet is more magnesian than elsewhere in the rock (Table 3), due to local retrograde exchange. It is reasonable to assume that $K_D$ calculated from garnet-rim and matrix-biotite compositions gives an indication of the last continuous retrograde metamorphic equilibration. However, it is a serious problem to estimate how much the matrix-biotite composition might have been changed by retrograde (and prograde) reactions from the composition it had when it was in equilibrium with intermediate or core garnet compositions. It can be reasoned that the amount of biotite composition change during a retrograde continuous reaction would be proportional to the extent that bulk garnet participated in the reaction. In cases where the rock contains very little garnet and/or the retrograde outer rims are extremely narrow (and there are no other abundant Fe-Mg-Mn phases), the matrix biotite may have been close to being an infinite reservoir, and there is no way that the biotite Fe/Mg ratio could have increased substantially from what it was earlier. Here, $K_D$ determined from garnet interior and matrix biotite should give a substantially correct estimate of prograde temperature. On the other hand, when the rock contains very abundant garnet and/or shows very extensive retrograde rims as exemplified by specimen 933B (Table 2, Figs. 3c, 4), the Fe/Mg ratio of the matrix biotite should have increased substantially from what it was earlier. In this case, $K_D$ calculated using interior-garnet and matrix-biotite compositions results in
a "false" high temperature estimate (Table 3, 933A, 933B, T12A).
Gar–Bio pairs from Zones I and II yield temperatures which are lowest for cores and outermost rims,
diagram (Fig. 6) showing the temperatures and pressures at which garnets of the indicated composition would be in equilibrium with Fe–Mg–Mn Crd, Sil, and Qtz. Pressures determined from this Fe–Mg–Mn data necessarily give lower pressure estimates than if the experimental Fe–Mg data (corrected for Mn) of Hensen and Green (1973) or Currie (1971) had been used. The calculated Mg end-member reaction used here is about 3 kbar below that of Hensen and Green.

The assemblage Gar–Crd–Sil–Qtz–Ksp is known only in Zone VI, and yields estimates of pressure of 6.2–6.3 kbar (Table 3, column a). In the more common assemblage Gar–Bio–Sil–Qtz, the garnet is necessarily more Fe-rich than garnet in the assemblage Gar–Crd–Sil–Qtz at the same P and T. Consequently, due to the orientation of the Gar–Crd P–X loop, with garnet on the high-P side, Gar–Sil–Qtz (+ Bio) without cordierite must indicate higher pressure than garnet of the same composition with cordierite. Garnet composition in the assemblage Gar–Bio–Sil–Qtz, applied to Figure 6, should then yield an estimate of minimum pressure (Table 3, column a). Because reaction (9) is metastable in the kyanite zone, P–X loops and an Fe–Mg–Mn triangle were constructed for reaction (9) with kyanite (see caption Fig. 6), and pressure estimates for Zone I samples were obtained from these.

Other continuous reactions involving Gar–Bio–Sil–Qtz can be used for thermometry and barometry. If muscovite is present with Gar–Bio–Sil–Qtz, as in Zones II, III and IV, then continuous reaction (3), which has values of dP/dT for end-members approaching zero, could be a useful barometer, but not thermometer. This continuous Fe–Mg reaction has been calibrated (neglecting Mn because of the paucity of data) using the calculated dP/dT for the pure-Fe reaction, the location of an invariant point through which this curve must pass, and Δμ°FEMS₁, to calculate the Mg reaction (see Appendix 1). The pressures estimated from this method...
GARNET COMPOSITION AND ZONING  

(Table 3, column b) are considered to represent maximum values because the effect of Mn would be to lower the pressure of the continuous Fe-Mg reaction. This calibration is even less dependable than Gar-Crd-Sil(Kya) because it is not tied to experimentally investigated equilibria.

A further attempt at quantitative geobarometry uses the compositions of coexisting garnet and plagioclase, with \( \text{Al}_2\text{SiO}_5 \) and quartz (see Appendix 2). Calibrations of reaction (7) have been used to obtain the pressure estimates shown in Table 3, column c.

**Difficulties in use of zoned garnets for geothermometry and geobarometry**

While the data presented here are considered to illustrate the importance of prograde continuous reactions in the formation of growth zoning in garnet, difficulties in interpretation are apparent. First, modeling of garnet growth zoning with such models as Rayleigh fractionation (Hollister, 1966) can be successful only if the garnet is involved in a single continuous reaction during its growth. Second, with available data, we are unable to discriminate fully between garnet zoning due to continuous prograde reactions, retrograde reactions either between adjacent phases or within a larger volume around the garnet, homogeneous diffusion within garnet, exchange with Fe-Mg-Mn inclusions, and reactions involving a possible melt phase at the highest grades.

The observed zoning of garnets from Zones IV, V, and VI cannot be successfully explained by prograde continuous reactions involving iron, magnesium, and manganese. However, as discussed by J. B. Thompson (1972, p. 32), simultaneous reactions involving iron–titanium oxides, iron sulfides, or graphite can displace projected bulk compositions in the AKFM tetrahedron away from or towards (FeO) and consequently affect the nature of the Fe-Mg continuous reactions. Similarly, as discussed by A. B. Thompson et al. (1976 and in preparation), simultaneous reactions involving calcium and sodium phases such as white micas, feldspars, epidote, and calcite can displace projected bulk compositions in the AKFM reaction (7) and consequently displace the Fe-Mg continuous reactions. Reactions involving phases that display Tschermak's exchange, for example, Al\(_2\)Mg\(_4\)Si\(_6\)O\(_{24}\) in muscovite, biotite, chlorite, and possibly staurolite, will have the same effect. Such reactions operating simultaneously with Fe-Mg-Mn exchange reactions could actually lead to garnet consumption or a net change in zoning patterns contrary to those implied by continuous Fe-Mg-Mn reactions.

The role of diffusion in producing the observed zoning is difficult to assess. In fact, we have taken definite advantage of the slow diffusion rates within garnet that have led to the preservation of growth zoning, at least for Zones I, II, and III. This suggests that the exchange reactions within these samples have involved all the phases in the rock outside the garnet. This implied mobility of exchangeable species may be related to the presence of some transporting medium, such as the unseen “intergranular film.” Further evidence that garnets from the lower-grade zones preserve continuous reaction zoning is the progressive decrease from core to rim of the ratio Mn/Fe in both host garnet and included ilmenite (see Fig. 2 and Table 4). For these coexisting phases, the ratio (Mn/Fe)\(_{\text{Garn}}/(Mn/Fe)_{\text{Ilm}}\) changes slightly from core to rim. If this \( K_D \) could be calibrated as a function of temperature, then it might be possible to distinguish prograde continuous Fe-Mg-Mn reactions from retrograde two-phase cation exchange between garnet and ilmenite.

If mass balance across mineral contacts in exchange equilibrium can be evaluated, then the scale of equilibration can be determined. Moreover, the sense of the Fe–Mg exchange may be related to the change in the two-phase \( K_D(\text{Fe-Mg}) \) and the appropriate relative temperature change deduced. The demonstration of total mass balance across garnet–cordierite and garnet–biotite junctions in Zone VI rocks (Richardson, 1975) and the absence of hydrated minerals at grain boundaries (Hess, 1971) is taken to indicate diffusional cation exchange between adjacent mineral grains only. The observed change in \( K_D(\text{Fe-Mg}) \) indicates diffusion in response to falling temperature during a “dry” period of retrograde

**Table 4. Compositions of ilmenite inclusions and adjacent garnet in specimen 908**

<table>
<thead>
<tr>
<th>Code</th>
<th>Distance from center</th>
<th>Atomic percent Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Mn/Fe</th>
<th>(Mn/Fe)(<em>{\text{Garn}}/(Mn/Fe)</em>{\text{Ilm}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>Gar</td>
<td>1.000</td>
<td>0.072</td>
<td>0.16</td>
<td>7.2</td>
</tr>
<tr>
<td>B</td>
<td>0.8 mm</td>
<td>Gar</td>
<td>0.885</td>
<td>0.110</td>
<td>0.10</td>
<td>7.0</td>
</tr>
<tr>
<td>C</td>
<td>1.3 mm</td>
<td>Gar</td>
<td>0.890</td>
<td>0.008</td>
<td>0.10</td>
<td>7.8</td>
</tr>
<tr>
<td>D</td>
<td>1.8 mm</td>
<td>Gar</td>
<td>0.900</td>
<td>0.008</td>
<td>0.10</td>
<td>9.0</td>
</tr>
</tbody>
</table>

*See Figure 5a.*
772 TRACY, ROBINSON AND THOMPSON

metamorphism (Lasaga and Richardson, 1975). Homogeneous interior compositions of Zone VI garnets could be taken to indicate that, during prograde growth, diffusion rates within the garnet exceeded the rate of growth on the exterior, or that increased homogeneous diffusion rates at the inferred temperatures (650-695°C) were able to eliminate earlier growth zoning.

If the near-rim zoning in garnets from Zone VI represents a retrograde exchange in response to cooling, it could be suggested that the near-rim zoning in garnets from Zone I and the core to rim zoning in garnets from Zones IV and V are also due to retrograde processes. The more concentric patterns of near-rim zoning in garnets of Zones I–V, however, which occurs irrespective of the adjacent phase, indicates a more complex mechanism than local two-phase cation exchange. Moreover, other phases in the assemblage appear to be internally homogeneous in composition. The reequilibration may have involved other phases in the rock, thereby representing retrograde continuous reaction, operating in a reverse sense from the prograde counterpart.

**Speculations on significance of temperature and pressure estimates**

Although the $P$ and $T$ estimates of this study are tentative and will, of course, be subject to major correction on the basis of additional and improved experimental work, it is useful to consider some of the geological implications. The estimates of temperature and of pressure (or minimum pressure) are plotted directly on a $P$-$T$ diagram (Fig. 7) together with three conflicting sets of experimental data on the stability of the $\text{Al}_3\text{SiO}_5$ polymorphs (Newton, 1966; Richardson et al., 1969; Holdaway, 1971). Minimum pressures for most zones lie within 1 kbar below estimated pressure for Zone VI and suggest that the last prograde equilibration may have been near 6 kbar over the entire area, well above any of the conflicting experimental triple points. Only specimens from Zone I have minimum pressures for estimated temperatures that lie on the kyanite side of all of the experimental Kya–Sil equilibria. All the Zone I specimens studied actually occur close to the kyanite-sillimanite isograd, and would be expected to fall close to this equilibrium in Figure 7.

Reclit kyanite is fairly common in some rocks of Zone II, particularly near the Keene gneiss dome, in the north center of Figure 1. Detailed work on gedrite–cordierite gneisses in this vicinity (Robinson and

![Fig. 7. $P$-$T$ diagram summarizing the pressure and temperature estimates made for samples in this study: Zone I (squares), Zones II and III (open circles), Zones IV and V (closed circles) and Zone VI (triangles). Symbols with arrows are minimum pressure estimates. Bars are used for samples with minimum (from Gar–Crd–Sil[Kya]–Qtz) and maximum (from Gar–Bio–Mus–Sil–Qtz—see Appendix 1) pressure estimates. $\text{Al}_3\text{SiO}_5$ triple points shown for comparison are $N$ (Newton, 1966), RGB (Richardson et al., 1969) and $H$ (Holdaway, 1971).

Jaffe, 1969) suggests late-stage crossing of the pressure-sensitive reactions

$$\text{Gedrite} + \text{Sillimanite} + \text{Quartz} = \text{Cordierite} + \text{H}_2\text{O} \quad (10)$$

and

$$\text{Gedrite} + \text{Sillimanite} = \text{Cordierite} + \text{Corundum} + \text{H}_2\text{O} \quad (11)$$

to lower pressure, interpreted as the product of tectonic unloading associated with the rise of the gneiss domes.

Several of the rocks of Zone VI, including FW-283 and FW-122 (Field, 1975), contain columnar aggregates of sillimanite crystals with textural features similar to those at Gap Mountain, New Hampshire (Rosenfeld, 1969). These may be interpreted as sillimanite pseudomorphs after andalusite. Interestingly, the estimated temperature and pressure for
specimen FW-122 (Table 3) lie close to the "isomeke" determined using quartz inclusion piezothermometry by Adams et al. (1975, Fig. 10) for specimen γ612 from Gap Mountain. However, they suggest temperatures between 500 and 600°C for their specimen. Regardless of precise temperatures, it appears that the rocks forming much of this part of the Merrimack synclinorium followed a trajectory on the high-temperature side of the Al₂SiO₅ triple point and, at least in the case of Zone VI in Massachusetts, suffered rather severe late-stage compression to pressures above any of the experimental triple points. The overall impression of late-stage unloading, due to uplift, in the Bronson Hill anticlinorium, and simultaneous late-stage compression due to downbuckling in the adjacent Merrimack synclinorium is consistent with the presently available picture of late-stage regional tectonics and gravity in central Massachusetts (J. B. Thompson et al., 1968; Kick, 1975).

Summary

We have attempted to illustrate the importance of continuous reactions involving the whole assemblage in the formation of growth zoning within garnets of medium- to high-grade metamorphism, and to emphasize that adequate petrologic characterization of natural samples is mandatory. Appropriate continuous reactions controlling the compositions of coexisting minerals must be identified and scales of equilibration considered.

We are unable at this time to assess the total effect of the amount of diffusional mass transfer (Blackburn, 1968; Anderson and Buckley, 1973, 1974), which is a function of additional unknown variables, including relative time of annealing, initial magnitude of concentration gradients between garnet and matrix, and complex relations between chemical potentials and diffusive fluxes. It appears that the minor zoning of Zone VI garnets represents diffusional cation exchange in the absence of H₂O. If the marginal zoning of Zone IV and V garnets and the near-rim zoning reversal of Zone I garnets are due to retrograde continuous reactions in the presence of an aqueous fluid or film and not the result of complex prograde continuous reactions not represented by the AKFM pelite projection (with Mn), then a continuum of retrograde effects during cooling may be indicated, and these assemblages may be used to deduce some aspects of the cooling history. It is not yet known if this fluid requires an external source or reflects prograde dehydration fluids unable to escape and hence available for partial rehydration during a change in local temperature conditions.

Any attempt to refine the methods outlined here requires further calibrations from precise experimental studies, particularly P-T location of all end-member reactions and binary or ternary continuous reactions, and additional data on the activity-composition relations of the crystalline solutions, particularly cordierite. Also important are information on the nature and rates of diffusion in major metamorphic minerals and the mechanisms of crystal growth and intergranular diffusion. If the techniques described in this paper can be applied with greater precision, it will provide a powerful tool for better understanding the development of metamorphic rocks.

Appendix 1. Calibration of a Gar-Bio-Sil-Mus-Qtz Fe-Mg geobarometer

An attempt has been made to calibrate crudely the divariant isothermal P-X(Fe-Mg) loops for the continuous Fe-Mg reaction, involving ideal garnet and biotite solutions,

\[
\text{Gar} + \text{Mus} \rightarrow \text{Bio} + \text{Sil} + \text{Qtz} \tag{3}
\]

for use as a geobarometer. A value for \(dP/dT\) of +8 bars deg⁻¹ for the pure Fe-reaction was estimated (Thompson, 1976b, Table 2). The P-T location of the Fe and Mg end-member curves is constrained by Fe and Mg invariant points generated by the intersections of

\[
\text{Crd} = \text{Gar} + \text{Sil} + \text{Qtz} \tag{9}
\]

and

\[
\text{Crd} + \text{Mus} = \text{Bio} + \text{Sil} + \text{Qtz} \tag{12}
\]

in the end-member systems. This intersection is close to that between (9) and the reaction

\[
\text{Mus} + \text{Qtz} = \text{Ksp} + \text{Sil} + \text{H}_2\text{O} \tag{13}
\]

in end-member systems in P-T space. Thus, the pure-Fe reaction (3) is assumed to pass through the points 500°C, 2.8 kbar and 700°C, 4.2 kbar, even though metastable. By analogy with experimentally investigated and calculated reactions in the Mg-system, reaction (3) is assumed to pass through 500°C, 17.4 kbar and 700°C, 19 kbar, even though metastable in the pure Mg-system. Alternatively, the Mg-reaction (3) can be calculated from the P-T location of the Fe-reaction (3) and the (FeMgₓ₋₁) exchange potential for Gar-Bio (Thompson, 1976b, Fig. 1). Isothermal P-X(Fe-Mg) sections were calculated from these P-T...
Appendix 2. Calibration of a garnet-plagioclase-Al$_2$SiO$_5$-quartz geobarometer

The calculated breakdown reactions for plagioclase at high pressures (Thompson, 1974b, Fig. 8) were used as a base for the calculation of isothermal $P$-$X$ sections for reaction (7). One-site ideal solution was assumed for plagioclase, and solution of grossular was assumed ideal through Car-(Fe, Mg, Mn)$_3$. The $X_{Ca}$ values of coexisting garnet and plagioclase with sillimanite and quartz were used to estimate pressures for the temperatures shown in Table 3. The resulting pressures, shown in column c in Table 3, were necessarily determined from the asymptotic limb of an exponential curve and as such carry considerable uncertainty.

Acknowledgments

The authors thank an anonymous reviewer for his very helpful comments on the manuscript, and Dr. M. T. Field for providing us with some of his samples for study. This research was supported by National Science Foundation Grants GA-31989 (to H. W. Jaffe and Robinson) and DES-75-15012 (to Robinson). We also gratefully acknowledge the use of the automated microprobe at the University of Massachusetts, Amherst, which is supported by N.S.F. and state funds.

References


—— (1974b) The instability of feldspar in metamorphism, in,