Fluid-assisted modification of garnet composition along rims, cracks, and mineral inclusion boundaries in samples of amphibolite facies schists

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Abstract

Compositional zoning patterns in garnet from schists in central Vermont and western Connecticut suggest that prograde garnet growth was followed by an episode of compositional modification during fluid-assisted metasomatism. Prograde garnet zoning patterns are modified, with characteristic depletion of $X_{Gr}$ and corresponding increases in $X_{Amp}$, $X_{Sp}$, and $X_{Py}$, in a region 50–150 μm thick near the rim of garnet and along cracks and mineral inclusion boundaries. These regions of garnet compositional modification have a clouded appearance in thin section because they contain abundant secondary inclusions of both minerals and fluid 1–2 μm in size. Metasomatic reactions among the matrix mineral assemblages produced an assemblage more hydrous than the original prograde assemblage. The dissolution and concomitant reprecipitation of garnet in these samples occurred at lower amphibolite facies conditions.

Introduction

Garnet compositions are commonly a basis for thermobarometric calculations, and thus modifications to prograde garnet zoning have been the subject of many previous studies. Volume diffusion can modify garnet compositions at temperatures greater than ca. 550–650 °C (Loomis et al., 1985; Florence and Spear, 1991). The prograde composition of garnet around primary mineral inclusions, trapped during garnet growth, can be modified by exchange reactions (Tracy, 1982) and by net transfer reactions (Whitney, 1991). Yardley (1977) suggested that modifications to prograde garnet zoning could be regionally mapped and used to define an isograd comparable to the breakdown of muscovite to form sillimanite and feldspar. Zones of abrupt change in prograde garnet zoning patterns, such as those described in the present study, can be formed by sequential episodes of garnet growth without volume diffusion (Rumble and Finnerty, 1974), by discontinuous reactions (Thompson et al., 1977), and by resorption with volume diffusion (de Bethune et al., 1975; Tracy, 1982; Karabinos, 1984).

This study focuses on modifications to prograde garnet zoning patterns in two locations, representing two different metamorphic episodes. These garnets abruptly change composition in a zone 50–150 μm wide at their rims, around a variety of mineral inclusions, and along some cracks in the garnet interiors. The zones are decorated by small mineral and fluid inclusions 1–2 μm in diameter. These zones are interpreted to have formed by metasomatic dissolution and reprecipitation of preexisting garnet.

Sample locations

Rocks in this study were sampled from two locations in the Acadian zone of western New England (Fig. 1). Peak metamorphic minerals west of the Proterozoic massifs were produced mainly during Middle Ordovician (Taconian) metamorphism and during Early to Middle Devonian (Acadian) metamorphism east of the massifs (Sutter et al., 1985). Both metamorphisms produced Barrovian facies series mineral assemblages. The Acadian metamorphic front (Fig. 1) represents a zone of transition from rocks in which the mineral assemblages, textures, and structures are dominantly the result of Taconian metamorphism to those in which they are due to Acadian metamorphism (Hames et al., 1991). Pre-Silurian rocks east of the Acadian front, as at the locality described below, locally contain polymetamorphic mineral assemblages that reflect both events.

Rocks within the Sharon Quadrangle and vicinity, northwestern Connecticut (Fig. 1), were initially metamorphosed at middle amphibolite-facies conditions (Zen, 1981; Wang and Spear, 1991) during the Taconian orogeny and were again metamorphosed at varying grades during the Acadian orogeny (Hames et al., 1991). Sample WH141 is a metamorphosed shale, part of the Walloomsac Formation, which in New York, Massachusetts, and Vermont contains Middle Ordovician faunas (Ratcliffe, 1974; Finney, 1986).

The structure and stratigraphy of the Strafford Quadrangle and vicinity in east-central Vermont (Fig. 1) were described by Doll (1943), White and Jahns (1950), Hov...
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and (1969), and Ralph (1982), and the metamorphism of
the area was described by Menard (1991). Devonian rocks
exposed in the quadrangle were deformed and metamor-
phosed during the Acadian Orogeny. The major structural
feature in the Strafford Quadrangle is the Strafford Dome (Fig. 1), which exposes a sequence of rocks increasing
inward from chlorite grade to kyanite grade. The sam-
ple described here is from a region that Ferry (1990) pro-
posed to have experienced high synmetamorphic fluid
flow.

Methods

Mineral compositions for the sample from Connecticut
were determined at the Virginia Polytechnic Institute and
State University on a Cameca SX50 electron microprobe.
Areal maps of Fe, Mg, Mn, and Ca concentration were
based on X-ray intensity data accumulated from wave-
length-dispersive spectrometers. Similarly, mineral com-
positions for samples from Vermont were determined using
the Jeol 733 Superprobe at Rensselaer Polytechnic
Institute. Analytical conditions for spot analyses of all
samples were 15 kV and 15–20 nA for a maximum of 40
s per element analyzed. Natural and synthetic silicates
and oxides were used as standards. FTIR and Raman
spectroscopic study was conducted at Virginia Polytech-
inic Institute and State University.

Sample Descriptions

Taconian garnet overprinted by Acadian metamorphism,
Sharon, Connecticut

Sample WH141 (Fig. 1; UTM coordinate B33234370)
is a schist in which Taconian metamorphism produced
the assemblage kyanite + staurolite + garnet + biotite
+ quartz + muscovite + plagioclase + ilmenite with
minor apatite, graphite, and pyrite (Hames, 1990). Com-
positional layering in the exposure defines a crenulated,
composite surface that is overgrown by the garnet, kya-
nite, and staurolite (T. porphyroblasts of Sutter et al.,
1985; Hames et al., 1991). This composite surface and
the porphyroblasts are deformed by both northwest- and
northeast-trending Acadian folds (the D4 and D5 folds of
Ratcliffe and Harwood, 1975).

Porphyroblastic garnet, kyanite, and staurolite have ir-
regular, rounded shapes and are surrounded by coarse,
randomly oriented muscovite, suggesting resorption of
early-formed, less hydrous porphyroblasts and formation
of a more hydrous assemblage. Traces of acicular sill-
imanite are present on the resorbed margins of garnet por-
phyroblasts in sample WH141. Plagioclase porphyro-
blasts are texturally zoned, with fractured, inclusion-rich
cores and clear subhedral rims; however, they have a uni-
form composition of about An48. The porphyroblast re-
sorption, coarse muscovite, and acicular sillimanite are
interpreted as having formed during Acadian metamor-
phism (Hames et al., 1991). The rim compositions of
porphyroblasts in WH141 define P-T conditions of 510
± 25 °C and 4 ± 0.5 kbar; from this sample locality,
Acadian metamorphic P-T conditions increased mono-
tonically to greater than 650 °C and 7 kbar southeastward
along the present erosion surface (Hames et al., 1991).

Textures of garnet representative of this locality are
shown in Figure 2. The garnet interior is characterized by
concentric changes in major cation concentrations that
are consistent with growth zoning. In contrast, there is an
abrupt decrease in $X_{Ca}$, and accompanying increases
in $X_{Mg}$, $X_{Si}$, and $X_{Fe}$ within ~100 μm of the garnet rim.
Identical compositional changes in garnet occur along
some cracks and around some primary apatite, musco-
vite, biotite, and ilmenite inclusions. These composi-
tional changes are uniform and do not vary with respect to
which mineral is in contact with garnet along the rim or
inclusion interface.

The regions of sharp compositional change are marked
by abundant secondary fluid and mineral inclusions, up
to ~2 μm in diameter, that impart a clouded appearance

Fig. 1. Regional geologic maps of western New England indicating the general areas of Taconian and western Acadian metamorphisms (adapted from Sutter et al., 1985). One sample is from post-Taconian metasedimentary rocks of the Acadian zone in Vermont, and the other is from the Taconian-Acadian polymetamorphic zone in northwestern Connecticut. Geology of the 15’ Strafford Quadrangle is based upon Doll (1943), White and Jahns (1950), Howard (1969), Rolph (1982), and Menard (1991): WR = Waits River Formation, SP = Standing Pond Volcanic Member, GM = Gile Mountain Formation. Geology of the 15’ Sharon Quadrangle is based upon Gates (1959), Zen (1981), and Hames et al. (1991): HM = Housatonic massif, EV = Everett Formation, S = Stockbridge Formation, W = Walloomsac Formation.
in thin section (Fig. 2A, 2C). The clouded regions along cracks in the garnet cross the concentric growth zoning pattern, and thus these small inclusions are secondary with respect to prograde garnet growth. Mineral inclusions in these regions are highly birefringent and appear to be muscovite and sphene. The fluid inclusions are generally equant, and negative crystal shapes (reflecting the host isometric structure) are common. Spacing between these inclusions ranges from 2 to 10 μm. Some inclusions are arranged in parallel, linear arrays: these arrays are generally perpendicular to the garnet surface. The largest fluid inclusions (~1–2 μm in diameter) have distinct vapor bubbles that adhere to the inclusion wall, suggesting that the fluids are H₂O-rich. FTIR and laser Raman spectroscopic data from garnets in sample WH141 (and others in the vicinity) detect both CO₂ and H₂O in the fluid inclusions.

Garnet in the prograde Acadian zone, Sharon, Vermont

Sample 8516g is a calcic pelitic schist from the Devonian Gile Mountain Formation collected from a roadcut on the northbound entrance ramp of I-89 in Sharon, Vermont (Fig. 1). The matrix assemblage is kyanite + staurolite + garnet + biotite + plagioclase (An₃₅) + quartz + muscovite + graphite, with minor rutile + ilmenite + tourmaline + zircon. Ilmenite and the first generation of muscovite and biotite define a crenulated S₁ schistosity. Orientation of a second generation of biotite defines the S₂ schistosity. The garnet core has straight inclusion trails,
Fig. 3. Garnet from the Acadian zone in central Vermont.
(A) Sketch of garnet in 8516g. Late, coarse muscovite porphyroblasts, appearing as inclusions in the section, crosscut the garnet and the included S1 surface (defined principally by ilmenite inclusions). The distribution of micrometer-scale fluid and mineral inclusions is indicated by the darker shaded pattern as in Fig. 2A. Line A–D refers to the compositional half-profile in C; the inset represents the location of the photomicrograph in B.
(B) Photomicrograph of a muscovite inclusion and surrounding garnet showing the distribution and scale of the fluid and mineral inclusions. (C) Garnet compositions in sample 8516g (profile lines are interpolated between 116 data points). Note the sharp decrease of $X_{an}$ and increase of $X_{mg}$ and $X_{sm}$ from D to the garnet rim at A. Identical compositional changes occur around mineral inclusions, as shown in B. The 116 analysis points are along the traverse.

Garnet in this sample grew during Acadian metamorphism by the reaction (Menard, 1991) Chl + Ep + Ms + Qtz + Gr = Grt + Bt + Pl + H2O + CO2. Garnet was interpreted to have grown along a computed P-T path of heating during a 1-kbar pressure increase up to conditions of 550 ± 25 °C and 7.5 ± 0.6 kbar (Menard, 1991). The subsequent development of sharp compositional zoning at the rim of the garnet probably formed without a large change in P and T; the distribution coefficient of Ca between garnet and plagioclase inclusions does not change substantially across the sharp compositional zoning in the garnet. The large change of garnet and plagioclase compositions under seemingly isothermal, isobaric conditions indicates open-system behavior and metasomatic loss of Ca from the rock.

composed of epidote and graphite, that define an included S1 surface at a high angle to the matrix S2 foliation (Fig. 3).

Garnet in sample 8516g is intensely resorbed (Fig. 3) and replaced along its rim and interior by coarse, unoriented muscovite that crosscuts the internal S1 fabric in the garnet (Fig. 3). The garnet rim and surfaces of the garnet adjacent to the late muscovite have a zone 30 μm wide with abundant micrometer-scale fluid and mineral inclusions. Garnet compositions (Fig. 3C) are similar to those in sample WH141. $X_{gr}$ in the garnet core is high and fairly uniform. However, in the outer 50 μm of the garnet rim, $X_{gr}$ decreases sharply as $X_{al}$ and $X_{sp}$ increase; similar sharp zoning patterns are evident adjacent to some muscovite, ilmenite, and plagioclase inclusions.
Compositional modification by volume diffusion

One interpretation for the observed sharp compositional zoning of the garnet near its rim is that it results from volume diffusion within existing garnet following a change of equilibrium compositions. This phenomenon has been documented in middle amphibolite and higher grade settings where temperatures exceeded ca. 650 °C. Several studies have concluded that temperatures below ca. 600 °C are insufficient to produce significant modification of prograde garnet zoning in garnets larger than a few millimeters in diameter for the duration of most metamorphic episodes (e.g., Florence and Spear, 1991). Thermobarometry from each of the present sample sets indicates that temperatures did not exceed 550 °C during the garnet resorption episodes, and thus it is difficult to account for the observed changes by volume diffusion. Previous studies have also suggested that surface diffusion, assisted by an intergranular metamorphic fluid, may have enhanced compositional changes along garnet rims (Karabinos, 1984).

Models of multicomponent volume diffusion generally predict a smooth, curved compositional zoning profile as a result of modifications to growth zoning patterns (Florence and Spear, 1991, their Fig. 5). Ordinary volume diffusion tends to smooth out sharp shoulders and compositional breaks in zoning patterns. In contrast, the $X_{\text{Gr}}$ profile from the samples of this study have a straight-line decrease of $X_{\text{Gr}}$ at the rim that is separated from the core compositions by a shoulder—a distinct change in the slope of the zoning profile. Ordinary volume diffusion would tend to smooth out such a shoulder. The natural zoning profiles also contrast with typical patterns of volume diffusion in that the magnitudes of modification of $X_{\text{Sp}}$ and $X_{\text{Gr}}$ in these samples are quite similar. In contrast, the magnitude of modification for $X_{\text{Sp}}$ predicted for volume diffusion is much greater than for $X_{\text{Gr}}$ at any specific time. Relative to the modification of $X_{\text{Gr}}$, the observed modification of $X_{\text{Gr}}$ was enhanced over that expected for simple volume diffusion. Thus the petrologic and textural data suggest that diffusion mechanisms alone are not responsible for the modifications to growth zoning in the present study samples.

Fluid-assisted metasomatism of garnet

The prominent features discussed earlier indicate a mineral replacement process across a reaction layer 50–150 μm wide in which a metamorphic fluid participated—a metasomatic process. Lindgren (1928) defined metasomatism as a process of mineral replacement by simultaneous dissolution and reprecipitation, with accompanying mass transfer of components, via capillary metamorphic fluids. A dissolution reaction can occur most readily upon mineral surfaces where intracrystalline defects (especially vacancies) are concentrated. Previous studies have documented preferential dissolution of a mineral in pits or tubes that formed on surface defects (e.g., Blum et al., 1990, and references therein). Mineral growth can be promoted along the edges of pits, even as the garnet is being resorbed, because of their high surficial energy and resulting thermodynamic instability. Local equilibrium during metasomatism (Thompson, 1959; Korzhinskii, 1970) could fractionate cations between the garnet edges, other minerals, and the metamorphic fluid as the garnet dissolves and reprecipitates. If the equilibrium was controlled by the fluid, then the equilibrium composition of the reprecipitated garnet should be the same along every surface to which the fluid had access, irrespective of which minerals are in contact with the garnet. This metamorphic fluid could also be trapped during the metasomatism as pits are sealed by growth along their edges.
We propose that this single-crystal style of metasomatism formed the textural and compositional discontinuities along garnet surfaces in these samples. The garnet resorption textures, presence of fluid inclusions, and accompanying compositional changes suggest that the outer surface of the garnet was dissolved in a metamorphic fluid. The garnet being resorbed probably had relic, disequilibrium compositions and the equilibrium garnet compositions changed as a result of the resorption. This mineral-surface scale metasomatism modified the original prograde garnet zoning pattern along every pathway accessed by the metamorphic fluid, even along cracks and some inclusion boundaries inside the garnet. Reprecipitation of garnet in equilibrium with the fluid, concomitant with the dissolution, trapped both fluid and mineral inclusions in pits near the garnet surface.

We cannot prove that the new garnet was in equilibrium with the fluid, yet fluid-controlled equilibrium is strongly suggested because (1) garnet composition is similar along every surface that contains the mineral + fluid zone, irrespective of which mineral is in contact with garnet across the zone; (2) we obtain consistent pressure-temperature estimates (i.e., consistent mineral \( K_\text{eq} \) and thus \( P-T \) estimates) from the garnet rims and matrix minerals in these samples; and (3) the \( P-T \) estimates based upon garnet rim and matrix mineral compositions are compatible with the sample matrix assemblages and the regional metamorphic setting.

**Implications**

These samples provide evidence of compositional modification interpreted to result from fluid-assisted metasomatism in metapelitic rocks at lower to middle amphibolite facies. The extent to which processes more rapid than volume diffusion can modify composition in minerals places limits on the applicability of models based on volume diffusion. Thus the validity of a volume diffusion model to establish guidelines for which natural minerals are safe to analyze in polymetamorphic rocks (Jiang and Lasaga, 1990) relies upon the extent to which volume diffusion is the fastest process for effecting a change in a particular garnet sample. Tracy (1982) suggested that hydration reactions can modify garnet rim compositions more effectively than volume diffusion. This study documents that these reactions occurred at amphibolite facies conditions and were metasomatic in the sense of Lindgren (1928). This study also emphasizes and expands a conclusion of Loomis (1983) and Whitney (1991): postentrapment net-transfer reactions can occur among garnet, primary mineral inclusions, and the matrix if there are cracks or inclusion boundaries that provide a link with the matrix assemblage.

The data of this study are from two areas in the New England Appalachians. In addition, previous studies in a variety of metamorphic settings have documented zones 10–300 \( \mu \)m wide enriched in fluid and mineral inclusions that precede a reaction front. Zhou and Fyfe (1989) noted that an inclusion zone precedes reaction fronts in altered volcanic glass. Features analogous to the present study have been reported in a separate part of Vermont by Karabinos (1984), in the Italian and Swiss Alps by de Bethune et al. (1975), and in the Dalradian of Scotland by Yardley (1977), indicating that this style of garnet compositional modification is more extensive than previously recognized.

**Conclusions**

Garnets from a prograde metamorphic zone in Vermont and a polymetamorphic zone in Connecticut changed composition by a similar, crystal-scale metasomatic process. This metasomatism dissolved garnet with disequilibrium compositions and reprecipitated garnet with a composition in equilibrium with the metamorphic fluid and the evolving matrix assemblage. Fluid and mineral inclusions trapped within garnet and associated abrupt compositional changes are the principal indications of this process. The metasomatism also changed the composition of garnet along cracks that linked the garnet interior with the matrix.

**Acknowledgments**

The research represented in this study was completed during the dissertation work of the authors, and we gratefully acknowledge the advice, guidance, and support of R.J. Tracy and F.S. Spear in our respective work. W.E.H. wishes to thank R.J. Bodnar for advice in this work and assistance with the Raman and FTIR analyses. Comments and reviews from Donna Whitney, Doug Smith, R.J. Tracy, Frank Florence, and K.V. Hodges promoted considerable improvements in the final manuscript. Financial support was provided for W.E.H. through Connecticut and New York Geological Survey grants, and NSF grants EAR-88-16382 and EAR-86-96064 (Tracy). Financial support was provided for T.M through NSF grant EAR-89-16417 (Spear).

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Manuscript received January 24, 1992
Manuscript accepted November 21, 1992