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Ca-METASOMATISM AND CHEMICAL ZONATION OF GARNET IN CONTACT-METAMORPHIC AUREOLES, JUNEAU GOLD BELT, SOUTHEASTERN ALASKA

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Abstract

Calcic pelite from the contact aureoles around plutons in the Grand Island diorite complex, southeastern Alaska, records episodic flow of metamorphic fluid and Ca-metasomatism. Grains of garnet adjacent to quartz veins are comprised of almandine, spessartine, grossular, and pyrope components and show oscillatory zoning in mole fraction of grossular (ranging from 0.10 to 0.35) and antipathetic zoning in mole fraction of almandine. With some exceptions, the mole fraction of spessartine decreases and Fe/(Fe + Mg) increases toward the rim. Na, Y, Yb, and Zr zoning in these garnet grains have opposite trends to grossular, but Ti in garnet is positively correlated with grossular content. Garnet grains *ca.* 2 m from the veins have fewer cycles of zoning, indicating that infiltration started near veins and that some infiltration events penetrated only a short distance into the pelite. In contrast, andradite-rich garnet and epidote in the veins contain negligible concentrations of Y, Yb, and Zr, consistent with growth of andradite-rich garnet from infiltrating fluids containing low concentrations of these elements. The data on zoning can be explained by episodic Ca-metasomatism, with or without mobility of other components, producing episodic growth of garnet, plagioclase, and epidote. The reason for pulses of fluid flow or changes in fluid compositions is unclear, but may be related to episodic plutonism in the complex. Staurolite and other minerals in the amphibolite-facies rocks were partially replaced in a series of fluid-infiltration pulses. The first produced a second generation of garnet, the second produced retrograde clinozoisite + albite + muscovite + sulfide in the contact-metamorphic rocks and the plutonic rocks, and a later event produced chlorite + sericite. Retrograde metamorphism is inferred to be associated with emplacement of plutons in the Coast plutonic–metamorphic complex 10 km to the east, and possibly with mineralization in the Juneau gold belt.

Keywords: garnet, zoning, trace elements, contact metamorphism, metasomatism, southeastern Alaska.

Sommaire

Les roches pélitiques calciques prélevées dans les auréoles de contact autour du complexe plutonique dioritique de Grand Island, dans le sud-ouest de l'Alaska, contiennent des vestiges du flux d'une phase fluide métamorphique et de métasomatose calcique. Les cristaux de grenat voisins de veines de quartz contiennent les composants almandin, spessartine, grossulaire et pyrope; ils font preuve de zonation oscillatoire dans la proportion du pôle grossulaire (dans l'intervalle 0.10 à 0.35), et d'une zonation complémentaire dans le pôle almandin. Sauf quelques exceptions, la proportion de spessartine diminue, et le rapport Fe/(Fe + Mg) augmente vers la bordure. Dans ces mêmes cristaux, la distribution de Na, Y, Yb et Zr va dans le sens inverse à la teneur en grossulaire, tandis que le Ti varie dans le même sens. Des cristaux de grenat situés à environ 2 m des veines possèdent des oscillations moins nombreuses, indication que l'infiltration a débuté près des veines, et que dans le cas de certains épisodes d'infiltration, la phase fluide n'a pas pénétré très loin dans l'encaissant pélitique. Par contre, dans les veines, le grenat, enrichi en andradite, et l'épidote contiennent des quantités négligeables de Y, Yb et Zr; le grenat riche en andradite aurait donc cristallisé suite à l'infiltration d'une phase fluide appauvrie dans ces éléments. Les données obtenues concordent avec l'hypothèse d'une métasomatose calcique épisodique, avec ou sans mobilité d'autres composants, menant à la croissance épisodique de grenat, plagioclase et épidote. Les raisons ultimes des flux épisodiques et des changements dans la composition de la phase fluide demeurent méconnues; elles pourraient être liées à un plutonisme épisodique dans ce complexe. La staurolite et les autres minéraux de ces roches équilibrées dans le faciès amphibolite ont été partiellement remplacés dans une série de pulsations de fluide. La première a donné une deuxième génération de grenat; la seconde a causé une rétrogression à l'assemblage clinozoïsite + albite + muscovite + sulfures dans l'auréole de contact et dans les roches plutoniques. Un événement plus tardif encore a donné l'assemblage chlorite + séricite. La rétrogression métamorphique serait associée à la mise en place de plutons du complexe plutonique et métamorphique de la chaîne côtière 10 km à l'est, et peut-être aussi à la minéralisation responsable de la ceinture aurifère de Juneau.

(Traduit par la Rédaction)

Mots-clés: zonation, grenat, éléments traces, métamorphisme de contact, métasomatose, sud-est de l'Alaska.

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Introduction

Major advances in understanding the flux of metamorphic fluid and metasomatism have resulted from study of the cumulative, time-integrated effects of metasomatic events. To evaluate such effects, researchers have examined reaction progress (*e.g.*, Ferry 1991), compared whole-rock composition of altered rocks to that of the protolith (*e.g.*, Gresens 1966), and evaluated results of bulk isotopic analyses (*e.g.*, Cartwright 1994). Such time-integrated approaches, however, ignore the temporal variability of fluid flux and metasomatism during metamorphism. This variability is potentially important because it reflects processes external to the metamorphic rocks, such as structural events or multiple intrusive events, and internal processes, such as fluid flow between rock types in an outcrop. Methods used to study temporal variability include field-based studies of overlapping aureoles (*e.g.*, Morgan & London 1987), measurement of elemental zoning in minerals (*e.g.*, Kwak & Tan 1981, Jamtveit *et al.* 1993), and studies of isotopic zoning (Chamberlain & Conrad 1993, Kohn *et al.* 1993).

In this paper, we describe contact metamorphic rocks from aureoles around the Grand Island diorite complex in the western metamorphic belt of the Coast plutonic-metamorphic complex near Juneau, southeastern Alaska. On the basis of oscillatory major- and trace-element zoning in garnet and on the sequence of hydration reactions, we conclude that (1) several episodes of fluid infiltration and metasomatism occurred near the thermal peak of metamorphism, and (2) additional events involving fluid infiltration occurred during retrograde metamorphism.

Regional Setting

The Coast plutonic-metamorphic complex in southeastern Alaska comprises (Fig. 1) (Crawford *et al.* 1987): 1) a western metamorphic belt of Paleozoic to Mesozoic metasedimentary and metavolcanic rocks, 2) a central pluton-gneiss belt of Tertiary granodiorite plutons, migmatites, high-grade gneisses, and a narrow belt of granodiorite and tonalite plutons known as the Coast plutonic-metamorphic-complex sill or Great Tonalite sill (Brew & Ford 1981), and 3) an eastern metamorphic belt. Metamorphism and deformation in the Coast plutonic-metamorphic complex occurred during collision of the Insular and Intermontane terranes that lie to the west and east, respectively (Monger *et al.* 1982, Crawford & Hollister 1982, Crawford *et al.* 1987, Stowell & Crawford, in press).

The rocks in the Coast plutonic-metamorphic complex show evidence for at least six metamorphic events, as reviewed by Stowell & Crawford (in press). Contact and regional metamorphic events comprise pre-101 Ma regional metamorphism (M_1^R), 101–90 Ma contact metamorphism (M_2^C), 90–85 Ma regional metamorphism associated with thrusting that inverted metamorphic isograds (M_3^R), 72–58 Ma metamorphism associated with the emplacement of Coast plutonic-metamorphic complex sill plutons (M_4^C), *ca.* 55 Ma high-grade metamorphism in the central pluton-gneiss belt (M_5^{C-R}), and *ca.* 20 Ma contact metamorphism associated with Miocene plutons (M_6^C).

The Grand Island diorite complex near Juneau, Alaska, consists of diorite and quartz diorite plutons that intruded the western metamorphic belt of the Coast plutonic-metamorphic complex (Fig. 1). Plutons in the diorite complex display various mineral assemblages, styles and intensities of alteration, and magnetic susceptibilities (Drinkwater *et al.* 1992, Stowell, Inman & Ridgway, unpubl. data). The presence of the igneous assemblage epidote + garnet + hornblende and thermobarometry of the contact-metamorphic rocks indicate a pressure of crystallization in excess of 6 kbars (Zen & Hammarstrom 1984, Inman 1992, Stowell & Crawford, submitted). The only published age for the plutons is 94 Ma (U/Pb zircon) for garnet–biotite granodiorite from Butler Peak (Brew *et al.* 1992) (Fig. 1).

To the north, along strike from the Grand Island diorite complex, are the largest mines in the Juneau gold belt, the foremost lode-gold-producing district in Alaska. The age of mineralization is estimated at ~55 Ma, when crustal stresses changed in response to shifting motions of the plate in the northeastern Pacific (Goldfarb *et al.* 1991). Mineralization may have occurred in less than a million years as a result of metamorphic dewatering and focusing of fluid flow along fault or shear zones (Goldfarb *et al.* 1988, 1991). The Treadwell deposit, near Juneau (Fig. 1), is hosted by a diorite dike similar in age (91 ± 2 Ma; Gehrels, in press) and mineralogy to the Grand Island diorite complex, but other deposits occur in metasedimentary rocks.

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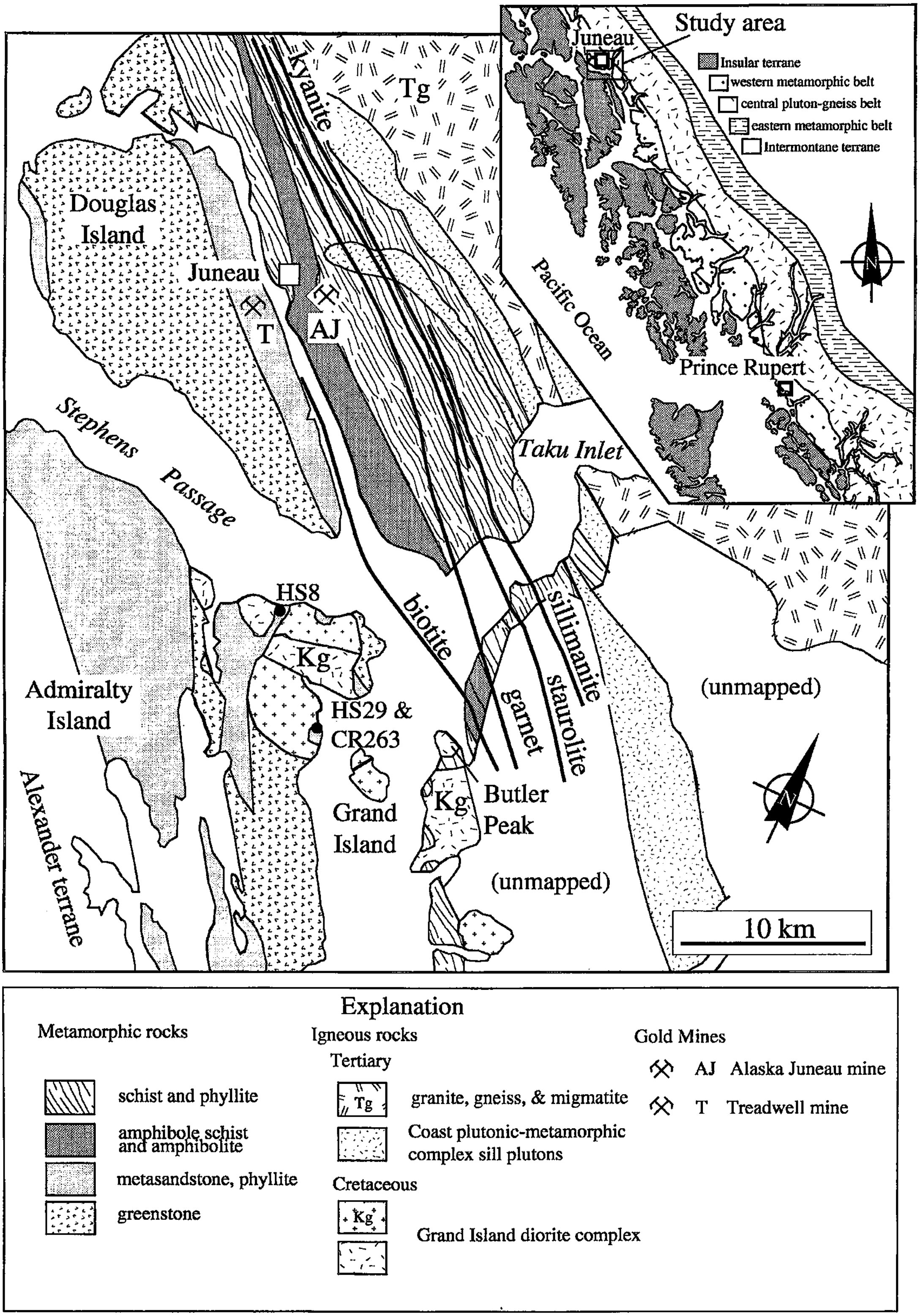
FIG. 1. Simplified geological map of the northern part of the western metamorphic belt near Juneau, modified from Lathram *et al.* (1965), Brew & Ford (1985), and Drinkwater *et al.* (1992). Inset shows geological terranes of southeastern Alaska and adjacent British Columbia (modified from Monger *et al.* 1982).


Study area
Juneau
Insular terrane
western metamorphic belt
central pluton-gneiss belt
eastern metamorphic belt
Intermontane terrane
Pacific Ocean
Prince Rupert
N
Douglas Island
Juneau
T
AJ
kyanite
Tg
Stephens Passage
Taku Inlet
biotite
garnet
staurolite
sillimanite
HS8
Kg
HS29 & CR263
Admiralty Island
Grand Island
Kg
Butler Peak
Alexander terrane
(unmapped)
(unmapped)
10 km
Explanation
Metamorphic rocks
schist and phyllite
amphibole schist and amphibolite
metasandstone, phyllite
greenstone
Igneous rocks
Tertiary
Tg
granite, gneiss, & migmatite
Coast plutonic-metamorphic complex sill plutons
Cretaceous
Kg
Grand Island diorite complex
Gold Mines
AJ Alaska Juneau mine
T Treadwell mine

The country rocks around the Grand Island diorite complex include pelite, calcic pelite, marble, amphibolite, and layers and pods of calc-silicates. These rocks were affected by the following metamorphic events: a low-grade regional event (Himmelberg *et al.* 1992) that produced chlorite-zone mineral assemblages (Stowell & Crawford, in press) (M_1^R), contact metamorphism around the diorite plutons (M_2^C) and, finally, low-grade metamorphism associated with crustal thickening (M_3^R) or emplacement of the ≤72 Ma plutons in the Coast plutonic-metamorphic complex 10 km to the east (M_4^C) (Fig. 1) (Gehrels *et al.* 1992, Stowell & Crawford, in press).

Contact metamorphism caused by intrusion of plutons in the Grand Island diorite complex (M_2^C) produced narrow (20–200 m) aureoles with peak metamorphic grade increasing from chlorite-zone outside the aureoles up to a maximum of staurolite + kyanite zone at the contact with the plutons (Hooper & Stowell 1990, Stowell & Inman 1991, Inman 1992). The mineral assemblages indicate a relatively uncommon medium-pressure aureole (Pattison & Tracy 1991), although other examples occur elsewhere in the western metamorphic belt (Stowell & Crawford, in press). Mylonitic fabrics and rotated staurolite and garnet porphyroblasts indicate synchronous deformation and contact metamorphism (Hooper & Stowell 1989, 1990).

The most recent metamorphism observed in the western metamorphic belt near Juneau (M_3^R or M_4^C or both) produced mineral assemblages that range from sillimanite zone near the Coast plutonic-metamorphic-complex sill to chlorite zone at Grand Island. The Grand Island plutons and their aureoles contain greenschist-facies mineral assemblages produced by this event (Stowell & Crawford, in press, Stowell & Pike, in press). These mineral assemblages may have resulted from emplacement of plutons in the central pluton-gneiss belt or thermal equilibration after thrusting of hot rocks over cooler rocks to the west (Himmelberg *et al.* 1991). Faulting and associated flow of metamorphic fluid during the waning stages of this event were responsible for mineralization in the Juneau gold belt (Goldfarb *et al.* 1988, 1991).

TABLE 1. REPRESENTATIVE COMPOSITIONS OF METAMORPHIC GARNET FROM CONTACT–METAMORPHIC AUREOLES OF THE GRAND ISLAND DIORITE COMPLEX, SOUTHEASTERN ALASKA

Major elements	8d core	8d rim	29j core	29j rim	263m rim matrix	263m core matrix	263m rim vein
SiO_2 wt.%	37.57	37.12	38.49	38.79	37.33	37.27	38.04
Al_2O_3	20.82	21.39	21.96	21.48	21.31	21.29	18.63
TiO_2	0.10	0.05	0.22	0.13	0.07	0.18	1.68
Fe_2O_3*	n.c.	n.c.	n.c.	n.c.	n.c.	0.21	2.02
FeO	27.53	30.62	21.03	24.25	19.08	21.94	7.89
MgO	3.08	2.72	2.42	1.28	2.17	2.74	0.66
MnO	7.23	2.87	12.36	5.73	7.97	7.57	2.47
CaO	2.24	4.45	5.76	10.65	9.79	7.99	27.63
total	98.57	99.22	102.23	102.31	97.72	99.18	99.02
Cations based on 12 atoms of oxygen							
Si	3.041	2.990	3.000	3.018	3.009	2.980	2.981
Al	1.987	2.030	2.017	1.970	2.025	2.007	1.721
Ti	0.001	0.003	0.013	0.008	0.004	0.011	0.099
Fe^{3+}*						0.012	0.119
Fe^{2+}	0.383	2.063	1.371	1.578	1.286	1.467	0.517
Mg	0.077	0.327	0.281	0.148	0.261	0.326	0.077
Mn	0.102	0.196	0.816	0.378	0.544	0.512	0.164
Ca	0.040	0.384	0.481	0.888	0.846	0.685	2.322
total	7.960	7.992	7.979	7.989	7.975	8.000	8.000
Mg #	0.166	0.137	0.170	0.086	0.169	0.182	0.130
Alm	0.637	0.695	0.465	0.527	0.438	0.491	0.168
Prp	0.127	0.110	0.095	0.050	0.089	0.109	0.025
Sps	0.169	0.066	0.277	0.126	0.185	0.171	0.053
Grs	0.066	0.129	0.163	0.297	0.288	0.223	0.689
Adr*						0.006	0.065
ppm							
Cr	711	328	582	622	n.a.	n.a.	76
Zn	—	—	64	26	n.a.	n.a.	26
Y	6010	10	1620	23	n.a.	n.a.	30
Zr	46	135	292	30	n.a.	n.a.	43
Yb	390	42	45	136	n.a.	n.a.	—

Mg# = Mg/(Fe + Mg). * Fe_2O_3, Fe^{3+}, and Adr estimated from charge balance, n.a. = not analyzed, n.c. = not calculated, Alm: mole fraction of almandine, Prp: mole fraction of pyrope, Sps: mole fraction of spessartine, Grs: mole fraction of grossular, Adr: mole fraction of andradite

Analytical Procedures

The major-element chemical compositions of garnet and other minerals were determined using wavelength-dispersion spectrometry on the JEOL 8600 electron microprobe (EMP) at the University of Alabama. Operating conditions were: accelerating potential 15 kV, beam current 20 nA, counting time 30 s (major elements), and a beam 2 to 15 μm in diameter. Mineral standards and the methods of Bence & Albee (1968) or Doyle & Chambers (1981) were used to calculate the weight percent of oxides or elements, respectively. Representative compositions of garnet are given in Table 1.

The concentrations of trace elements in garnet were assessed using the synchrotron X-ray fluorescence microprobe (SXRF) at Brookhaven National Laboratory and using the University of Alabama EMP. SXRF analytical data were collected with a 10-μm-wide beam using the techniques described by Lu *et al.* (1989) and have detection limits of about 2 ppm for Y and Zr, and about 10 ppm for Yb. EMP operating conditions were: accelerating potential 15 kV, beam current 80 nA, counting time 5 minutes, and a beam 2 μm in diameter, which gives semiquantitative determinations of concentrations above ~100 ppm. The precision and reproducibility of the EMP data are better than 20% relative, which is sufficient to show trends of compositional zoning. Representative trace-element concentrations in garnet are given in Table 1.

Compositional Zoning in Garnet from Calcic Pelitic Schists

Contact-metamorphic aureoles around plutons in the Grand Island diorite complex have been mapped at a scale of 1:50,000 (Inman 1992, Ridgway, Inman &

Stowell, unpubl. data). Petrographic descriptions of over 100 thin sections from the metamorphic rocks provide a data base for the description of the aureoles. Numerous grains of garnet from twenty-five of these samples have been analyzed for thermobarometry (Inman 1992, Stowell & Inman 1991). Four samples that illustrate variations in the chemical zonation of garnet from the pelitic rocks (Inman 1992) were chosen for detailed major- and trace-element studies. Backscattered electron images of garnet grains from HS8d (*ca.* 25), HS29k (*ca.* 50), HS29j (*ca.* 50), and CR263m (*ca.* 10) were examined in order to characterize the nature of chemical zonation. Over 3,500 EMP analyses and 150 SXRF analyses were obtained on a total of 20 grains of garnet from these four samples. These data are used to infer 1) the effects of metasomatism in calcic pelitic schists from the aureoles around plutons in the Grand Island diorite complex, and 2) the variation in metasomatic history found in different aureoles.

Sample HS8d

Sample HS8d is a staurolite-zone pelite collected 10 m from a diorite pluton on the shore of Admiralty Island (Fig. 1). The matrix assemblage is staurolite + garnet + biotite + plagioclase + muscovite + quartz + graphite + retrograde chlorite (Fig. 2a). Muscovite and biotite are foliated and crenulated. Porphyroblastic staurolite overgrew the early foliation, has curved trails of inclusions, and contains relatively few randomly oriented inclusions of graphite. The graphite crystals in the matrix are foliated; therefore, staurolite grew during deformation. The staurolite was partially replaced by biotite and small, euhedral crystals of garnet (Fig. 2a).

The grains of garnet from the schist matrix have an inclusion-free interior mantled by a graphite-rich rim. The garnet in the rim overgrew the crenulation cleavage, and hence postdates staurolite. Compositional zoning divides the garnet into three zones (Figs. 2b, c). The core has a high proportion of the grossular component ($X_{Grs} = 0.22$), a middle portion has less ($0.06 < X_{Grs} < 0.11$), and grossular increases to 0.16 at the rim. The sharp decrease of grossular from the core to the mid-region could reflect resorption of garnet during production of staurolite or loss of epidote from the assemblage (Menard & Spear 1993). Garnet resorption, however, is unlikely because the garnet core is euhedral (Fig. 2b). Therefore, although there are too few inclusions to demonstrate a change of assemblage, we prefer the latter interpretation.

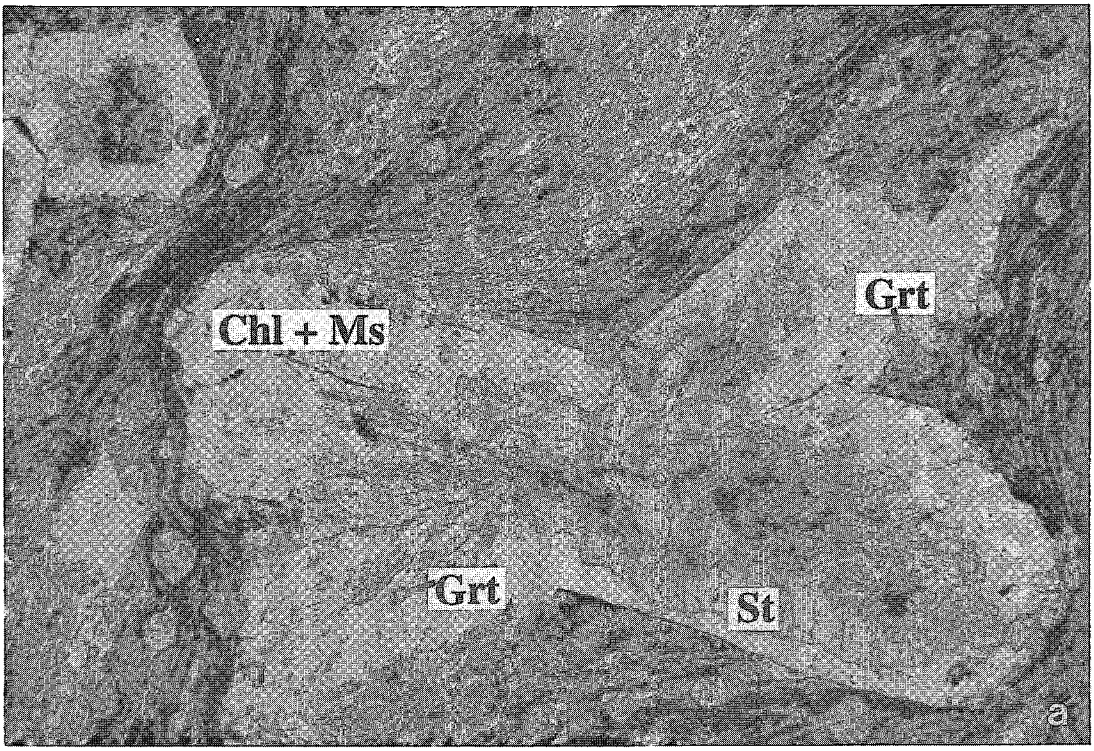
Concentrations of Y and Yb in two grains of garnet from HS8d were determined using SXRF. The zonation of these elements is simple, with high concentrations in the core and low concentrations in the rim (Fig. 2d). The pattern of zoning, which is similar to the pattern of Mn in growth-zoned garnet (Hollister 1966, Tracy 1982), is compatible with depletion of these elements in the matrix of the rock during growth of garnet. A decrease in the availability of these elements could reflect growth of epidote; however, there is no epidote in sample 8d. The simple zonation in Y and its similarity with zonation of the major elements in sample 8d are distinctly different from the oscillatory distribution of Y and the simple bell-shaped major-element zonation described by Lanzirotti (1995) in garnet from similar staurolite-bearing schist from The Straits Schist, Connecticut. We cannot rule out the possibility of metasomatism during the growth of garnet in sample HS8d, but the zonation in major- and trace-element contents is compatible with growth without significant changes in bulk-rock composition. This is in contrast to samples HS29j, HS29k, and CR263m, discussed below.

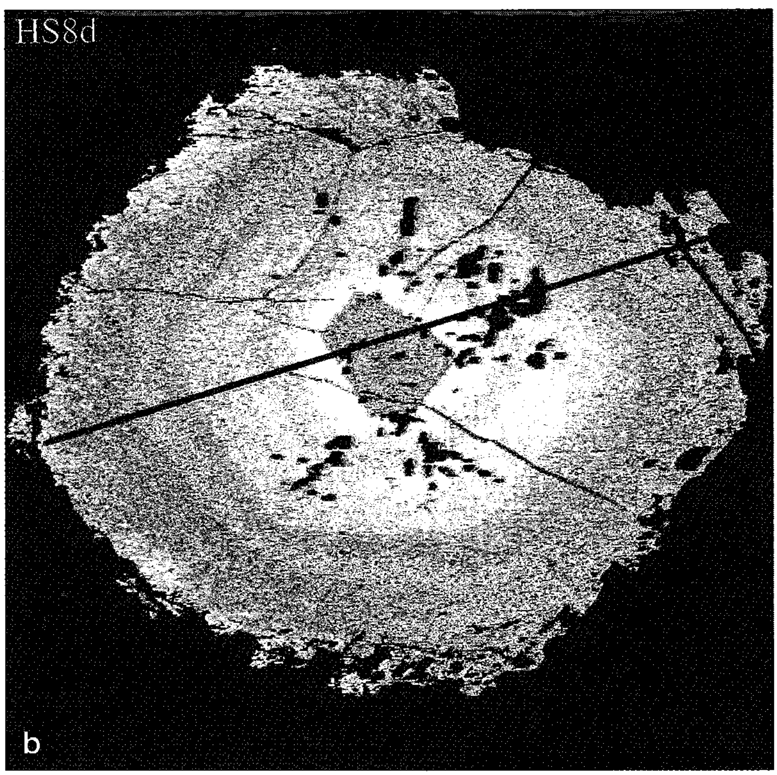
Chlorite and muscovite partially replaced (by pseudomorphism) staurolite, garnet, and biotite, and overgrew both deformation fabrics. This retrograde hydration event also affected the pluton and probably correlates with metamorphism adjacent to plutons to the east in the central pluton-gneiss belt (Stowell & Pike, in press, Stowell & Crawford, in press).

Samples HS29j, HS29k, and CR263m

Samples HS29j, HS29k, and CR263m, all considered calcic pelitic schist, were collected within 25 m of a diorite pluton (Fig. 1). Samples HS29j and HS29k were collected from schist that is exposed in a wave-cut bench within the tidal zone. Sample HS29j is fine-grained schist that contains a deformed quartz vein (<5 cm thick). Sample HS29k is a fine-grained schist, collected 0.8 m from HS29j, that contains several thin (<0.5 cm thick) lenses of quartz. Sample CR263m was collected from a low ridge near the high-tide line, about 3 m from an outcrop of diorite and about 10 m from HS29j and HS29k. Sample CR263m is a garnet–biotite schist that contains a 5-cm-wide garnet-bearing vein. Rocks in the contact aureole display a penetrative muscovite + biotite schistosity, and some also display a crenulation cleavage. The penetrative schistosity must have formed during contact metamorphism because it is defined by contact-metamorphic minerals of the garnet zone.

The peak metamorphic assemblage in these samples was garnet + biotite + plagioclase + epidote + quartz + muscovite + titanite, with minor tourmaline, apatite, and zircon. Grains of garnet in the schist are small, 0.2 – 0.5 mm, and some have been partially resorbed to chlorite. The garnet grains contain inclusions of quartz and epidote. Tiny (1 to 3 μm) inclusions of compositionally zoned, rare-earth-element-rich epidote in the garnet grains occur adjacent to euhedral cores of grossular-rich garnet (Fig. 3a) and are inferred to have grown contemporaneously with cores of allanite found in matrix epidote.


Chl + Ms
Grt
Grt
St
a


HS8d
b

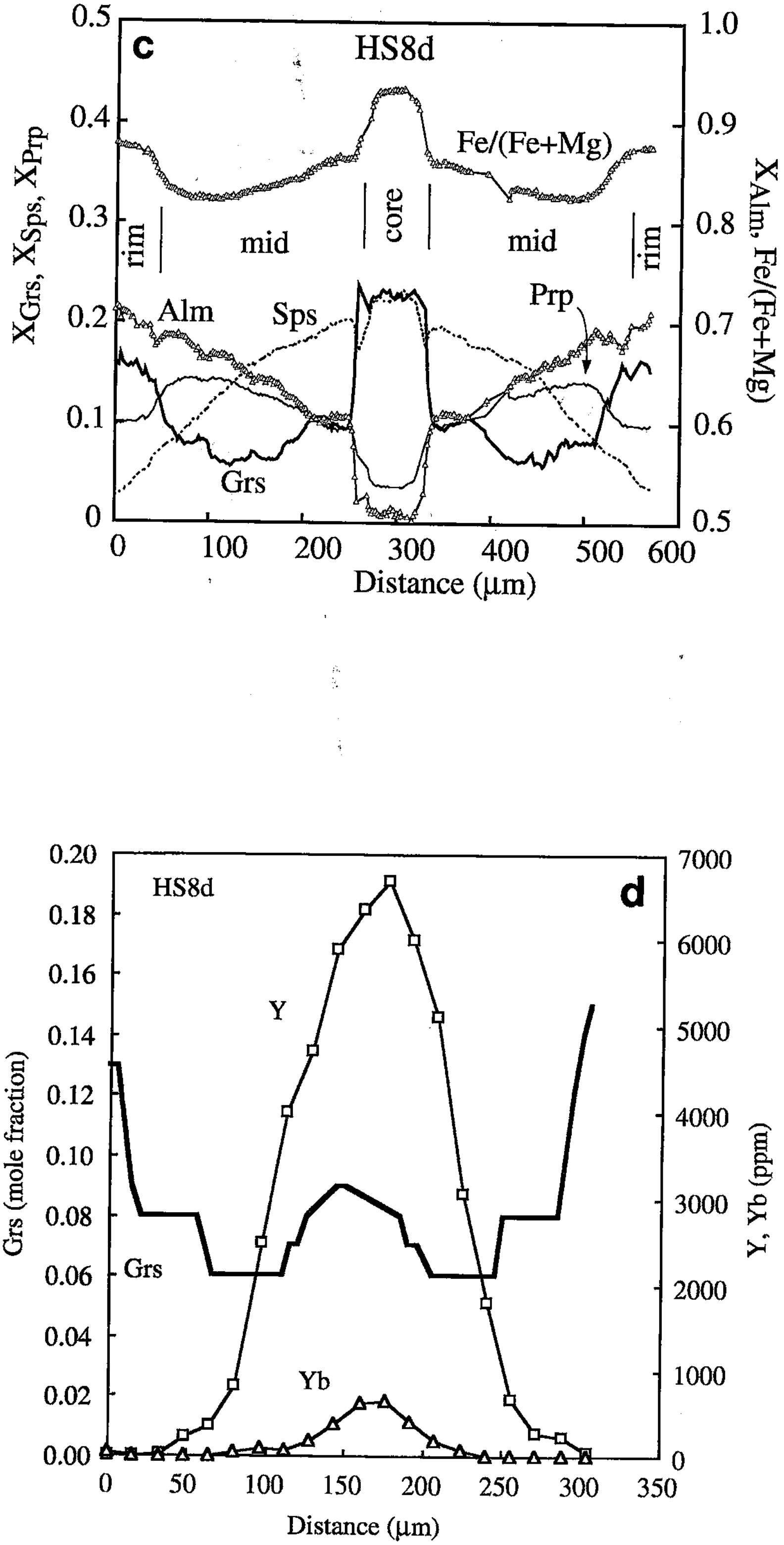
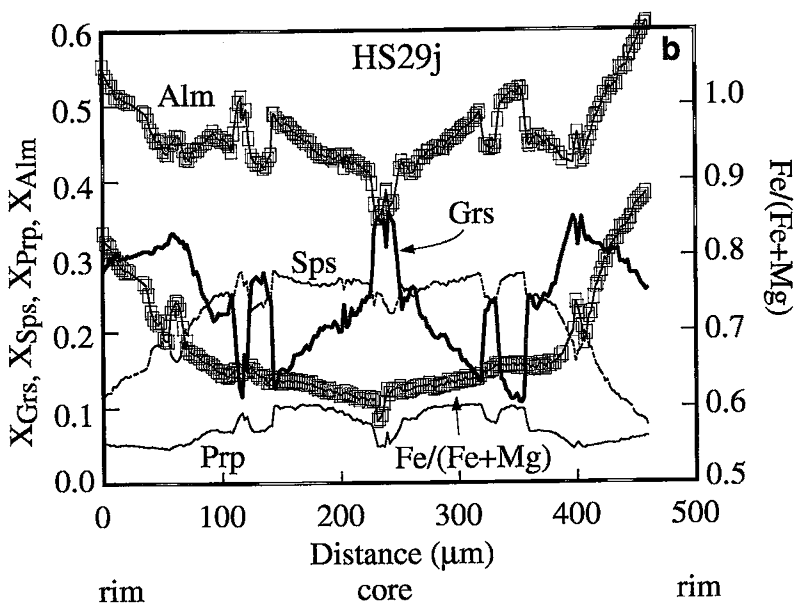


FIG. 2. Compositional zoning in garnet from sample HS8d. a. Photomicrograph of twinned staurolite partially replaced (pseudomorphism) by garnet, biotite, and muscovite. The matrix foliation is defined by muscovite, biotite, and graphite. Garnet cores and staurolite overgrew the early fabric, and garnet rims overgrew a crenulation (not apparent in photo). Plane-polarized light. Base of photo is 1 mm. b. Back-scattered electron image of garnet; the red areas correspond to the highest Fe and Mn contents, and the purple areas, to the lowest. Most of the black inclusions are quartz. The sides of the image have 512 pixels and represent 500 μm. c. Compositional zoning of pyrope, grossular, spessartine, and almandine components along the line shown in (b). Note the different scales on the left and right. Symbols on X_{Alm} and Fe/(Fe + Mg) show positions of analyzed points. The decrease of grossular content from the core to mid-region marks the likely loss of epidote from the assemblage; the increase of grossular from the mid-region to the rim reflects changed P–T conditions. The rim grew after the growth of staurolite. d. Y and Yb zoning along a traverse across a second grain of garnet. Also shown is X_{Grs}, which allows correlation with Figure 2b. The simple zonation in the distribution of these elements is compatible with consumption of a trace-element-rich phase (*e.g.*, epidote).


HS29j
a


HS29j
b
Alm
Grs
Sps
Prp
Fe/(Fe+Mg)
X_{Grs}, X_{Sps}, X_{Prp}, X_{Alm}
Fe/(Fe+Mg)
Distance (μm)
rim
core
rim

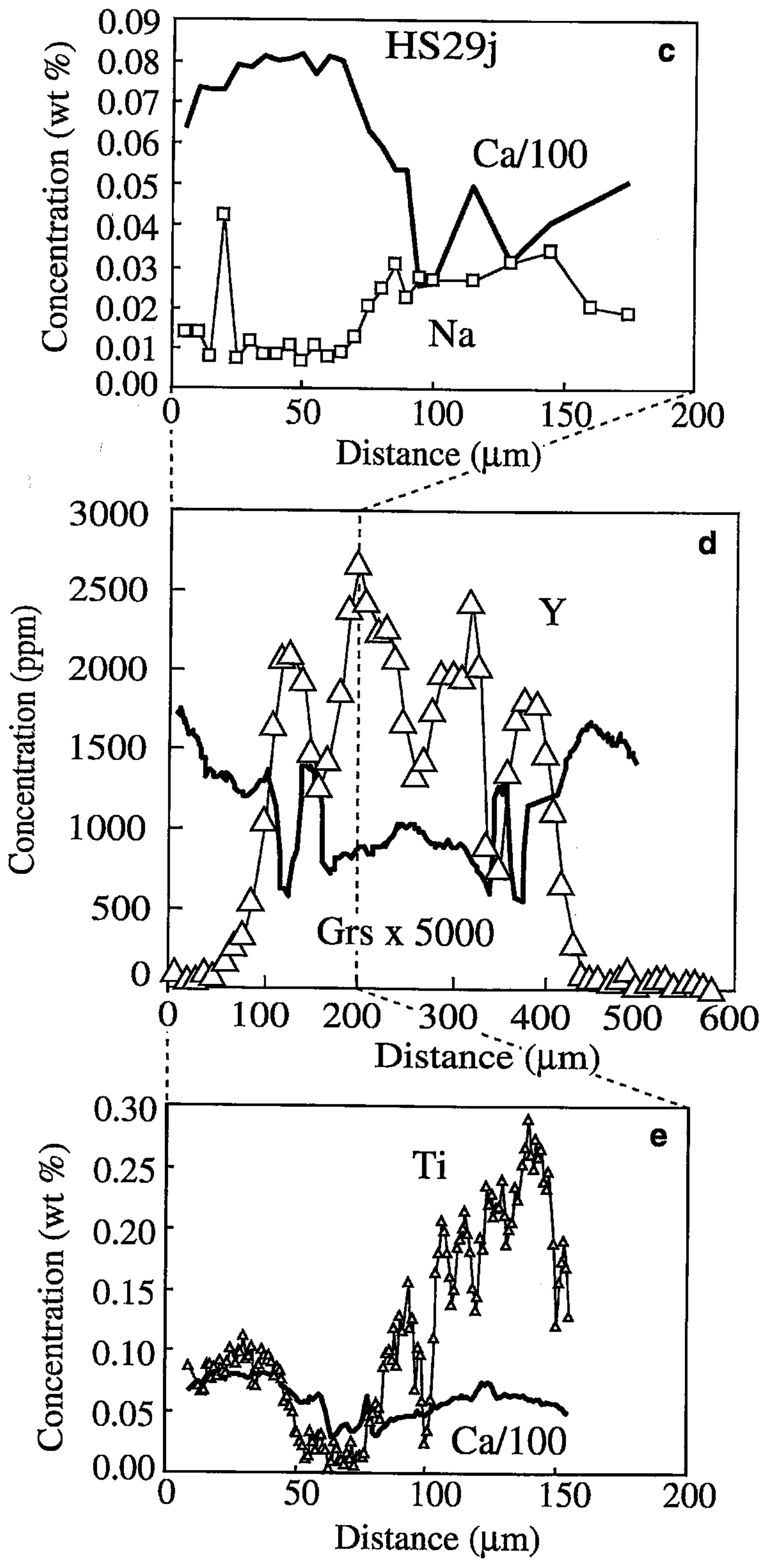


FIG. 3. Compositional zoning in garnet from sample HS29j. a. Back-scattered electron image of garnet; the red areas correspond to the highest Fe and Mn contents, and the purple areas, to the lowest. The small, bright spots near the core are *REE*-rich epidote; most of the black inclusions are quartz. The sides of the image have 512 pixels and represent 500 μm. The three concentric purple bands indicate peaks in Ca-concentrations. b. Compositional zoning of garnet from HS29j along line shown in (a). Note the different scales on the left and right. Symbols on X_{Alm} and Fe/(Fe + Mg) show positions of points analyzed. c. Na zoning along a traverse from a second grain of garnet in HS29j (EMP), with the weight percent of Ca shown for comparison. Note the negative correlation of Na with Ca content. d. Y zoning along a traverse from the second grain of garnet in HS29j. Also shown is X_{Grs}, which allows correlation with Figures 3a–c. Note that the center with high X_{Grs} in Figures 3a, c is not shown here. Yb and Zr (not shown) also have similar patterns of zoning as does Y. Note the negative correlation of Y with Ca content. e. Ti zoning along a traverse from a third grain of garnet in HS29j (EMP), with the weight percent of Ca shown for comparison. Note the positive correlation of Ti with Ca content.

The outcrop exposes several generations of dikes and quartz + feldspar veins with differing relationships to the deformational fabrics. Sample HS29j, for example, contains a quartz vein that was deformed during formation of the schistosity and again during development of the crenulation. The vein is surrounded by a selvage of chlorite + sericite 1–2 mm thick. Garnet is most abundant within 3 mm of the vein and may have been part of a medium-grade selvage, but subsequent retrograde alteration obscures the relationships. Late, cross-cutting, undeformed veins, in contrast, have selvages of only retrograde minerals. Sample CR263m includes a 5-cm-wide vein containing quartz + amphibole + clinozoisite + sulfides + andradite-rich garnet ($X_{Adr} \leq 0.20$); it formed after the penetrative schistosity and subsequently was folded. Amphibole within veins and vein selvages (CR263m), coarse-grained muscovite selvages, and garnet adjacent to veins (HS29j and HS29k) suggest that all of these veins formed at or near the thermal peak of contact metamorphism.

Compositional zoning in garnet from HS29j and HS29k can be seen optically with transmitted light because zones with different indices of refraction have sharp boundaries, and in back-scattered electron images (Figs. 3a, 4a). Garnet exhibits oscillatory zoning in grossular (X_{Grs} ranges from 0.10 to 0.35) and antipathetic zoning in almandine (Figs. 3b, 4b). Spessartine decreases, and Fe/(Fe + Mg) increases, from the core toward the rim. Grains of garnet in sample HS29j have three peaks in grossular concentrations (Fig. 3b), those in HS29k have only two peaks (Fig. 4b). Approximately fifty grains of garnet were examined in each of these samples, which should be a large enough number to avoid the problem of non-centered sections. Andradite-rich garnet from the quartz vein in CR263m is less strongly zoned than any of the garnet grains from the schist (not shown), but also shows numerous oscillations in grossular content (X_{Grs} ranges from 0.40 to 0.58); andradite is antipathetic (X_{Adr} ranges from 0.04 to 0.17).

The level of Na in garnet is negatively correlated with grossular content (Fig. 3c). As suggested by Hickmott & Spear (1992), incorporation of traces of Na in garnet can mirror the Na content of plagioclase. If that applies here, the garnet-zoning data suggest that levels of grossular in garnet and of anorthite in plagioclase increased (and decreased) together. Concentrations of Y (Fig. 3d), Zr (not shown), and Yb (not shown) are negatively correlated with grossular and positively correlated with Mn in the garnet from the schist and may reflect simultaneous growth of epidote and grossular-rich garnet, and epidote consumption during growth of grossular-poor garnet. The strong negative correlation of Y and grossular is similar to the zonation of garnet in calcic pelites from Massachusetts described by Hickmott & Spear (1992), but contrasts with oscillatory Y and simple major-element zonation described by Lanzirotti (1995) for garnet in The Straits Schist. Ti concentrations in the garnet, on the other hand, are positively correlated with grossular (Fig. 3e), which may reflect consumption of ilmenite or rutile to liberate Ti during growth of grossular-rich garnet, or metasomatic addition of Ti.

In contrast with the garnet in the schist, andradite-rich garnet in a quartz vein at the same location contains lower concentrations of Y and Yb (<700 ppm), higher concentrations of Ti, and similar concentrations of Zr throughout the grains. The relatively low concentrations of Y and Yb in andradite-rich garnet in the veins compared to garnet from the schist suggests that 1) these elements were less abundant in the Ca-rich vein-forming fluid than in the schist, or 2) these elements were less strongly partitioned into the andradite-rich garnet from the vein.

Matrix epidote from the schist in sample HS29j contains small, 10-μm, subhedral cores of zoned, rare-earth-element-enriched epidote (~0.2 – 0.3 mole fraction pistacite) that contain Ce, and are generally zoned with increasing La and decreasing Sm and Eu from the center outward. Approximately 3 μm from the center of the grains, a 1-μm-wide ring has higher Ce concentrations than the rest of the grain, which may reflect an episode of epidote consumption and concentration of rare-earth elements (*REE*) at the grain edges. The rim zone on matrix epidote is unzoned clinozoisite in textural equilibrium with the retrograde assemblage.

The mineral assemblage developed at the peak of metamorphism in the schist was extensively retrograded to clinozoisite + albite + muscovite + sulfide. Finally, during later retrograde metamorphism (<400°C), minor growth of chlorite and sericite indicates another event of fluid infiltration. Thus, there were four (sample HS29k) or five (sample HS29j) events of fluid infiltration.

Plagioclase is zoned from oligoclase to albite, from core to rim. It has equilibrium textures with the retrograde assemblage, and hence all the plagioclase likely postdates the formation of garnet. Correlation of compositional zoning in garnet and in plagioclase has been used to interpret pulses of metasomatic fluids (Crawford 1977), but that cannot be done in these rocks owing to the pervasive character of the later metasomatic events.

Pyrrhotite, chalcopyrite, and sphalerite replaced the rim zones of the peak metamorphic minerals, but do not occur as inclusions; thus, the sulfides probably were added to the rock during retrograde alteration. Similar textures and assemblages also occur locally in the diorite plutons of the Grand Island diorite complex. More extensive alteration, and gold and sulfide mineralization, also occur in the Treadwell Dike near Juneau (Spencer 1906). On the basis of mineralogy and

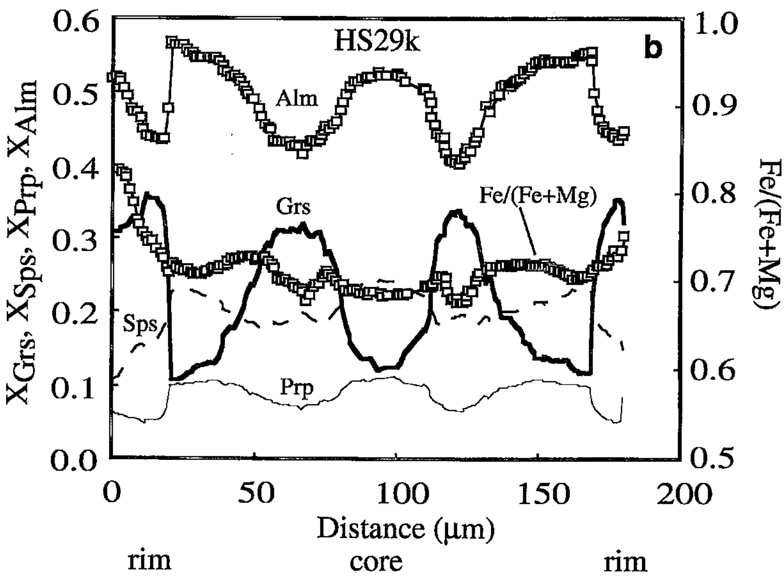


FIG. 4. Compositional zoning in garnet from sample HS29k. a. Back-scattered electron image of garnet; the red areas correspond to the highest Fe and Mn contents, and the purple areas, to the lowest. Most of the black inclusions are quartz. The sides of the image have 512 pixels and represent 250 μm. The two concentric purple bands indicate peaks in concentration of Ca. b. Compositional zoning of garnet from HS29k along line shown in (a). Note the different scales on the left and right. Symbols on X_{Alm} and Fe/(Fe + Mg) show positions of points analyzed.

timing, we speculate that the S and minor Co, Cu, and Zn were added in the same event that produced the Juneau gold deposits 20 km to the north along strike.

Discussion

The interpretation given above, that the compositions of both types of garnet from locations HS29 and CR263 suggest the importance of pulses of fluid during metamorphism, is discussed further here.

Zoning of major elements

Compositional zoning in garnet can be produced by metasomatism, or changes in pressure and temperature. The magnitude of the oscillatory compositional zoning, observed in samples from HS29, would require large changes in temperature (possibly >200°C at constant pressure) or pressure (possibly a few kbars). These estimates are made by comparison with modeling by Menard & Spear (1993) in calcic pelitic assemblages. Such large episodic changes of pressure or temperature, however, seem unreasonable for a contact-metamorphic aureole that displays no other physical evidence for such major variations. Whereas large changes in temperature can accompany metamorphism, such large variations would involve a sequence of discontinuous and continuous reactions not observed here. Therefore, we conclude that the observed patterns of compositional zoning in the garnet are not the result of changes in pressure and temperature.

Changes of mineral assemblage can also affect the compositional zoning of minerals (*e.g.*, Menard & Spear 1993), but this does not seem to be a likely explanation for the oscillatory zoning described here, which would require the improbable cyclic addition and loss of a mineral or a series of minerals.

Instead, the simplest interpretation is that the sharp increases of grossular content shown in the profiles of samples HS29j and HS29k (Figs. 3, 4) reflect successive Ca-metasomatic events that drove metamorphic reactions, produced garnet, and increased the equilibrium grossular content. This stage of mineral growth may have been rapid, as suggested by the inclusion of tiny grains of *REE*-rich epidote preferentially in these zones. Garnet growth continued with decreasing grossular content after each of these events, allowing the interpretation that Ca was fractionated into the growing garnet and plagioclase when volatiles were the only mobile components.

The relatively grossular-poor zones in the garnet from HS29 schist samples may have grown by a reaction such as:

$$\text{Chl} + \text{Ep} + \text{Ms} + \text{Qtz} = \text{Grt} + \text{Pl} + \text{Bt} + \text{fluid}.$$

The breakdown of epidote in this assemblage has been correlated with growth of grossular-rich garnet (Menard & Spear 1993). Note that even the relatively low concentrations of grossular in garnet from HS29 (X_{Grs} between 0.12 and 0.22) are higher than those from pelites that were interpreted to have grown in a mineral assemblage lacking epidote (Menard & Spear 1993). The grossular-rich zones of in the garnet may have grown by a reaction such as:

$$\text{Chl} + \text{Ms} + \text{Qtz} + \text{Ilm} + \text{Ca}^{\text{fluid}} = \text{Grt} + \text{Pl} + \text{Ep} + \text{Bt} + \text{fluid}.$$

Consumption of chlorite, muscovite, and quartz in the schist and growth of biotite were chosen to balance the reaction, consistent with reactions observed in calcic pelite elsewhere (Menard & Spear 1993). The hypothesis for influx of a Ca-rich fluid can be evaluated further by considering the concentrations of trace elements in the garnet.

Zoning of trace elements

Data on trace-element zoning provide a useful supplement to major-element data for petrological interpretations (Hickmott *et al.* 1987, Hickmott & Shimizu 1990, Hickmott & Spear 1992, Schwandt *et al.* 1993). Some trace elements are indicators of particular petrological reactions; for example, a zonal distribution of Zn in garnet can reflect reactions involving staurolite (or sulfides), Y can reflect reactions involving epidote, Ti can reflect reactions involving ilmenite–rutile (or titanite), and Na can reflect reactions involving plagioclase (Hickmott & Spear 1992). A correlation of Na zonation in garnet with the Na content of plagioclase would be particularly important in rocks where compositions of early plagioclase are not preserved (*e.g.*, samples HS29j and HS29k). These elements provide additional monitors of the assemblage present in the rock, of the progress of reactions (*e.g.*, epidote-consuming reactions will liberate Y into the system), and of metasomatism. Hickmott & Spear (1992) concluded that concentrations of Y, Zr, and *REE* in garnet should vary with Ca concentrations because these elements substitute into epidote-group minerals. Therefore, reactions involving consumption of these phases should supply both Ca and these trace elements for garnet growth.

The simple zonation in Y and Yb and the positive correlation with Ca in garnet from sample 8d are compatible with consumption of a trace-element-rich phase (*e.g.*, epidote) during growth of garnet. Y and Yb concentrations, in contrast, show oscillatory zonation and appear to be negatively correlated with Ca in garnet from sample HS29j (Fig. 3d). This is compatible with addition of a Ca-rich and Y- and Yb-poor fluid during growth of garnet. The andradite-rich garnet and epidote in the vein in sample CR263m also display patterns of zoning consistent with growth from a

Ca-rich and Y- and Yb-poor fluid; both minerals probably grew mainly by precipitation from the same hydrothermal fluid (*e.g.*, Jamtveit *et al.* 1993) that infiltrated the surrounding schist.

Correlation of Y and major-element zonation (*e.g.*, negative correlation with calcium content) observed in garnet from the Grand Island area is similar to the zonation in garnet from calcic pelites described by Hickmott & Spear (1992), but contrasts with a lack of any correlation between Y and major elements described by Lanzirotti (1995) in garnet from The Straits Schist. Sample 8d and samples described from The Straits Schist are staurolite-bearing biotite muscovite schist; however, samples 29j and 29k differ from the Connecticut samples: they contain abundant clinozoisite and do not contain staurolite. Maximum temperatures in the Grand Island rocks were 515 and 555 ± 50°C for 8d and 29k, respectively (Stowell & Inman 1991, Stowell & Crawford, submitted). Maximum temperatures in The Straits Schist may have been considerably higher: 650 to 700°C (Miller & Tracy 1991). Contact metamorphic garnet from the Grand Island area must have grown rapidly over a brief time-interval during emplacement of plutons into low-grade metamorphic rocks. Regional metamorphic garnet from The Straits Schist could have remained at metamorphic temperatures for ≥20 m.y. or have been reheated long after growth (Lanzirotti & Hanson 1995). Therefore, although diffusion is not likely to have affected garnet from Grand Island, it may have redistributed major elements in garnet from The Straits Schist (Lanzirotti 1995).

The concentration of Na in garnet from HS29 is negatively correlated with grossular content (Fig. 3c). If the Na content in garnet mirrors the Na content of plagioclase, then this negative correlation indicates that grossular in garnet and anorthite in plagioclase increased and decreased together. Such a correlation is compatible with episodic Ca-metasomatism or episodic breakdown of a Ca-bearing mineral (*e.g.*, epidote). Addition of Ca would drive reactions producing garnet (X_{Grs} increases), plagioclase (X_{An} increases), and epidote, whereas reactions during a hiatus in metasomatism would return X_{Grs} and X_{An} to previous levels. The Ti in garnet from HS29 is positively correlated with grossular (Fig. 3e). This correlation may reflect consumption of ilmenite or rutile to liberate Ti during growth of grossular-rich garnet, or metasomatic addition of Ti. In summary, the zoning of Na, Ti, Y, and Yb in garnet is consistent with incorporation of these elements from within the pelites. Other trace elements may have been added during the proposed Ca-metasomatism, but their concentrations were not monitored. Hickmott & Spear (1992) inferred that trace-element concentrations in garnet should reflect fluid-infiltration events. The trace-element chemistry of garnet, presented here, suggests that some of the trace elements (*e.g.*, Y and Yb) may be locally derived. However, the concentrations of these elements apparently do reflect the flux of Ca-rich fluids because these elements are negatively correlated with grossular content.

The simplest interpretation for the chemical zonation of garnet from samples HS29j and HS29k is that the sharp increases of grossular content and Ti, and decreases of Y, Yb, and Na contents (Figs. 3, 4) reflect successive Ca-metasomatic events that produced garnet with a higher equilibrium content of grossular and lower Y and Yb contents. The interpretation of infiltration by high-Ca fluids is further supported by the andradite-rich garnet found in veins from sample CR263m.

Variability of chemical zonation of garnet with respect to distance from veins

Garnet sampled from within veins, adjacent to veins, and far from veins provides information about the nature and extent of fluid flux. Garnet within the veins (CR263m) is the most Ca-rich of the three and contains the lowest concentrations of Y and Yb. Garnet adjacent to some of the veins (HS29j) has three peaks in Ca concentration, suggesting that these samples were affected by three phases of metasomatism during garnet growth. Garnet further from these veins (HS29k) has only two peaks in Ca concentration, suggesting that these samples were affected by fewer phases of metasomatism during garnet growth.

Variability between outcrops

Fluid flow and metasomatism may vary in different parts of the aureoles in response to successive intrusive events in the Grand Island diorite complex. Samples from HS29 and HS8, for example, record a different sequence of metasomatic and fluid-flow events for two aureoles in the complex. This difference may be related to the presence of a different number of overlapping aureoles, or may be related to fluid flow through different rock-types in the two locations. Samples from HS29, which is from a sequence that contains interbedded calc-silicates, experienced Ca-metasomatism during garnet growth and during retrograde metamorphism, whereas sample HS8d, which is from a sequence lacking interbedded calcic rocks, did not experience Ca-metasomatism.

Conclusion

This paper presents mineral-chemical evidence for temporal variation in metasomatic alteration and intensity of fluid flux in pelites. In our examples, metamorphic reaction-histories and compositional zoning in minerals are interpreted as reflecting pulses of fluid influx and Ca-metasomatism during contact metamorphism.

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