Growth and retrograde zoning in garnets from high-grade metapelites: Implications for pressure-temperature paths

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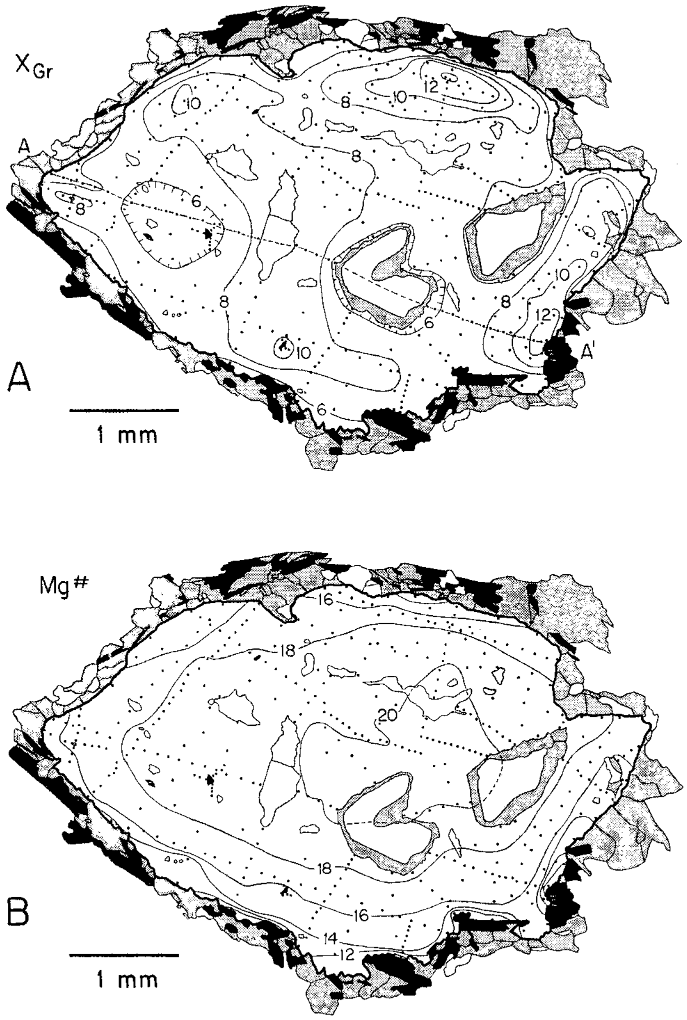
ABSTRACT

A previously unrecognized pattern of garnet zoning has been preserved in garnets from the upper amphibolite facies Britt domain, Ontario Grenville province. Some large garnets contain discrete regions of high grossular content as well as variations in the Mg/(Mg+Fe) and Mn nearly parallel to grain boundaries. The latter are superimposed on and cut across regions of high grossular content. Such crosscutting zoning patterns have not been previously recognized in garnets. The Ca zoning involves changes of 4 to 10 mol% grossular and is interpreted to represent growth zoning, whereas the decreasing Mg/(Mg+Fe) and increasing Mn from core to rim are believed to be a diffusional retrograde effect. The Ca zoning indicates a pressure drop of ca. 5 kbar at 700 ±50 °C (<5 °C/km). Preservation of grossular-rich areas also suggests that the diffusion rate of Ca is slower than those of Fe, Mn, and Mg in garnet.

INTRODUCTION

There is an extensive body of literature on chemical zonation in garnets. Zoning can be used to constrain the pressure-temperature (*P-T*) histories of metamorphic rocks because chemical variations preserved in garnets provide records of the equilibration histories of their host rocks and can yield *P-T* paths. Unfortunately, growth zoning is usually obliterated in high-grade garnets through volume diffusion (Blackburn, 1969; Grant and Weiblen, 1971; Anderson and Buckley, 1973; de Bethune et al., 1975; Tracy et al., 1976; Woodsworth, 1977; Yardley, 1977). At high temperatures, diffusion will tend to reduce existing chemical profiles, thereby homogenizing the garnets. Progressive homogenization of zoned garnets with increasing metamorphic grade has been documented by Anderson and Olimpio (1977), Woodsworth (1977), and Yardley (1977). In addition, high-grade garnets commonly exhibit zoning patterns that are reversed from those resulting from growth zoning. These trends are believed to be a retrograde effect caused by diffusion (e.g., Tracy et al., 1976; Grant and Weiblen, 1971; Woodsworth, 1977; Yardley, 1977; Freer, 1979; Tracy, 1982). The characteristic chemical profiles of garnets that have undergone homogenization and retrograde zoning include a core to rim increase in Mn, a decrease in Mg, and a flat Ca profile. This contrasts with growth zoning, which is usually characterized by bell-shaped Mn profiles and core to rim increases in Mg (Hollister, 1966; Atherton, 1968; Tracy, 1982; Loomis, 1983).

Growth histories are generally lost in garnets that have attained temperatures in excess of 600 °C. Woodsworth (1977) reported homogen-



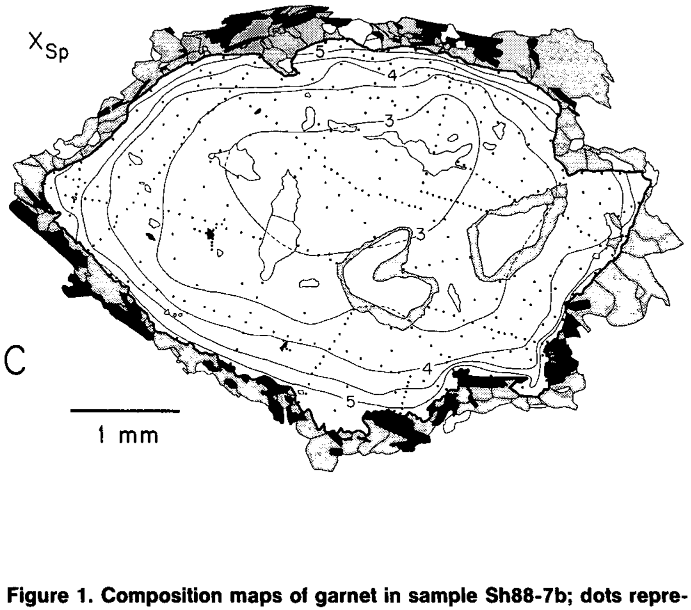


Figure 1. Composition maps of garnet in sample Sh88-7b; dots represent analytical points. Black is biotite, gray is plagioclase, white is quartz. A: X_{Gr} = 100 × Ca/(Ca+Mn+Mg+Fe). B: Mg# = 100 × Mg/(Mg+Fe). C: X_{Sp} = 100 × Mn/(Ca+Mn+Mg+Fe). Gr = grossular, Sp = spessartine.

ization of zoned garnets above 600 °C and Yardley (1977) estimated that volume diffusion begins to affect zoning profiles between 615 to 665 °C. However, Blackburn (1969) observed Mn-rich cores in garnets from high-grade pelitic gneisses from Gananoque, Ontario. Petrakakis (1986) found Ca- and Mn-rich relict cores to have been preserved in pelitic gneiss garnets from the Moldunabian zone in Austria that attained peak temperatures of 700 to 770 °C. In this paper, we also present evidence that growth zoning as well as retrograde zoning may be preserved in some high-grade garnets, and will discuss their significance for *P-T* paths.

ROCK AND MINERAL DESCRIPTIONS

The garnets studied occur in metapelitic gneisses from the Britt domain of the Central Gneiss belt in the Ontario Grenville province. The two samples most thoroughly examined, Sh88-7b and Sh88-42, were collected ~40 km northwest of the town of Parry Sound. Their respective locations are 45°31′30″N, 80°20′30″W, and 45°31′45″N, 80°23′00″W. These rocks have been subjected to the upper amphibolite facies (Davidson, 1984); Anovitz and Essene (1990) reported pressure and temperature values of 8.7–11.1 kbar (0.87–1.11 GPa) and 680–750 °C for this area. Samples Sh88-7b and Sh88-42 are well-foliated gneisses with the assemblage quartz-plagioclase-alkali feldspar-garnet-biotite-kyanite-sillimanite-rutile ± pyrite ± apatite ± sphalerite ± zircon ± monazite. In these samples, sillimanite overgrows ragged kyanite, chlorite is present as an alteration product, and porphyroblasts of late muscovite crosscut the foliation. Garnets in these rocks are irregularly shaped and display embayed edges; the few inclusions in these garnets are randomly distributed and consist of quartz, plagioclase, biotite, zircon, rutile, and sphalerite.

ANALYTICAL METHODS

Analyses were made using the University of Michigan Cameca Camebax electron microprobe at an accelerating voltage of 15 kV and a sample current of 10 nA. Natural and synthetic silicates and oxides were used as standards. Standards were analyzed as unknowns to check the calibrations and were periodically rechecked during analytical sessions. A combination of step scans and individual analyses were performed on the garnets to obtain reasonable coverage. Preliminary analyses showed little Cr and Ti, and the analyses compiled to map the grains included only the elements Si, Al, Fe, Mg, Ca, and Mn.

RESULTS

Analytical results are summarized in Figures 1 and 2 and Tables 1 and 2. The results of the microprobe analyses for a zoned garnet in sample Sh88-7b are illustrated in Figures 1 and 2; similar patterns were found in garnets from sample Sh88-42. In both samples, the distribution of Ca is highly irregular and the maxima do not occur at the centers of the grains. Ca-rich regions show steep gradients, changing by as much as 9 mol% over a distance of a millimetre, and the contours are roughly concentric within each region. The dramatic changes in grossular content are largely compensated by changes in the almandine component. The garnet in Sh88-7b also exhibits some Ca zoning of 2 to 3 mol% around the plagioclase (An_{33}) rimming the quartz inclusions (Fig. 1A; lower central and right parts of the grain). The Ca content also varies around the small plagioclase inclusion (An_{40}) on the far left side of the grain (circled by the 8 mol% contour in Fig. 1A).

A completely different zoning pattern is followed by the spessartine component and the Mg#, Mg/(Mg+Fe) (Fig. 1, B and C). The contours for these values are concentric and approximately parallel to the grain boundaries, but cut across the grossular contours. In both samples, the Mg# shows a decrease from core to rim, whereas the spessartine content increases slightly. The Mg# also decreases dramatically near biotite grains that are touching the garnet, a pattern observed in garnets of high-grade metapelites (e.g., Tracy, 1982; Edwards and Essene, 1988). The spessartine and Mg# contours are not concentrated near the rims of the grains, as is generally observed with zoning patterns of most high-grade garnets, but extend far into the grains (Figs. 1, B and C, and 2). In garnets of both samples the spessartine and Mg# contours also continue across major embayments in the grains. For example, they cross the large notch in the

TABLE 1. GARNET ANALYSES

	Sample*					
	1	2	3	4	5	6
Oxides (wt%)						
SiO_2	37.9	37.8	37.4	38.0	37.4	37.7
Al_2O_3	21.6	21.6	21.5	21.7	21.0	21.2
FeO	30.7	32.4	33.2	30.8	33.9	33.9
MnO	1.6	1.3	1.9	0.8	1.0	1.0
MgO	3.6	4.6	3.7	3.8	3.9	4.0
CaO	5.2	2.6	1.9	5.3	2.1	1.5
Total	100.6	100.3	99.6	100.4	99.3	99.3
Elements (moles)						
Si	2.99	2.98	2.98	2.98	3.00	3.00
Al	2.01	2.01	2.02	2.02	1.99	1.99
Fe	2.03	2.14	2.21	2.03	2.27	2.25
Mn	0.11	0.09	0.13	0.05	0.07	0.06
Mg	0.42	0.55	0.44	0.44	0.47	0.47
Ca	0.44	0.22	0.17	0.44	0.19	0.13
Components (mol %)						
Gr	14.8	7.5	5.6	15.0	6.1	4.5
Py	14.0	18.1	15.0	14.8	15.5	16.1
Alm	67.6	71.4	74.9	68.3	76.0	77.2
Sp	3.6	3.0	4.4	1.8	2.3	2.2
Mg#	17.1	20.2	16.7	17.9	17.0	17.3

Note: All Fe was assumed to be Fe^{2+}. Formulae were calculated on the basis of eight cations. Gr = grossular, Py = pyrope, Alm = almandine, Sp = mol % spessartine, Mg# = Mg/(Mg+Fe)

*1: Sh88-7b, high X_{Gr} region, top area of grain in A. 2: Sh88-7b, intermediate X_{Gr}, same area. 3: Sh88-7b, low X_{Gr}, touching plagioclase, same area. 4: Sh88-42, high X_{Gr}. 5: Sh88-42, intermediate X_{Gr}. 6: Sh88-42, low X_{Gr}, touching plagioclase.

TABLE 2. PLAGIOCLASE ANALYSES

	Sample*					
	1	2	3	4	5	6
Oxides (wt%)						
SiO_2	59.4	58.6	58.8	57.6	59.7	60.3
Al_2O_3	25.1	25.6	25.8	26.6	25.1	25.0
Fe_2O_3	0.0	0.4	0.1	0.7	0.0	0.4
CaO	7.1	7.4	7.1	8.6	6.6	5.9
Na_2O	7.6	7.4	7.4	6.8	8.0	7.9
K_2O	0.2	0.3	0.5	0.1	0.3	0.3
Total	99.4	99.7	99.7	100.4	99.7	99.8
Elements (moles)						
Si	2.66	2.63	2.64	2.57	2.67	2.69
Al	1.33	1.36	1.36	1.40	1.32	1.31
Fe	0.00	0.01	0.00	0.02	0.00	0.01
Ca	0.34	0.35	0.34	0.41	0.32	0.28
Na	0.66	0.64	0.64	0.59	0.69	0.68
K	0.02	0.01	0.03	0.01	0.02	0.02
Components (mol %)						
Ab	64.7	63.5	63.5	58.5	67.4	69.4
An	33.7	35.0	33.7	40.9	30.8	28.9
Or	1.6	1.5	2.8	0.7	1.8	1.7

Note: All Fe was assumed to be Fe^{3+}. Formulae were calculated on the basis of eight oxygens. Ab = albite, An = anorthite, Or = orthoclase.

*1: Sh88-7b, matrix plagioclase. 2: Sh88-7b, plagioclase touching garnet. 3: Sh88-7b, plagioclase inclusion surrounding quartz. 4: Sh88-7b, plagioclase inclusion. 5: Sh88-42, matrix plagioclase. 6: Sh88-42, plagioclase near garnet.

northeast corner of the garnet depicted in Figure 1 while the grossular contours do not.

DISCUSSION

Zoning of Mg, Mn, and Fe

The observed Mn and Mg# zoning profiles in the garnets analyzed are produced by retrograde diffusion processes (e.g., Grant and Weiblen, 1971; Tracy et al., 1976; Anderson and Olimpio, 1977; Woodsworth, 1977; Edwards and Essene, 1988). Grant and Weiblen (1971) described the resorption of garnet to form other ferromagnesian phases such as biotite and cordierite. Because the K_D between garnet and biotite or cordierite decreases with decreasing temperature (Evans, 1965), garnet will become enriched in Fe relative to Mg during resorption. Because Mn is not easily incorporated into biotite or cordierite, it will diffuse into the garnet, creating an enrichment in Mn on the rim. Biotite is the only phase in our samples that is likely to have undergone Fe-Mg-Mn exchange with the garnet. A possible reaction is:

$$\text{Garnet} + \text{K-feldspar} + H_2O = \text{Biotite} + \text{Al-silicate} + \text{Quartz} \qquad (1)$$

(Tracy et al., 1976). We believe the Mg# and Mn zoning seen in the garnets to be the result of resorption; the Fe and Mn are redistributed in the garnets.

Zoning of Ca

Crawford (1977) postulated that the processes that produce Ca zoning in metapelitic garnets are different from those that produce zoning in Fe, Mg, and Mn. Garnets showing grossular zonation may occur in conjunction with zoned plagioclases, and the compositions of these two minerals may be controlled by equilibria involving each phase. One such reaction applicable to our samples is:

$$\text{Grossular} + \text{Al-silicate} + \text{Quartz} = \text{Anorthite (GASP).} \qquad (2)$$

Because grossular is on the high-pressure side of the reaction, the pattern of decreasing grossular content in the grains is consistent with growth of these garnets under conditions of decreasing pressure. For calculation of pressures using the GASP barometer, we have used the calibration of Koziol and Newton (1988), thermodynamic data from Moecher et al. (1988), and mixing models of Anovitz and Essene (1987) and Fuhrman and Lindsley (1988). We have assumed an infinite reservoir of Al-silicate, quartz, and plagioclase of fixed composition in the samples relative to garnet. Thus, garnet would be the only phase to undergo significant compositional change as a result of the reaction. Pressures were calculated with the GASP barometer at temperatures of 650 and 750 °C. Temperatures were chosen based on estimates of 680–750 °C from Anovitz and Essene (1990) and the coexistence of Al-silicate and K-feldspar. For the garnet in sample Sh88-7b, the maximum grossular value of 14.8 mol% yields pressures of 9.8 kbar at 650 °C and 11.8 kbar at 750 °C. Pressures of 5.5 and 6.8 kbar at 650 and 750 °C are obtained for a grossular component of 5.6 mol%, where garnet touches plagioclase. This observed pressure drop corresponds to a gradient <5.4 °C/km. The estimated uncertainty in the barometry is ±1 kbar (Essene, 1989).

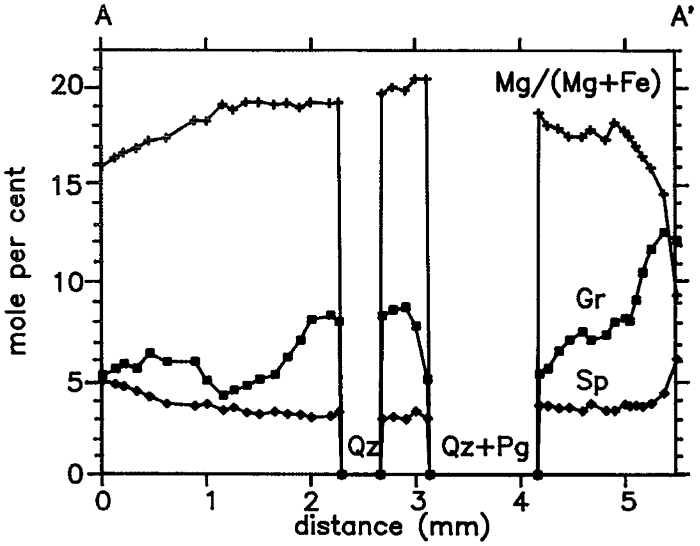


Figure 2. Composition vs. distance plot along traverse A-A' in Figure 1A. Areas where values are zero represent inclusions. Crosses are Mg#, squares are X_{Gr}, and diamonds are X_{Sp}. Qz, = quartz, Pg = plagioclase, Gr = grossular, Sp = spessartine.

We interpret the Ca zoning as having formed first because the contours for Mn and Mg# crosscut the Ca contours. The concentric nature of the zoning in the localized high grossular areas suggests that these may have originated as separate smaller garnets that coalesced during growth. Garnet growth may have occurred during the late prograde or early retrograde history of the rocks by some combination of reactions 1 and 2 and possibly under conditions of variable H_2O activity. There is some evidence for minor resetting of the Ca contours around the edges of the grain, which may have occurred through resorption of garnet to form plagioclase. The overall Ca growth zoning pattern, however, has been retained, whereas the Mg# and Mn growth patterns have not. It is concluded that Ca is the slowest of the R^{2+} cations to diffuse in garnet, because these specimens were able to preserve their grossular growth zoning during retrogression.

Experimental work by Loomis et al. (1985) and Chakraborty and Ganguly (1990) suggests that the intrinsic diffusion coefficient of Ca is smaller than those of Mg and Fe in pyrope-almandine couples. One possible explanation for the lesser diffusivity of Ca may be the size of the Ca atom. Freer (1981) noted a relation between ionic radius and diffusion coefficients, and Morioka (1981) found experimentally that diffusion coefficients in olivine decrease with increasing ionic radius. Petrakakis (1986) observed varying degrees of homogenization of the R^{2+} cations in garnets, increasing in the order Ca, Mn, Fe, Mg; i.e., that of decreasing ionic radius. Petrakakis (1986) based his discussion on concentric zoning patterns, but the composition gradients he found among the various cations may also be related to the original zoning and not to relative diffusion rates. Our data do, however, support Petrakakis's inferences. Because the Ca contours are crosscut by the Fe, Mg#, and Mn contours in the garnets from the Britt domain, it is clear that there is a significant difference in the behavior of the diffusing cations.

Implications for the *P-T* path

Pressure values obtained by applying the GASP barometer to the Ca zoning in the analyzed garnets have enabled us to unravel a critical part of the *P-T* history of the host rocks. Estimates from the GASP barometer indicate that the rocks have undergone a pressure drop of ca. 5 kbar during their late prograde and/or early retrograde history. This substantial pressure drop indicates a shift from the kyanite field into the sillimanite field and is consistent with observed textures of sillimanite overgrowing kyanite. The range of possible paths that these data represent is illustrated on a *P-T* diagram (Fig. 3). The diagram shows that the steep pressure decrease is part of a clockwise path, which is characteristic of terranes that have undergone thrusting (Thompson and England, 1984). Such a path is consistent with structural observations for this part of the Grenville province. Mapping by Davidson et al. (1982) has shown the Central Gneiss belt to

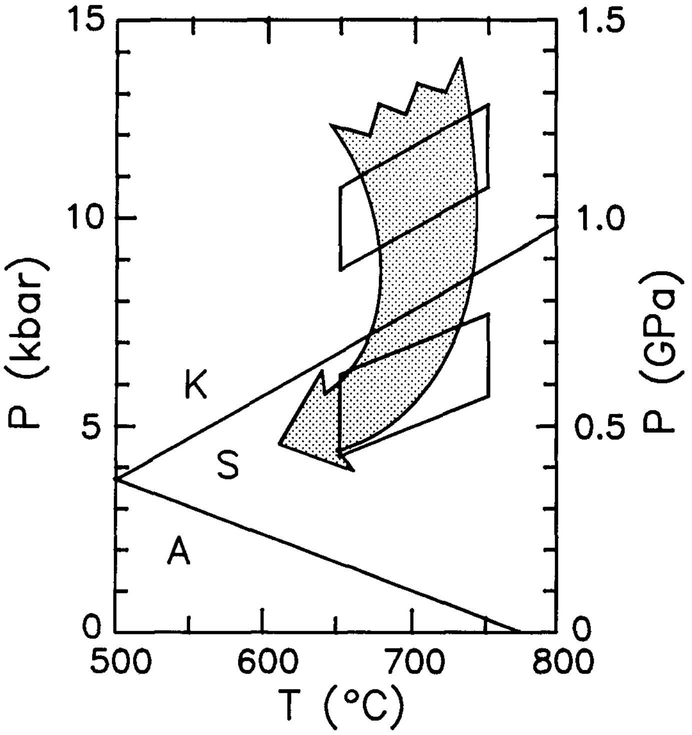


Figure 3. Pressure-temperature diagram based on data from sample Sh88-7b, showing late prograde or early retrograde "clockwise" path. Upper box represents pressures obtained using maximum grossular value of 14.8 mol% over temperature interval of 650 to 750 °C. Lower box represents pressures obtained with 5.6 mol% grossular over same temperature interval. Al-silicate phase diagram after Holdaway (1971).

consist of several domains, or thrust sheets, that are separated by ductile shear zones. The Britt domain is structurally the lowest of these and is overlain by the Parry Sound domain. The part of the *P-T* path for the Britt domain that we have obtained using the garnet zoning lends further support for a history of ductile thrusting for the Central Gneiss belt of the Grenville province.

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