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HOMOGENIZATION OF ZONED GARNETS FROM PELITIC SCHISTS

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Abstract

Garnets from low-variance pelitic assemblages in the garnet and staurolite zones of the Mt. Raleigh area, B.C., generally show strong compositional zoning. A decrease in Mn outwards from the core is balanced by an increase in Fe and Mg. Zoning in garnets from the cordierite zone is weak or absent. Mn commonly increases slightly from core to rim; Mg shows a corresponding decrease. There is little or no Ca zoning in either high or low-grade rocks. At all metamorphic grades, the garnet rims are in partition equilibrium with adjacent ferromagnesian minerals. Ilmenite inclusions in low-grade rocks are in equilibrium with immediately adjacent garnet, but inclusions in cordierite-zone garnets are not in equilibrium with garnet.

The data suggest: (1) growth of zoned garnets by a fractionation-depletion process at lower grades; (2) homogenization of zoned garnets at temperatures above about 600°C; (3) modification of the bulk composition of homogeneous garnets by exchange equilibria involving garnet and cordierite; and (4) formation of Mn-rich rims on both high and low-grade garnets during retrogression of the garnet. Volume diffusion was the main process which created and modified the zoning in the cordierite zone, but was of only minor importance in lower grade rocks. The onset of significant volume diffusion may have initiated changes in the equilibria with other minerals.

Sommaire

Des grenats provenant d'associations pélitiques de faible variance, tirées de zones à grenat et à staurolite de la région de Mt. Raleigh, C.-B., montrent généralement une forte zonation de composition. Une diminution de la teneur en Mn, en direction éloignée du centre, est équilibrée par une augmentation des teneurs en Fe et Mg. Il y a peu ou pas de zonation dans les grenats provenant de la zone à cordiérite. La teneur en Mn augmente légèrement du centre en direction de la bordure; le contenu en Mg subit une diminution analogue. Il n'y a que peu ou pas de zonation en Ca dans les roches de haute ou de faible intensité. Les bordures des grenats des roches métamorphiques de toutes intensités sont en équilibre de partage avec les minéraux ferromagnésiens adjacents. Les inclusions d'ilménite présentes dans les roches de faible grade sont en équilibre avec le grenat immédiatement adjacent, mais celles qui se trouvent dans les grenats de la zone à cordiérite ne sont pas en équilibre avec le grenat.

Les données suggèrent qu'il y a: (1) une croissance de grenats zonés sous de faibles intensités métamorphiques par un procédé de fractionnement-appauvrissement; (2) une homogénéisation des grenats zonés à des températures au-dessus de 600°C environ; (3) une modification de la composition globale des grenats homogènes par un équilibre d'échange entre le grenat et la cordiérite, et (4) la formation de bordures riches en Mn sur les grenats de faible et de haute intensité pendant la rétrogresion du grenat. La diffusion volumique fut responsable de la création et de la modification de la zonation dans la zone de cordiérite, mais n'a eu qu'un rôle mineur dans les roches de faible grade. L'action d'une importante diffusion volumique a pu causer des changements dans les équilibres entre les autres minéraux.

(Traduit par la Rédaction)

Introduction

Most almandine garnets from pelitic schists are compositionally zoned. Zoning is most spectacular in low and medium-grade garnets, which generally show bell-shaped Mn profiles with Fe increasing from core to rim to balance the Mn, and varied and complex profiles for Ca, Mg, and Ti. Hollister (1966, 1969) interpreted such Mn zoning as resulting from preferential incorporation, in the growing garnet, of Mn released by reactant phases. This model and its variants have been successfully applied by many authors to garnets from low and medium-grade environments. Implicit in this fractionation-depletion model are the assumptions that volume diffusion in the growing garnet is negligible, i.e. garnet is a refractory phase (Hollister 1969), whereas intergranular diffusion in the matrix surrounding the garnet is relatively rapid.

In garnets from high-grade rocks, bell-shaped Mn profiles are commonly absent. Zoning is generally weak; Mn may increase from core to rim in marked contrast to lower grade garnets. The fractionation-depletion model cannot be applied to such zoning, and most authors attribute zoning in high-grade garnets to exchange reactions between garnet and matrix (e.g. Loomis 1975) or to resorption of the garnet (e.g. Grant

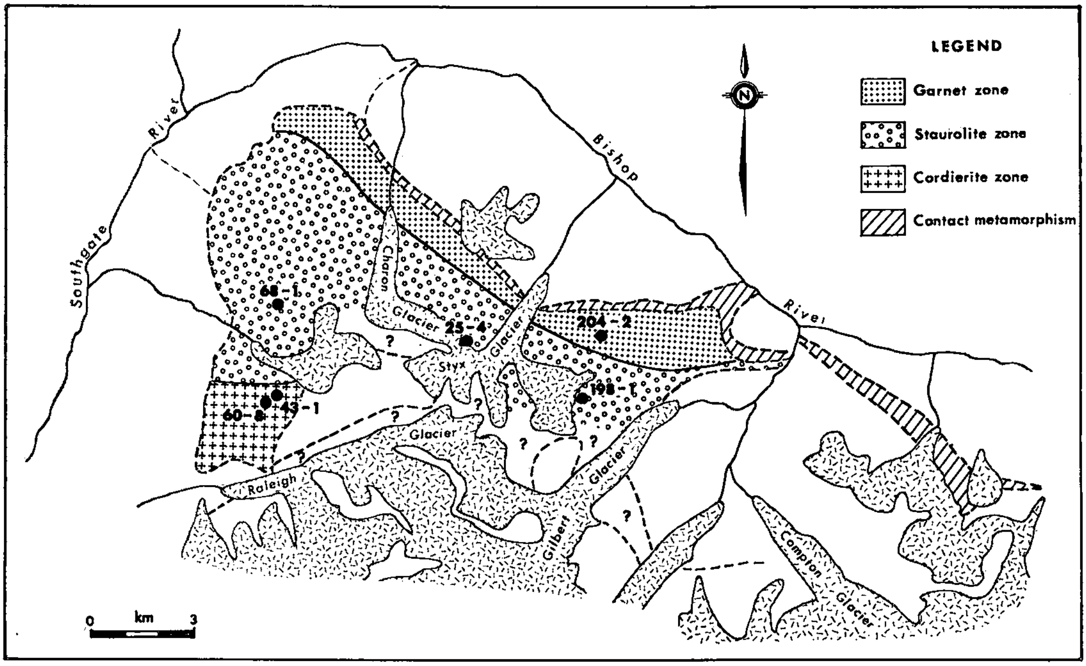


FIG. 1. Generalized map of metamorphic zones in the Mount Raleigh pendant. Question marks indicate areas of the pendant where pelitic rocks are absent. Granitoid rocks bound the pendant on all sides.

& Weiblen 1971) or to homogenization of originally zoned garnets (e.g. Blackburn 1969). These processes require considerable volume diffusion within the garnet: i.e. garnet is not a refractory phase.

This paper evaluates the relative importance of fractionation-depletion and volume diffusion processes in the production and modification of garnet zoning in the garnet, staurolite, and cordierite zones of the Mount Raleigh area, British Columbia. The examples discussed are from low-variance assemblages in meta-greywackes that have undergone only one period of prograde regional metamorphism.

Geological Setting

The Mount Raleigh pendant (Woodsworth, in press) comprises approximately 4000 m of metamorphosed strata surrounded by plutonic rocks, predominantly quartz diorite and granodiorite, of the Coast Plutonic Complex. The stratified rocks are mainly intermediate volcaniclastics, conglomerate, amphibolite, and aluminous greywacke of probable Early Cretaceous age deposited on a basement of quartz diorite and folded migmatite.

Strata in the pendant have undergone one period of regional metamorphism. Metamorphic grade increases from garnet in the north to cordierite and sillimanite in the southwestern part of the pendant (Fig. 1). Maximum temperatures and pressures reached about 750°C and 4 kbar at the cordierite isograd (Woodsworth, in press). Retrograde effects range from absent to almost complete obliteration of prograde assemblages and textures. Deformation of the pendant and diapiric emplacement of quartz diorite plutons accompanied metamorphism. Large post-tectonic plutons have superposed a narrow contact aureole along the northern margin of the pendant.

General Petrography

Metamorphic zones in the greywacke

Metamorphic grade in the pendant strata increases from north to south (Fig. 1). The lowest grade metapelitic rocks are in the garnet zone; consequently the garnet-producing reaction is not known. Staurolite appears as a product of the idealized net reaction

$$\text{chlorite} + \text{muscovite} = \text{staurolite} + \text{biotite} + \text{garnet} + SiO_2 + H_2O \quad (1)$$

At higher temperatures staurolite breaks down to cordierite according to the continuous reaction

staurolite + quartz = garnet + cordierite +
sillimanite + staurolite (more zincian) + H_2O(2)

Staurolite persists for about 1 km upgrade from the cordierite isograd, but always in rocks containing cordierite. The staurolite occurs in the matrix as anhedral grains surrounded by cordierite and sillimanite and as anhedral grains enclosed in euhedral garnet. Staurolite inclusions in garnet are rare below the cordierite isograd.

Three aluminum silicate isograds, not shown on Figure 1, are discussed in Woodworth (in press). Below the fibrolite isograd, andalusite is the only aluminum silicate species present. The fibrolite isograd, midway between the staurolite and cordierite isograds, marks the appearance of the aluminum-silicate assemblage andalusite+fibrolite. Above the sillimanite isograd, which is roughly coincident with the cordierite isograd, andalusite, fibrolite, and coarse sillimanite may all be present in the same sample. Above where andalusite disappears, about 1 to 2 km south of the cordierite isograd, fibrolite and coarse sillimanite are the only aluminum-silicate phases present.

Mineral assemblages

Only samples from low-variance pelitic assemblages were used in this study. Such samples from the garnet and staurolite zones generally consist largely of quartz, plagioclase, biotite, and aluminum silicate, with lesser ilmenite, graphite, garnet and (in some samples) muscovite. Modal biotite increases markedly on the upgrade side of the staurolite isograd; modal garnet remains about the same. Garnet seldom exceeds 3% of the rock volume. The garnets are euhedral to subhedral, and are generally less than 1.0 mm across. Inclusions of ilmenite are common. The garnets in the upper part of the staurolite zone are commonly slightly discoid in shape.

In the cordierite zone the assemblage with

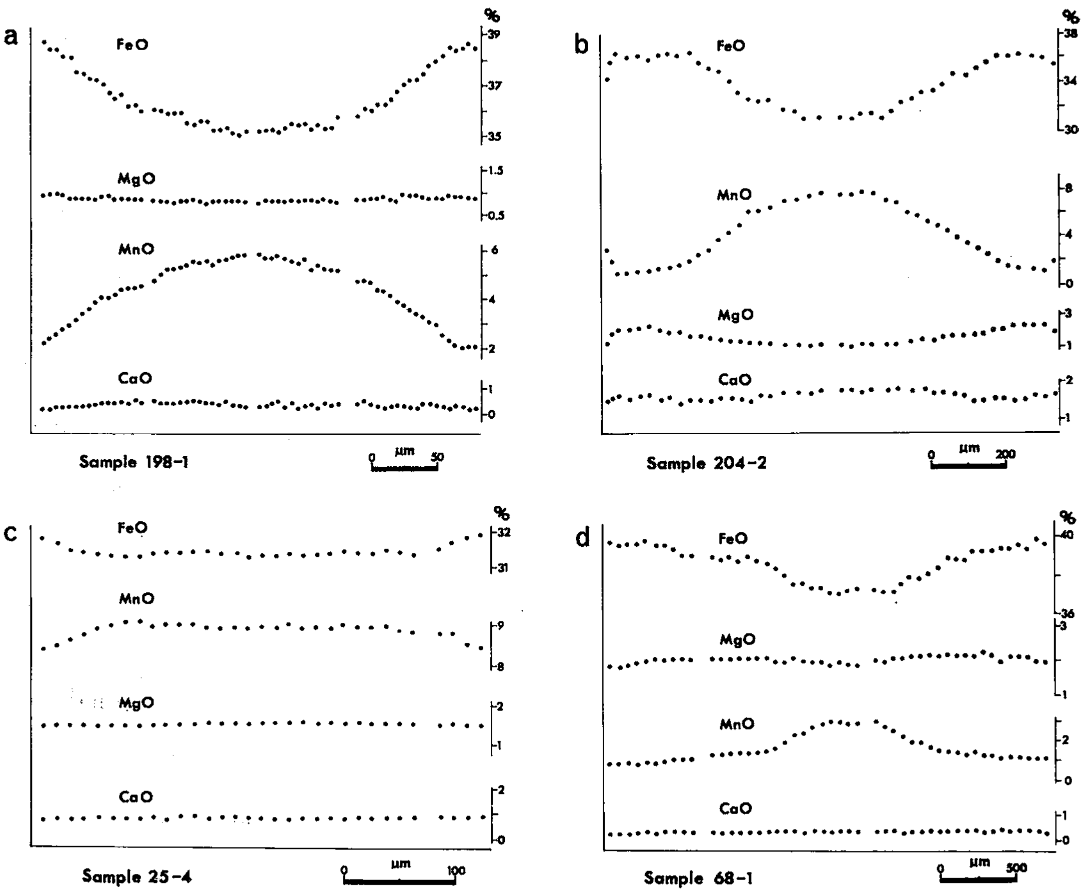


FIG. 2. Electron microprobe profiles across four garnets from the garnet and staurolite zones. All analyses made with a beam diameter of less than 1 µm. Al, Si, and Ti are unzoned in all garnets.

the maximum number of phases is quartz+plagioclase+garnet+biotite+cordierite+staurolite+Al_2SiO_5+ilmenite+graphite. Garnets are larger and more abundant than in the staurolite zone, but they seldom exceed 7% of the rock volume. Common inclusions in the garnets are ilmenite, biotite, staurolite, and quartz. Many of the garnets are flattened parallel with the foliation defined by biotite. Textural evidence (Woodsworth, in prep.) suggests that most garnet growth in the cordierite zone was syntectonic, whereas that in the staurolite and garnet zones was post-tectonic.

Analytical Methods

Chemical analyses were made using an ARL-EMX electron microprobe. Operating conditions and data reduction methods are given in Woodsworth (in press). For each sample, successive thin sections were made until one was found that contained all the minerals of the assemblage in an area of about 1 cm²; the analyses were obtained from this one area.

Garnets were examined early in the thin-sectioning process and only garnets that were sectioned close to the centre were probed. For most samples, step-scans were made across two different garnet grains and several other grains were analyzed at cores and rims. Rim and core "spot" analyses were used to calibrate the step-scans. Representative step-scans for Fe, Mn, Mg, and Ca are given in Figures 2 and 4. In all samples, Ti, Si, and Al are unzoned and thus are not shown on the step-scans. The Al analyses indicate that little andradite is present: all Fe is shown as almandine. The precision of the analyses is about 1% of the amount present for Ca and Mg, about 0.5% for Mn, and about 0.3% for Fe.

Garnet Zoning: Description

Garnet and staurolite zones

Garnets from the garnet and staurolite zones have zoning characteristics that are distinctly different from cordierite-zone garnets. Zoning patterns in garnets in samples 198-1 (Fig. 2a) and 204-2 (Fig. 2b) are typical of most garnets from the staurolite and garnet zones, respectively. The garnets in both samples are euhedral and contain a few inclusions of ilmenite. Garnets from 198-1 show no evidence of alteration. Those from 204-2 are commonly slightly embayed and replaced by chlorite around the margins.

Except for the outer 50 μm of 204-2, the general characteristics of the zoning in the two samples are the same. The bell-shaped Mn profiles are similar to those for many other medium-grade almandine garnets (e.g. Hollister 1969). Fe increases from core to rim to offset the decreasing Mn. Mg increases slightly from core to rim in 204-2, but in 198-1 Mg shows no significant variation. Most garnets from the staurolite zone, however, show a slight core to rim increase in Mg. Ca zoning is absent or very weak in all pelitic samples from the Mount Raleigh area, but slight fluctuations in Ca are present in samples 198-1 and 204-2.

The major difference between the two sets of profiles is the sharp increase in Mn in the outer 50 μm of 204-2, balanced by a drop in Fe and Mg. Such Mn-rich rims are common in garnets from the garnet and staurolite zones, but only in garnets that show evidence of retrograde alteration.

There is a good correlation between the maximum range in Mn zoning in each rock and the modal abundance of garnet (Fig. 3). The best-developed bell-shaped Mn profiles are found in specimens in which garnet is relatively abundant. In rocks where garnet is a trace constituent, zoning is very weak. For example, the step-scans across the largest garnet (0.4 mm) in a sample from the staurolite zone containing 0.1% garnet (Fig. 2c) reveal weak zoning; the difference in Mn between core and rim of smaller garnets from the same rock is even less.

Only one sample was available from the upper third of the staurolite zone (Fig. 2d). Although the general shapes of the profiles are similar to those at lower grade, the differences between core and rim compositions are much less: the zoning is greatly subdued.

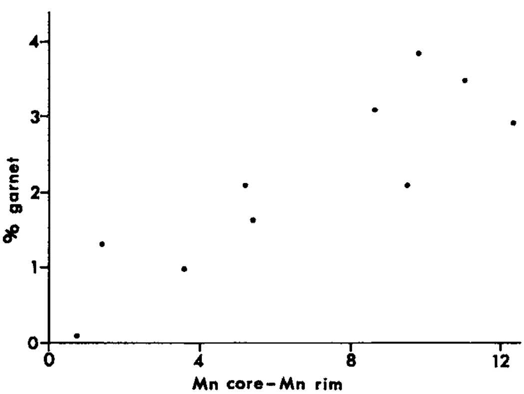
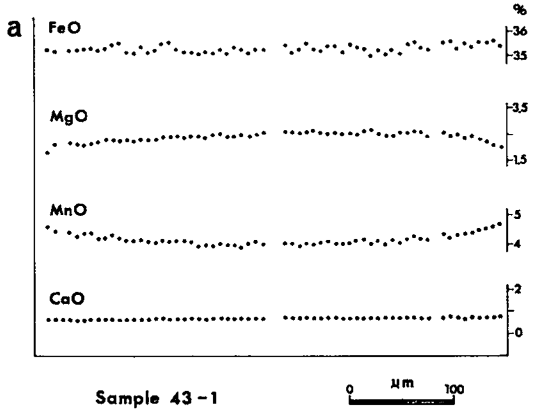


FIG. 3. Modal garnet (volume percent) versus maximum values for each sample of 100 Mn/(Mn+Fe+Mg+Ca) for the core minus that for the rim.



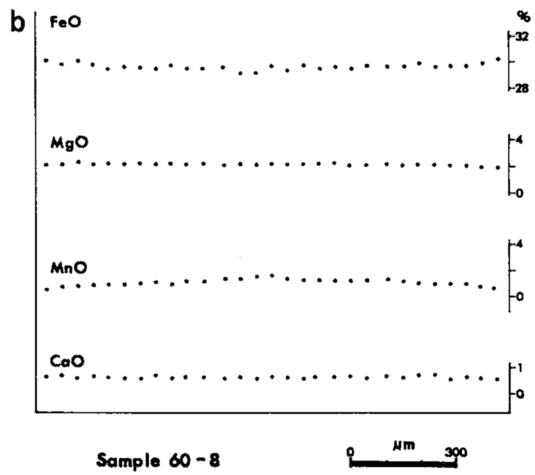


FIG. 4. Electron microprobe profiles across two garnets from the cordierite zone. All analyses made with a beam diameter of less than 1 μm. Al, Si, and Ti are unzoned in both garnets.

Cordierite zone

Zoning in cordierite-zone garnets is markedly different from lower grade samples: bell-shaped Mn profiles are absent. Two typical examples are shown in Figure 4. Both samples contain the prograde assemblage garnet+biotite+cordierite+ staurolite+Al_2SiO_5+ quartz+ plagioclase+ ilmenite+ graphite. In both samples staurolite is found as inclusions in garnet and as small anhedral grains in the matrix; hercynite is associated with matrix and included staurolite in 43-1. Sample 60-8 shows no evidence of retrogression whereas 43-1 is strongly altered: garnets are fringed by chlorite, and cordierite is pinitized.

The larger garnets (>1 mm) from sample 60-8 (Fig. 4) show a slight decrease in Mn from core to rim, balanced by an increase in Fe. Mg and Ca are unzoned. Smaller garnets (<1 mm) are unzoned in all elements. In sample 43-1, on the other hand, Mn is unzoned in the central area of the garnets and increases slightly in the outer parts. Fe and Ca are unzoned throughout and the Mg profile is the reverse of that for Mn.

ELEMENT PARTITIONING AND INCLUSION DATA

The partitioning of Fe, Mn and Mg between garnet rims and other phases is regular and provides the strongest evidence that equilibrium was approached during metamorphism. It is not possible in this paper to discuss all the partitioning data collected but several examples, relevant to discussion later in this paper, are described below.

The probe analyses of coexisting minerals indicate that Mg/(Mg+Fe) decreases in the order cordierite>biotite>staurolite>garnet>ilmenite, and that Mn/(Mn+Fe) decreases in the order garnet>ilmenite>staurolite>cordierite> biotite. This order is the same as that described by many authors (e.g. Thompson 1976).

The distribution of Mn between garnet rim and matrix ilmenite immediately adjacent to the garnet is shown in Figure 5. The data for both high and low-grade rocks fall close to the same line, indicating that the distribution of Mn between coexisting garnet and ilmenite is independent of temperature and pressure over the range of conditions found in the Mount Raleigh area, and that partition equilibrium was achieved between garnet rims and adjacent ilmenite. The partitioning of Mn between ilmenite inclusions in garnet and the immediately adjacent garnet

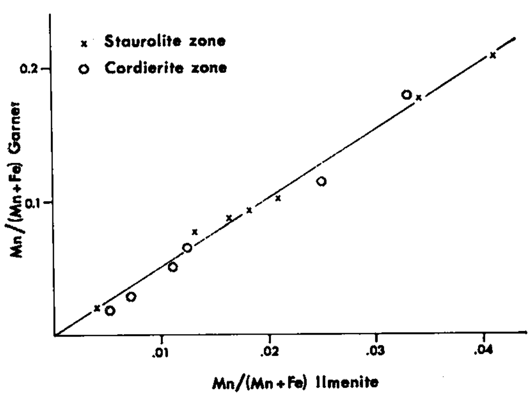


FIG. 5. Mol ratios Mn/(Mn+Fe) for garnet rims and immediately adjacent matrix ilmenite for rocks from the staurolite, garnet, and cordierite zones.

is more complicated (Fig. 6). For samples from the staurolite zone, data for ilmenite inclusions in garnet fall along or near the trend for matrix ilmenites, whereas cordierite-zone ilmenite inclusions plot beneath the equilibrium line of Figure 5. Ilmenite inclusions in staurolite and garnet-zone garnets seem to be in equilibrium with the adjacent garnet. Ilmenite included in cordierite-zone garnets is clearly not in equilibrium with the enclosing garnet, but is generally more manganiferous than would be expected from the rim partition data.

The distribution of Mg between garnet rims and adjacent staurolite is also regular (Fig. 7), and the data for staurolite-zone rocks define a reasonably good curve. Much of the scatter in the data appears due to the effects of Zn in staurolite; the ZnO content ranges from 0.13% to 2.6%.

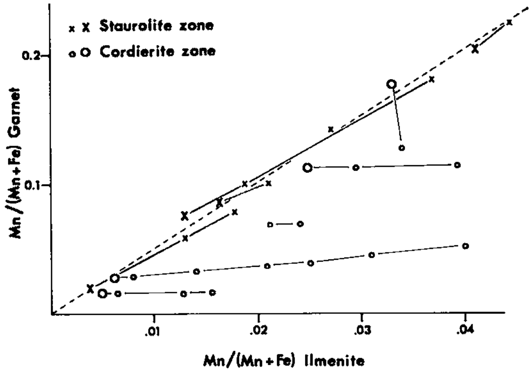


FIG. 6. Mol ratios Mn/(Mn+Fe) for ilmenite inclusions in garnet and immediately adjacent garnet (small x's, small o's). Large X's and O's indicate matrix ilmenite and rim garnet. Solid lines join all points from one garnet. Dashed line is line of best fit to rim and matrix data on Figure 5.

INTERPRETATION

Origin of bell-shaped Mn profiles

Garnets from the garnet and staurolite zones are generally characterized by decreasing Mn contents from core to rim, accompanied by increasing Fe (the reverse zoning near the rim of some garnets is discussed later). Several different models have been suggested for the origin of bell-shaped Mn profiles. These include growth during progressive metamorphism (e.g. Harte & Henley 1966), diffusion models involving exchange between initially homogeneous garnets and matrix minerals (Anderson & Buckley 1973), and a depletion model involving fractionation of Mn into garnet during its growth (Hollister 1966).

The view that the bell-shaped zoning profiles result from the increasing stabilization of Fe and Mg in the garnet structure with rising temperature is based largely on studies showing that the average MnO content of garnet decreases with increasing temperature (e.g. Sturt 1962; Müller & Schneider 1971). In rocks of the same bulk composition, however, this decrease seems to be due largely to the gradual increase in modal garnet with increasing temperature (Miyashiro & Shido 1973) and is readily explained by the fractionation-depletion model. Further, it is difficult to see why the form of the zoning profiles should be nearly identical in garnets from areas which have had different temperature-time histories. Although increasing temperature will affect the partitioning of Fe, Mg, and Mn among garnet and other phases, increasing temperature alone is insufficient to account for most zoning in medium-grade garnets.

Anderson & Buckley (1973) have proposed several pure diffusion models to explain bell-shaped zoning profiles. Beginning with initially homogeneous garnet of fixed composition and allowing exchange between garnet and surrounding reservoir, these models produce curves similar to many natural zoning profiles. A major problem, however, is the fate of the Mn that must have diffused out of the garnet. For example, in sample 204-2 (Fig. 2b), the mean MnO content of the garnet is between 2 and 3%. If the garnet was originally the same size as now and had a MnO content of 8% throughout the garnet (the present core composition), then more than two-thirds of the Mn originally present in the garnet must have diffused out. If

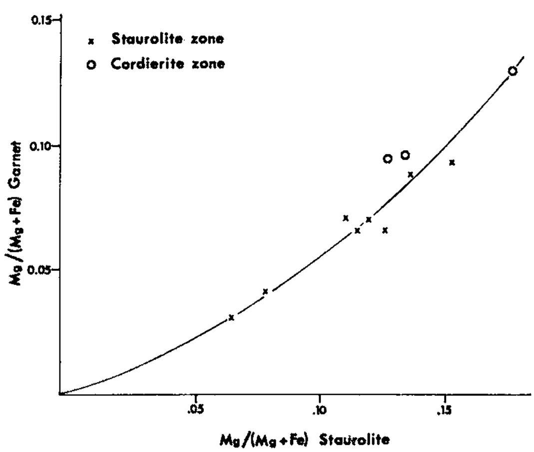


FIG. 7. Mol ratios Mg/(Mg+Fe) for garnet rims and immediately adjacent staurolite for rocks from the staurolite and cordierite zones.

partition equilibrium was maintained between garnet and other phases present, then the Mn lost from the garnet must have migrated out of the rock, as probe analyses indicate that the Mn could not be accommodated in other minerals present. As no outside sink for Mn is apparent, it seems that the bell-shaped Mn profiles in this rock did not originate by pure diffusion processes.

This leaves Hollister's (1966) fractionation depletion model, or some modification of it, as the most probable origin for the Mn profiles. The model is based on the fact that the fractionation factor λ, where λ = % MnO in garnet/ % MnO in rock, is large: Mn is strongly partitioned into garnet in preference to other minerals in pelitic schists. The model assumes that diffusion in the garnet is negligible, whereas diffusion in the surrounding matrix minerals is rapid enough to maintain relative homogeneity. The relationship shown in Figure 3, in which the range in Mn zoning correlates with modal garnet, is difficult to reconcile with the pure diffusion or increasing-temperature hypotheses, but is easily explained by the fractionation-depletion model. From equattion (10) of Hollister (1966), the difference in Mn content between garnet core and rim is proportional to the fractionation factor λ, the percentage of Mn in the rock, and the weight percent of crystallized garnet. Rocks with abundant garnet would thus be expected to have strong Mn zoning (e.g. sample 204-2 with 2.9% garnet), whereas zoning in rocks with only a trace of garnet should be weak or absent (e.g. sample 25-4, with 0.1% garnet).

The Mn zoning in the garnet and staurolite zones is concluded to have originated largely by a fractionation-depletion process. The Mn/Fe partition data for ilmenite inclusions in these garnets (Fig. 6) indicate that the garnets, at each stage in their growth, were in partition equilibrium with ilmenite. As each ilmenite grain was engulfed by the growing garnet it was effectively removed from the system. Ilmenites remaining in the matrix continued to equilibrate during garnet growth. Mn diffused out of the ilmenites to feed the growing garnet, whereas the ilmenite inclusions preserve a record of earlier conditions. Volume diffusion of Mn in the garnet must have been negligible during growth of the garnet.

Origin of homogeneous garnets in cordierite-zone rocks

Garnets in the cordierite zone are characterized by weak zoning and absence of bell-shaped zoning profiles. Two possible interpretations of the unzoned garnets are: (1) growth of unzoned garnets, and (2) homogenization of initially zoned garnets by diffusion. The first hypothesis implies that the garnets must have grown, unzoned, at temperatures high enough to permit internal re-equilibration of the garnets by diffusion. The second possibility, suggested by Blackburn (1969), implies that the garnets grew at temperatures below which diffusion was effective, but were subsequently raised to temperatures high enough to allow homogenization. Some support for the homogenization hypothesis is given by sample 68-1, containing 2.1% garnet, from the upper part of the staurolite zone (Fig. 2d). Although the Mn profile has the same shape as in lower grade rocks, the difference in core and rim compositions is only about 2% MnO, suggesting that this garnet has been partly homogenized. But the strongest support of the homogenization hypothesis comes from the element partitioning data. From Figure 6 it is clear that ilmenite inclusions in cordierite-zone garnets, unlike inclusions in lower grade garnets, are not in partition equilibrium with the host garnet. The inclusions have Mn/(Mn+Fe) ratios that could have been in equilibrium only with a garnet that was more manganiferous than at present. The garnet in Figure 8 provides an instructive example. This garnet, from sample 60-8, is only very weakly zoned in Mn (Fig. 4b), but evidence of former strong zoning is preserved by the ilmenite inclusions. Their Mn/ (Mn+Fe) ratios decrease systematically from garnet core to rim; core inclusions have ratios that are about six times higher than those at the rim, providing convincing evidence that the garnet was initially zoned with Mn decreasing out-

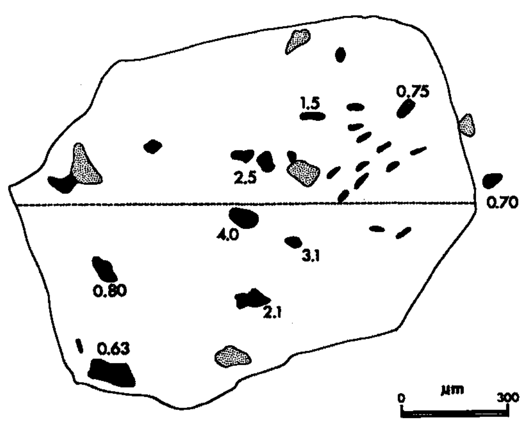


FIG. 8. Sketch of a garnet in sample 60-8. Ilmenite grains are black; staurolite is stippled. Numbers are 100 Mn/(Mn+Fe) in ilmenite grains. The profiles in Figure 4b were measured along the dashed line.

wards from the core. At temperatures reached in the cordierite zone, the garnet was homogenized by volume diffusion, leaving a relict zoning preserved by the inclusions.

Original zoning profiles of cordierite-zone garnets

If the Mn/(Mn+Fe) ratios of the ilmenite inclusions shown in Figure 8 have not changed since entrapment in the garnet, then it is possible to calculate a Mn/(Mn+Fe) profile for the garnet prior to homogenization. From Figure 5, Mn/(Mn+Fe) in garnet may be written as a function of $X^{ilm}{}_{Mn}$ = Mn/(Mn+Fe)$_{ilmenite}$:

$$\mathrm{Mn}/(\mathrm{Mn} + \mathrm{Fe})_{ga} = f_1(X^{ilm}_{Mn}) \quad (3)$$

If the growing garnet was in partition equilibrium with ilmenite, an assumption that seems reasonable based on the data in Figures 5 and 6, then equation (3) can be solved graphically from Figure 5 for each of the ilmenite inclusions in the garnet.

The ilmenite inclusions cannot be used to obtain original Mg/(Mg+Fe) ratios in the garnet, as Mg is below the limit of detection in most ilmenite grains, but the partitioning of Mg between staurolite and garnet may be used instead (Figs. 7, 9). If the staurolite inclusions shown in Figure 9 have not changed composition since entrapment, and if the inclusions were originally in equilibrium with garnet, then

$$\mathrm{Mg}/(\mathrm{Mg} + \mathrm{Fe})_{ga} = f_2(X^{st}_{Mg}) \quad (4)$$

where X^{st}_{Mg} equals Mg/(Mg+Fe) in staurolite. The assumption that the inclusions have remained constant in composition is supported by Zn analyses of staurolites from sample 60-8. The two staurolite inclusions shown in Figure 9 have 1.27% ZnO; the matrix staurolite has 0.44% ZnO. The matrix staurolite has reacted to form cordierite according to the continuous reaction (2), and the Zn released by staurolite has diffused into the remaining staurolite relicts (Woodsworth, in press). The included staurolites have not participated in reaction (2), and seem to preserve original ZnO contents and Mg/(Mg+Fe) ratios.

There are no Ca-rich inclusions in the garnets in sample 60-8. Because Ca is only weakly zoned in all garnets from the Mount Raleigh pendant, and as the CaO content of garnet 60-8 is about the same as that in most other garnets from the pendant, it seems probable that the CaO content of garnet 60-8 has not changed appreciably with time. This conclusion is supported by Ghent's (1976) model for plagioclase-garnet-Al_2SiO_5-quartz equilibria, which indicates that the *P-T* path during metamorphism of the pendant is such that the partitioning of Ca between plagioclase and garnet would have remained relatively constant during prograde metamorphism. Such relatively constant partitioning may explain

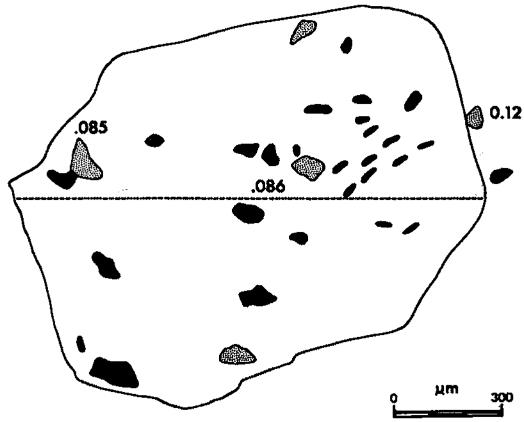


FIG. 9. Sketch of same grain as in Figure 8. Numbers are Mg/(Mg+Fe) in staurolite grains.

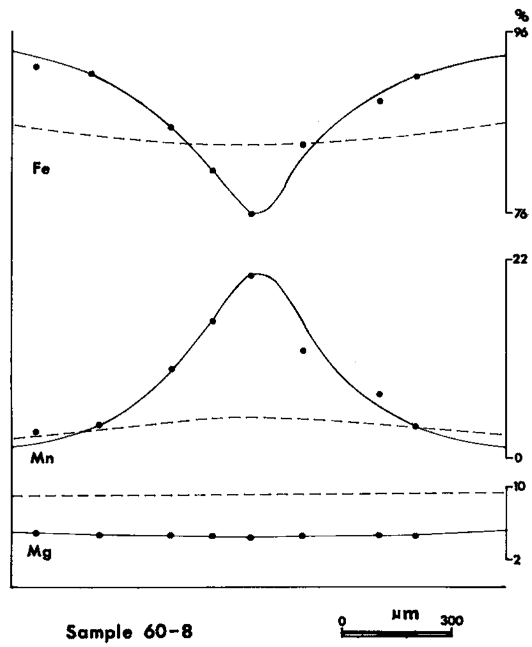


FIG. 10. Calculated and measured zoning profiles in the garnet grain of Figures 8 and 9. The dashed curves are the measured profiles of Figure 4b. The solid curves were calculated from the inclusion data in Figures 8 and 9. The profiles are calibrated in terms of molecular percentages, normalized so that Fe, Mn, Mg, and Ca total 100%.

why Ca zoning is weak in both garnet and plagioclase in most garnet-bearing samples from the pendant.

With the above assumptions and equations (3) and (4), the original garnet composition, prior to homogenization, may be calculated at each analyzed ilmenite in Figure 8, using an average value of X^{gt}_{Mg} of 0.855. The calculated zoning profile (Fig. 10) is remarkably similar to those measured for garnet and staurolite-zone garnets (e.g. Fig. 2a). The mean Mn content of the original garnet is the same as the mean Mn content of the garnet after homogenization: there was no net transfer of Mn across the garnet boundary as a result of homogenization. The mean Mg content of the homogenized garnet is, however, about twice as high as the original garnet. This addition of Mg to the garnet was balanced by a loss of Fe, possible causes of which are discussed below.

Modification of homogeneous garnets

Garnets that have reached temperatures sufficient to allow homogenization by volume diffusion are clearly not refractory. Such garnets must change their bulk composition upon a change in composition of any adjacent Fe-Mg phase (by a continuous reaction, for example) if equilibrium is to be maintained.

The formation of cordierite at the expense of staurolite, given by reaction (2), it at least divariant. Initially, garnet and the first bit of cordierite will have Mg/Fe ratios that are, in part, dependent on the prevailing temperature and pressure. As temperature increases, staurolite with an increasing Mg/Fe ratio will continue to be consumed, and the Mg/Fe ratios of garnet and cordierite will continuously increase in response to the changing conditions of metamorphism. Even after reaction (2) has gone to completion, exchange between garnet and cordierite will continue to modify the garnet composition. Figure 11 shows this possibility in a schematic view of equilibria in the system garnet-cordierite for the divariant reaction

$$3 \text{ cordierite} = 2 \text{ garnet} + 4 \text{ sillimanite} + 5 \text{ quartz} \qquad (5)$$

according to the data of Hensen & Green (1971). At some pressure and temperature, garnet of composition G_1 is in equilibrium with cordierite C_1. With increasing pressure and temperature the compositions of the phases change continuously according to reaction (5); modal garnet increases and garnet G_2 coexists with cordierite C_2. In systems with refractory garnet, such effects would result in garnet rims having high Mg/Fe ratios compared with the cores. In garnets where volume diffusion is sufficiently rapid to maintain homogeneity, the result would be a net diffusion of Mg into the garnet, balanced by a net loss of Fe from the garnet to the cordierite.

The equilibria in sample 60-8 are clearly more complex than those in Figure 11, but exchange reactions of this type seem adequate to account for the relatively high mean Mg content of the homogeneous garnet compared with that calculated for the original, zoned garnet. Conclusions based on the assumption that the core compositions of garnets reflect the composition of the garnet at time of nucleation may be invalid in garnets showing evidence of volume diffusion.

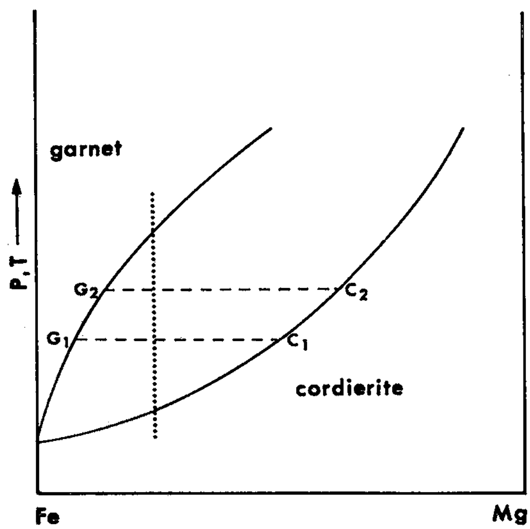


FIG. 11. Schematic phase equilibria in part of the system garnet-cordierite, based on data of Hensen & Green (1971). See text for discussion.

Formation of Mn-rich rims

Many garnets, both high and low grade, from the Mount Raleigh pendant are characterized by an increase in Mn near the rims accompanied by a decrease in Mg and Mg/(Mg+Fe) (Figs. 2b and 4a). Several origins have been proposed for such reverse Mn zoning (Hollister 1969; Kretz 1973; Grant & Weiblen 1971; de Béthune & Laduron 1975). Suggestions involving modifications of the fractionation-depletion model, either by increasing the Mn concentration in the reservoir surrounding the garnet or by changing the fractionation factor λ, are not applicable to non-refractory garnets. Other interpretations, favored here, involve resorption of the garnet with preferential retention of Mn in the remaining garnet.

All garnets from the Mount Raleigh pendant having reverse Mn zoning are from samples showing strong retrograde effects. Garnet is embayed and rimmed by chlorite; biotite is interleaved with chlorite; aluminum-silicate minerals are partly altered to shimmer aggregate, and coarse muscovite porphyroblasts cross-cut the foliation. The retrograde reactions were not studied in detail, but the restriction of garnets with Mn-rich rims to rocks with strong retrograde alteration suggests that these rims developed during retrograde alteration, as in the case described by de Béthune & Laduron (1975). During chloritization of the garnet, Mn was re-incorporated into the remaining garnet ahead of the dissolution front, because chlorite and the other retrograde minerals have very low Mn/(Mn+Fe) ratios. Probe analyses show that chlorite which rims the garnet has a Mg/(Mg+Fe) ratio greater than that of the garnet, requiring preferential removal of Mg from the shrinking garnet and resulting in a lowering of the Mg/(Mg+Fe) ratio at the garnet rim. These rims show no enrichment in Ca, and the chlorites have a very low Ca content. Presumably, the Ca released by resorption of the garnet has been taken up by another mineral such as plagioclase.

The inward migration of Mn during resorption of garnet- and staurolite-zone garnets creates problems, because retrogression of these garnets must take place at temperatures at which garnet is supposedly a refractory mineral. No satisfactory answer to this problem is currently available. Possibly, as was suggested by de Béthune *et al.* (1968), the garnet structure is unstable immediately ahead of the resorption front, allowing diffusion of ions in and out of the garnet. Possibly, as is discussed below, diffusion rates are strongly influenced by $P(O_2)$. If resorption of the garnet proceeded under relatively oxidizing conditions, the conversion of Fe^{2+} to Fe^{3+} near the rim of the garnet may have produced enough vacancies to enhance the diffusion rates for Mn, even under declining temperatures. The narrow width of the Mn-rich rims in garnet and staurolite-zone garnets (generally less than 20 μm compared with 100 to 200 μm for cordierite-zone garnets) may reflect the short distance over which diffusion is effective in the lower grade rocks. In cordierite-zone rocks, retrogression may have begun at temperatures at which diffusion in the garnet was still relatively effective, allowing Mn to diffuse far into the garnet, producing a wide zone of Mn enrichment.

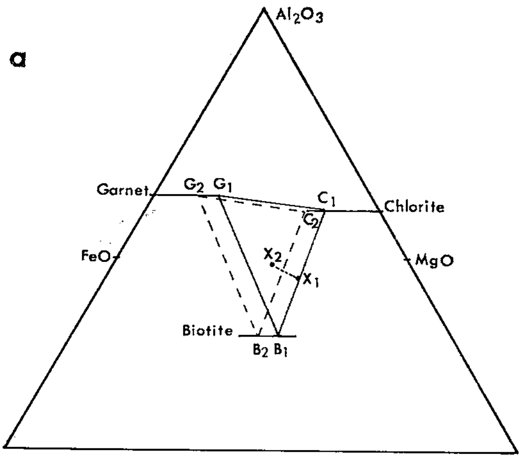
Discussion

Controls of volume diffusion

The above interpretation indicates that zoning in garnet- and staurolite-zone garnets was controlled primarily by fractionation-depletion processes, whereas volume diffusion was the main control in cordierite-zone garnets. It is not clear from this study at what temperature volume diffusion began to homogenize the garnets. Garnets from the one sample (68-1) available from the upper part of the staurolite zone have a subdued bell-shaped Mn profile (Fig. 2d) that may represent the beginning stages of homogenization. The maximum temperature reached by this sample was probably about 625°C (Woodsworth, in press). Garnets from near the staurolite isograd, which represents temperatures of about 550°C, show no evidence of volume diffusion aside from the Mn-rich rims, whereas at cordierite-zone temperatures of about 700°C original zoning is almost completely obliterated. Volume diffusion thus began to be important at some temperature between 550°C and 700°C, perhaps about 600°C.

Factors other than temperature may also control the extent to which volume diffusion may create or modify compositional zoning. The longer a zoned garnet is held at an elevated temperature, the greater will be the effects of diffusion. In the Mount Raleigh area, cordierite-zone rocks spent more time above 500°C than did staurolite-zone rocks (Woodsworth, in press), although the length of time spent at the maximum temperature may have been about the same in each zone. Diffusion may have been effective in homogenizing the cordierite-zone garnets partly because more time was available for diffusion to act than in lower grade rocks. Depending on the magnitude of the appropriate diffusion coefficients, garnets may survive high-level contact metamorphism without appreciable effect, such as in the Fanad aureole, Donegal (Edmunds & Atherton 1971). Garnets in regional metamorphic terrains, on the other hand, may be expected to show marked diffusion effects.

Little attention has been paid to the role of deformation in garnet zoning. Shearing stress may lower the activation energy needed for diffusion by causing the accumulation of lattice defects and raising the free energy of the crystal. Mueller (1967) pointed out that little shearing stress can be transmitted to a strong competent garnet growing in an incompetent matrix of sheet silicates, and thus shearing stress would have little effect on the rate of volume diffusion within the garnet. If, however, the garnet is about as competent as the other minerals in the rock, shearing stress may reduce the temperature at which diffusion becomes effective. Textural evidence indicates that garnets in the lower grade areas of the Mount Raleigh pendant are post-tectonic, whereas those in the cordierite zone are syntectonic and are flattened parallel with the foliation. Garnets in sample 68-1, in which the beginning of homogenization may be apparent, are also slightly deformed. The extent of volume diffusion in the garnets correlates roughly with increasing deformation of the garnets, as well as increasing temperature. The importance of shearing stress in promoting volume diffusion in the garnets is, however, impossible to determine and future attempts to estimate the duration of metamorphism from garnet zoning must consider the state of stress of the garnet at the time of metamorphism in addition to temperature.



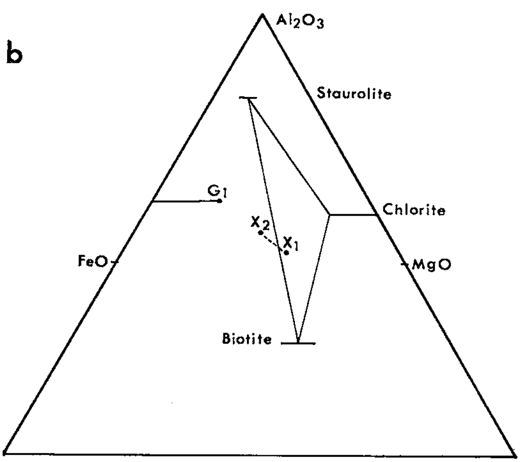


FIG. 12. a) AFM projection of the assemblage garnet+chlorite+biotite, with refractory (solid lines) and non-refractory (dashed lines) garnet.
b) AFM projection of the assemblage biotite+chlorite+staurolite, with garnet G_1 present as an inert phase. See text for discussion.

Diffusion rates in Fe-bearing minerals may also depend on $P(O_2)$ and the formation of vacancies associated with the conversion of Fe^{2+} to Fe^{3+}. For example, Buening & Buseck (1973) gave good evidence that Fe-Mg interdiffusion coefficients in Fe-Mg olivine are proportional to $P(O_2)^{0.172}$, suggesting that Fe^{3+} and associated vacancies are important controls of diffusion rates. Although a similar mechanism may operate in garnets, its importance cannot be evaluated from this study. All samples contain graphite and ilmenite and, although $P(O_2)$ may have increased with increasing temperature, the effects of temperature cannot be separated from the effects of $P(O_2)$. Comparisons of garnet zoning in rocks that have had the same *P-T* histories under different oxygen fugacities, such as adjacent beds of graphite-bearing and graphite-free rocks, are needed to evaluate the importance of this mechanism.

A puzzling feature of the present study is the preservation of original Mn/(Mn+Fe) ratios in ilmenites included in homogeneous cordierite-zone garnets. The ilmenite inclusions appear to be refractory, whereas matrix ilmenites are in partition equilibrium with the garnet rims. The implication is that diffusion of Mn and Fe in and out of ilmenite proceeded faster in the matrix ilmenite than in the inclusions. No satisfactory answer to this problem is apparent. However, the different environments of the two sets of ilmenites may provide a clue: inclusions inside the garnet may have been relatively insulated from the effects of shearing stress and from changes in $P(O_2)$ compared with matrix ilmenites. Diffusion rates in ilmenite are probably strongly dependent on Fe^{2+}/Fe^{3+} ratios; there is good experimental evidence for such a dependency in other iron oxides (e.g. Himmel *et al.* 1953). If the included ilmenites were subjected to a lower $P(O_2)$ than the matrix ilmenites, diffusion rates in the included ilmenites could be lower than in the matrix. Similar considerations may apply to staurolite and biotite inclusions in cordierite-zone garnets. These minerals are unzoned and are probably not refractory in the Mount Raleigh area, but inclusions in garnet preserve lower Mg/(Mg+Fe) ratios than are found in the matrix grains.

Effect of homogenization on phase equilibria

The concept of homogenization of zoned garnets has implications for phase equilibria. As discussed by Hollister (1969), the effective bulk composition of a rock containing refractory and non-refractory minerals is dependent only on the compositions and relative proportions of the non-refractory minerals because, at most, only the rim of the refractory mineral is part of the equilibrium system. This situation is illustrated by the assemblage garnet+biotite+chlorite+muscovite+quartz (Fig. 12a): the effective bulk composition X_1 of the system lies on the chlorite-biotite join. Homogenization of the garnet results in a shift in the garnet rim composition from G_1 to G_2 and a change in the bulk composition of the reactive system to X_2. If equilibrium is maintained, the Mg/Fe ratios of biotite and chlorite must decrease and the amount of chlorite relative to biotite must increase.

Conceivably, garnet could be sufficiently refractory that even the garnet rim is not in equilibrium with the other minerals in the assemblage. Figure 12b shows the equilibrium assemblage staurolite+chlorite+biotite+muscovite +quartz, with garnet G_1 present as an inert phase, at a temperature above the breaking of the garnet-chlorite join. Upon homogenization of the garnet the bulk composition of the system will move towards garnet, and the garnet and chlorite will react, possibly by a reaction such as garnet+chlorite=staurolite+biotite. The resulting equilibrium assemblage will be either garnet+biotite+staurolite+muscovite+quartz, or chlorite+biotite+staurolite+muscovite+quartz, depending on the "final" bulk composition of the system. The initiation of significant volume diffusion in garnet may promote reactions that had been suppressed because of the unreactive nature of the garnet.

Conclusions

The study is mainly concerned with deciphering the history of zoning in garnets from the Mount Raleigh area and evaluating the importance of volume diffusion in the production and modification of garnet zoning. The principal conclusions of the study are:

1. Most garnets from the garnet and staurolite zones are characterized by bell-shaped Mn profiles; the decrease in Mn from core to rim is balanced mainly by Fe. Such zoning results from a fractionation-depletion process; volume diffusion within these garnets is negligible.

2. Homogeneous garnets in cordierite-zone rocks nucleated and grew at lower grade. Zoning produced during growth by fractionation-depletion processes was obliterated by volume diffusion at cordierite-zone temperatures, producing homogeneous garnets. Exchange reactions involving garnet and cordierite modified the composition of the homogenized garnets, resulting in a net influx of Mg into the garnet and a net loss of Fe. Conclusions based on fractionation factors using garnet core compositions may not be valid in garnets showing evidence of volume diffusion.

3. Mn-rich rims on some garnets were produced during partial resorption of the garnet, and resulted from the diffusion of Mn released by garnet breakdown into the remaining garnet.

4. Ilmenite in the matrix of the rock was in partition equilibrium with adjacent garnet rims throughout garnet growth and homogenization. Inclusions of ilmenite and staurolite in cordierite-zone garnets have retained their original compositions since engulfment in the garnet and may be used to calculate the zoning profiles of the garnets prior to homogenization.

5. Modification of the garnet zoning profiles began at temperatures of perhaps 600°C. The effects of volume diffusion are most apparent in syntectonic garnets, and are least apparent in post-tectonic garnets. In addition to temperature, lattice defects produced by shearing stress and the conversion of Fe^{2+} to Fe^{3+} may be important controls of volume diffusion.

6. The change in garnet from a refractory to a non-refractory mineral may lead to changes in the effective bulk composition of the system, to changes in the compositions of other Fe-Mg phases, and possibly to reactions leading to the elimination of garnet or other minerals from the system.

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