

## **The relationship between chemical and textural (optical) zoning in metamorphic garnets, South Morar, Scotland**

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### **Abstract**

Textural (optical) zones and patterns of chemical zoning of Fe, Mn, Mg, and Ca in garnets from regionally-metamorphosed rocks in western Scotland correlate in a simple way where growth proceeded at a uniform rate into a homogeneous reservoir. Garnets with three zones predominate in garnetiferous mica-schists, whereas garnets in semi-pelite have two textural zones. In both types of garnet, each zone represents a separate growth stage. However, the outermost zone in many three-zone garnets is incomplete, which suggests that local changes in the effectiveness of intergranular diffusion in the matrix, combined with changes in distance to local sources of components such as Ca and Al, dominated the growth rate.

The evolution of textural zones closely reflects the amount of particulate matter and the local conditions in the reservoir into which the garnets grew. In contrast, chemical zoning resulted from distinct and universal stages in the metamorphic history of the rock. Where the incomplete development of textural zones in two- and three-zone garnets is due to partial growth, insufficient concentrations of particulate matter, or fragmentation, we believe the chemical data provide the firmest base for unraveling the history of garnet growth.

### **Introduction**

Metamorphic garnets of the Morar region provide a special opportunity to study the nature of crystal growth for two reasons: (1) they contain internal textural (optical) zones and inclusion fabrics that aid in relating periods of garnet development to periods of deformation and metamorphism; (2) they are found by electron microprobe analysis to be chemically heterogeneous, thus retaining a chemical record of their growth history. This paper is concerned with the relationship between textural zoning and chemical zoning; chemical variations associated with inclusion fabrics will be dealt with in a separate publication.

Since the papers of Atherton and Edmunds (1966) and Hollister (1966), compositional zoning in metamorphic garnets has been illustrated and modelled by a large number of authors; a review and analysis of the various models and the processes involved has been given by Atherton (1976). As yet, only a few studies have been completed of the relationships between chemical zoning and textural (optical) zones. Harte and Henly (1966) showed that distinct changes of slope in the chemical zoning profiles of garnets

from Sulitjelma, Norway, coincided with boundaries they described as growth discontinuities created by a change in metamorphic conditions. Atherton and Edmunds (1966) and Edmunds and Atherton (1971) found that chemical changes occurred at optical zone boundaries in garnets from regional metamorphic rocks. Recently, MacQueen and Powell (1977) superimposed the position of textural zone boundaries onto chemical profiles measured in a garnet from the Morar region. Their results indicated that each textural zone may have distinct chemical characteristics. The garnets examined here are from the same region as the samples studied by MacQueen and Powell. Our samples are from one stratigraphic unit of the Moine Schists—the Morar Pelite (Fig. 1). The petrography, mineralogy, and chemical composition of this unit have been described in detail by Richey and Kennedy (1939) and Lambert (1958). Garnets from the Morar Pelite contain well-preserved textural zones and inclusion fabrics (Powell, 1966; MacQueen and Powell, 1977) as well as complex chemical variations (Anderson and Olimpio, 1977). The term “textural zone” is used here in place of the term “optical zone” to denote an internal zone clearly visible in thin section.

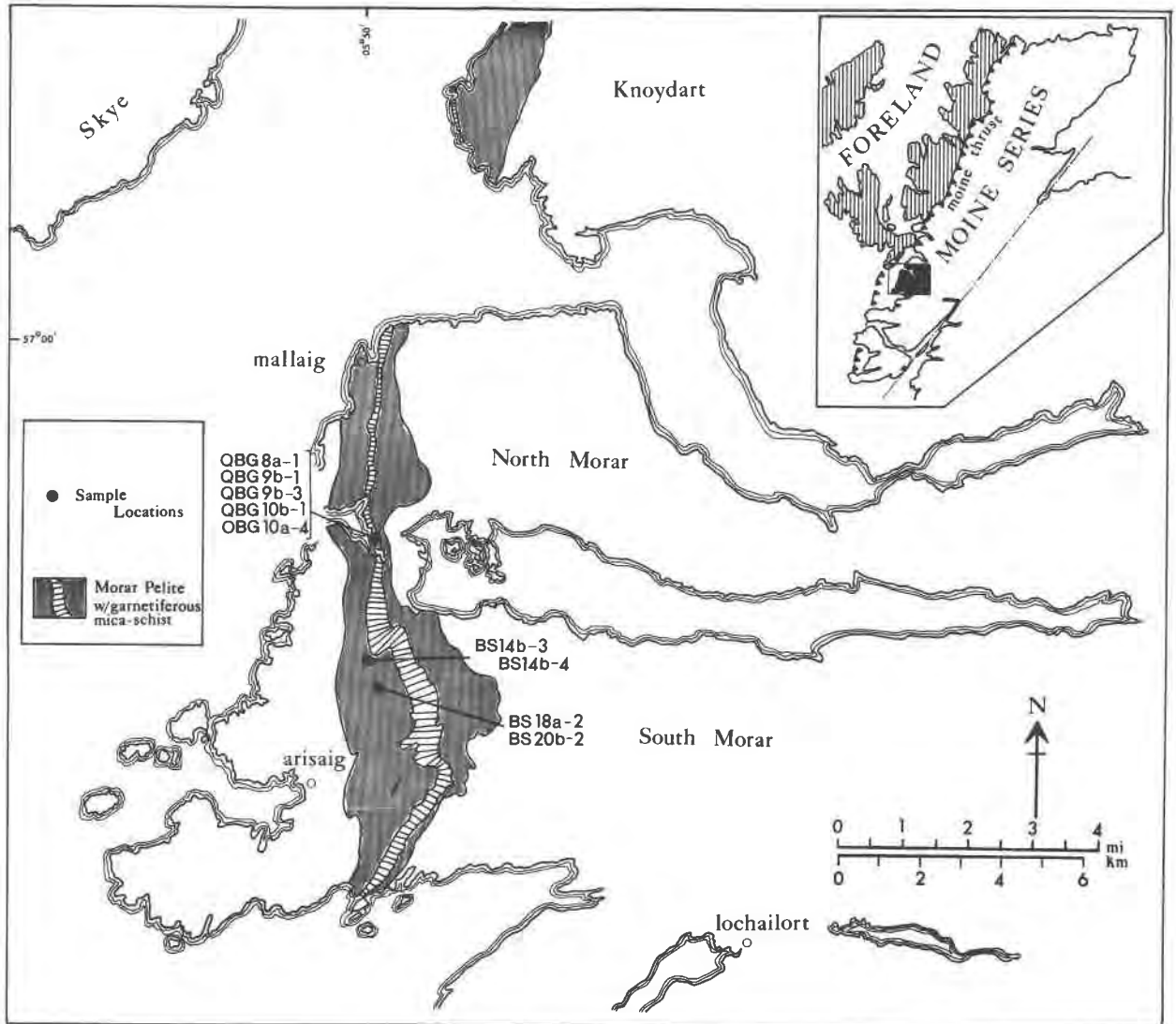


Fig. 1. Location of the South Morar region in western Scotland with positions of samples analyzed and discussed in text. The Morar Pelite is located within the garnet zone of regional metamorphism and has sustained partial chlorite-grade retrogression.

### Present investigation

Brook *et al.* (1977), using new isotopic data, have divided the tectonic and metamorphic history of the Morar region into Grenvillian (~1024 MA) and Caledonian (~450 MA) events. The Grenvillian event is composed of two distinct periods of deformation and metamorphism (Brook *et al.*, 1977; Powell, 1974): (a) isoclinal folding accompanied by low (garnet) grade metamorphism ( $M_1$ ) and (b) intense folding accompanied by medium grade metamorphism ( $M_2$ ). In the area from which our samples were taken,  $M_1$  metamorphism predominates;  $M_2$  metamorphism is represented by mild retrogression.

The Morar Pelite comprises three units (Richey and Kennedy, 1939; Powell, 1974). Garnets were sampled from the striped semi-pelites of the upper unit and the garnetiferous mica-schists of the middle unit. The mineralogical composition of the semi-pelites is biotite (20–25 percent), muscovite (20–25 percent), quartz (35–40 percent), plagioclase (10–15 percent), garnets (1–2 percent), and opaques (1–2 percent). The garnetiferous mica-schists are defined (Butler, 1965) by the presence of 2–10 percent of porphyroblastic garnets in a matrix of quartz (35–45 percent), plagioclase (20–25 percent), biotite (15–20 percent), muscovite (5–15 percent) and opaques (0.5–3 percent).

In both lithologies, ilmenite is the major opaque mineral and plagioclase is zoned in the range  $An_3$  to  $An_{25}$  (Lambert, 1958). Epidote, common as inclusions in garnets, is very rarely encountered in the matrix of either rock. Lambert noted that the garnetiferous mica-schists are too calcic to be classified as pelites. Butler (1965) proposed that they may have been derived from immature sediments of graywacke or silt composition in which epidote, calcite, and graphite were important minor components.

The garnets in the garnetiferous mica-schists are divided into two distinct groups: (1) small garnets (0.1–0.4 mm), located chiefly in micaceous bands, that are almost chemically homogeneous; (2) larger garnets (1.5–5 mm) that are strongly zoned in Mn, Fe, Ca, and Mg (McAteer, 1976). Only the larger garnets are examined in this paper.

### Textural zones

MacQueen and Powell (1977) have described and extensively illustrated the textural zones and internal fabrics of garnets from the Morar Pelite over a broad region of Morar, Knoydart, and Skye. They observed that in western Morar three textural zones are present in many, but not all, garnets. In some samples, garnets also contain two, or less commonly, four zones.

Our sampling of the Morar Pelite, admittedly over a much smaller region than that covered by MacQueen and Powell, suggests that the average number of textural zones present depends on the chemical composition of the rock. Garnets with three zones predominate in the garnetiferous mica-schists, whereas garnets with one, two, or four zones are rare. In contrast, garnets from the semi-pelite almost invariably have two textural zones. It is convenient through much of the following discussion to distinguish carefully between the textural and chemical properties of (a) two-zone garnets in the semi-pelite and (b) three-zone garnets in the garnetiferous mica-schists and, for the moment, to ignore the occurrence of garnets with one, two, or four zones in the latter unit. For brevity, the terms two-zone and three-zone garnets will be used to designate garnets from groups (a) and (b) respectively.

#### Three-zone garnets

The internal textural features of three-zone garnets from the garnetiferous mica-schists have been summarized in Table 1 of MacQueen and Powell (1977), and only a few additional comments are needed here. The innermost textural zone (zone 1) is commonly sub-spherical and relatively free of inclusions (Fig. 2);

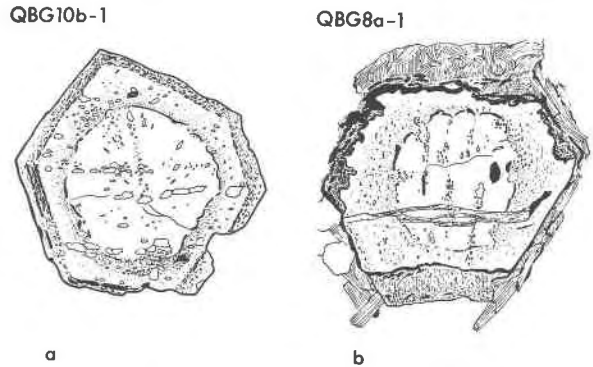


Fig. 2. Sketch of samples QBG10b-1 and QBG8a-1, both from one outcrop of garnetiferous mica-schist. The inclusions most frequent within all porphyroblasts are quartz (clear outline) and ilmenite/graphite (opaque).

in contrast, the middle zone (zone 2) is usually crowded, especially on its inner edge, with inclusions. The outermost zone (zone 3) is characterized in most garnets by a peculiar platy structure (Fig. 2a), formed by thin laminae separated by parallel, cleavage-like planes dusted with very fine inclusions. The same inclusions—quartz, ilmenite, graphite, epidote, and rutile—occur in all three zones, except that epidote is rare in zone 3. The  $Z_1/Z_2$  boundary is marked by thin, curved laminae of a low-reflectivity opaque (Fig. 2b). Tests with the electron microprobe have revealed that the laminae are composed of almost pure carbon, presumably graphite. The  $Z_2/Z_3$  boundary is rendered visible in transmitted or reflected light by one or more of the following features: (1) the laminated structure of zone 3; (2) concentrations of fine inclusions just inside zone 3; (3) trails of fine, evenly-spaced inclusions outlining an idioblastic form; (4) truncated quartz inclusions; (5) truncated or bent inclusions fabrics.

#### Two-zone garnets

Two-zone garnets from the semi-pelite are smaller (900–2000  $\mu\text{m}$ ) and less idioblastic than three-zone garnets (Fig. 3). The same inclusions, however, are present in both groups of garnets, although only a negligible amount of graphite is present in two-zone garnets.

The inner zone (zone 1) is sub-circular in outline and contains relatively few inclusions. The outer zone (zone 2) tends to form overgrowths that parallel the foliation ( $S_2$  of Powell, 1974) of the rock. Zone 2 is crowded with inclusions of quartz and, in the region adjacent to zone 1, finely-dispersed graphite.

The  $Z_1/Z_2$  boundary (Fig. 3) is defined by an

abrupt increase of quartz inclusions in zone 2 and a noticeable change in color. Laminae of opaques of the kind found along the  $Z_1/Z_2$  boundary in three-zone garnets are absent.

### Analytical procedure

The distributions of Fe, Mn, Ca, Mg, Ti, Si, and Al were determined with an ARL-EMX electron microprobe set at 20 kV and a beam current of approximately 0.6 microamps. Analytical procedures, standards and procedures for the correction of absorption, fluorescence, *etc.* correspond with those described by Sweatman and Long (1969) and Reed (1975). Continuous traverses for Mg and Ca were used to determine the spacing and location of subsequent spot analyses.

The whole-garnet analyses of Lambert (1958) show an average ferric oxide concentration of 1–3 percent. Ti, Si, and Al are homogeneously distributed in all the garnets analyzed.

### Compositional variation and textural zones

#### Three-zone garnets

Approximately 80 percent of the garnets in the garnetiferous mica-schists are idioblastic and have textural zones of uniform thickness. All the chemical data gathered for these garnets are from sections cut very close to their centers, so as to minimize “cut effects” in the matching of chemical and textural features, but cut effects cannot be eliminated in the examination of those 20 percent of garnets that are either xenoblastic or have irregular textural zones. We believe, however, that the experience gained with idioblastic garnets may be used to interpret and correlate chemical and textural data in the latter garnets.

The data in Figure 4 show a simple correlation between textural and chemical zoning. Chemically, zone 1 is characterized by a high Mn content and a nearly uniform distribution of Ca, whereas Ca and Mn decrease simultaneously across zone 2. In both zones, variations in Mn are almost exactly mirrored by antipathetic variations in Fe. Zone 3 typically has a low concentration of Mn accompanied by a higher concentration of Ca; changes of Ca in this zone tend to be compensated for by variations in Fe.

Concentration profiles measured in idioblastic three-zone garnets with zones of uniform thickness are reasonably symmetric (Fig. 4). As noted above, approximately 80 percent of all three-zone garnets fall into this category. Simple symmetrical relations of this kind are lacking in the other 20 percent of

garnets that have clearly experienced a more complicated growth history. But despite differences in their histories, certain features are common to all three-zone garnets:

1. A step of 2–4 percent in the concentration of Ca (designated the Ca-edge), accompanied by an increase of 3–5 percent in Fe, is located at the  $Z_2/Z_3$  boundary. The change in Ca and Fe may take place over a region as thin as 5–10  $\mu\text{m}$  (Fig. 4); in contrast, in other garnets—or in other parts of the same garnet—the two elements may change continuously over a region up to 90  $\mu\text{m}$  across (Fig. 5). The Mn and Mg profiles pass smoothly through this region with a rapid rise in Mn concentration beginning 50–150  $\mu\text{m}$  inside the  $Z_2/Z_3$  boundary.

2. The slopes of the profiles of Mn, Fe, and Ca may vary significantly from point to point in any garnet on the inner side of the Ca-edge, even where the shape of the edge is constant. The concentrations of elements, however, around the  $Z_2/Z_3$  boundary are approximately uniform in each garnet. For Ca and Fe, this means that their concentrations at the top and the bottom of the Ca-edge are respectively equal everywhere. Minor discrepancies, most obvious as variations of up to 0.5 percent in Mn, do occur; the overall uniformity, however, is significant.

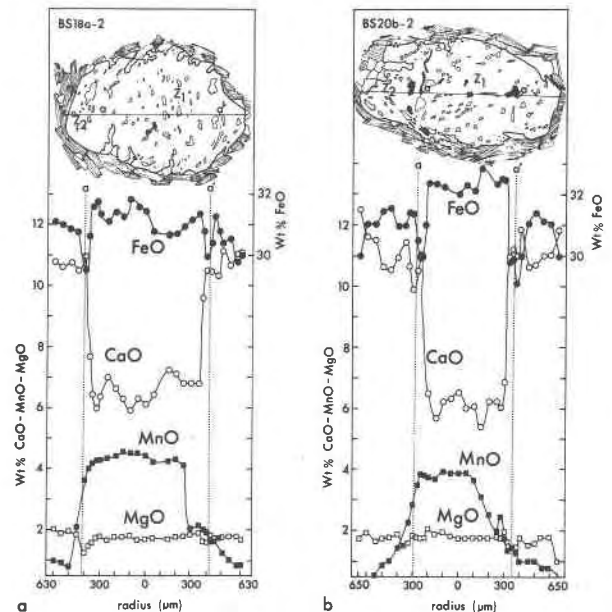


Fig. 3. Samples BS18a-2 and BS20b-2 from one outcrop of the uppermost semi-pelitic unit of the Morar Pelite. The positions of the textural zones, as observed in thin section and encountered along the line of microprobe traverse, are indicated by the dotted lines “a” and “a’” superimposed on the compositional profiles. In this and remaining diagrams, chemical compositions are given as oxide weight percentages.

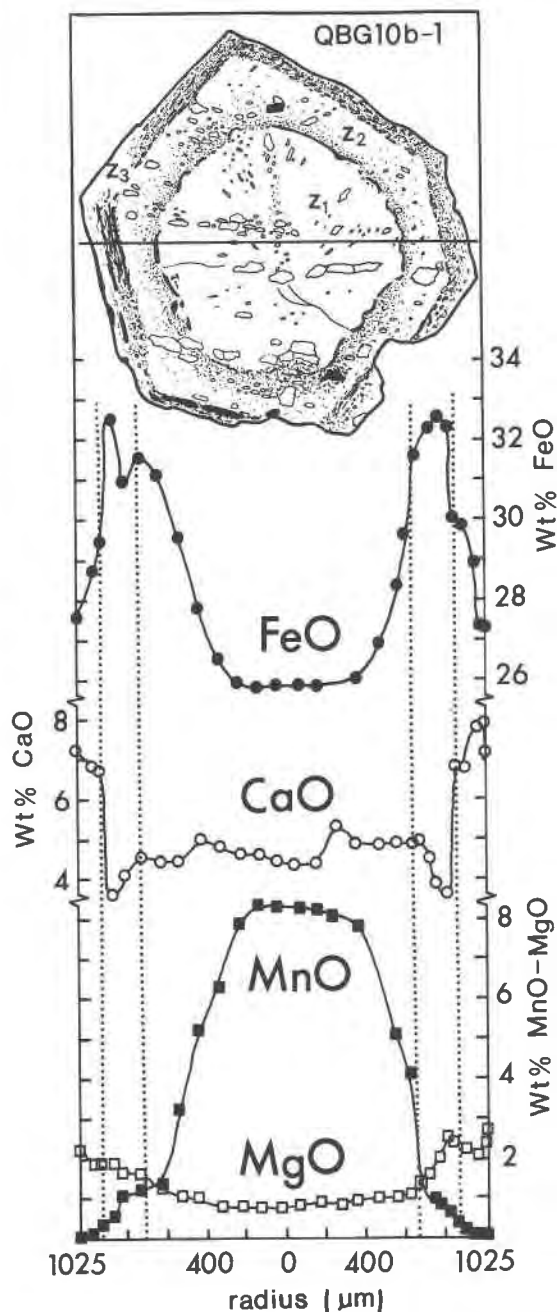


Fig. 4. Sample QBG10b-1 from the garnetiferous mica-schist; note the symmetrical distribution of textural zones and compositional fluctuations.

3. The  $Z_1/Z_2$  boundary coincides approximately with a break in slope of the Ca profile that marks the beginning of the gradual decrease of Ca through zone 2: where the boundary is clearly defined by laminae of graphite, the coincidence is exact; where the boundary is only visible because of changes in the density of

quartz inclusions and dispersed graphite, the break in slope may be up to  $100\ \mu\text{m}$  outside of the boundary. The concentration of Ca, with only a few exceptions (see below), drops by a uniform amount across zone 2, independently of the thickness of the zone on different sides of the garnet (Fig. 8).

Items 2 and 3 imply that each garnet was in local partitioning equilibrium with its reservoir throughout the growth of zones 1 and 2. The coincidence of the  $Z_2/Z_3$  boundary and the Ca-edge in well-formed garnets suggests a genetic relationship, the existence of which is reinforced by the data given in Figure 6. Binary garnets, two closely-spaced garnets of roughly equal size with similar patterns of chemical and textural zoning, are quite common in a thin transitional zone near the top of the garnetiferous mica-schists. A narrow zone 3 is irregularly developed around the two garnets. Where zone 3 is present, a Ca-edge is located exactly at the  $Z_2/Z_3$  boundary; on the other hand, wherever zone 3 is absent, the Ca-edge is also missing. In the latter situation, the concentrations of Ca and Mn at the rim of the garnet equal those just inside of the Ca-edge elsewhere in the garnets.

In a small number of three-zone garnets, the correlation between textural and chemical zoning is not as simple. The presence of a Ca-edge on the right-hand of garnet QBG10a-4 (Fig. 7), in a region where zone 3 appears to be absent, is one example. The irregular form of zones 1 and 2 is unusual, although the ten-

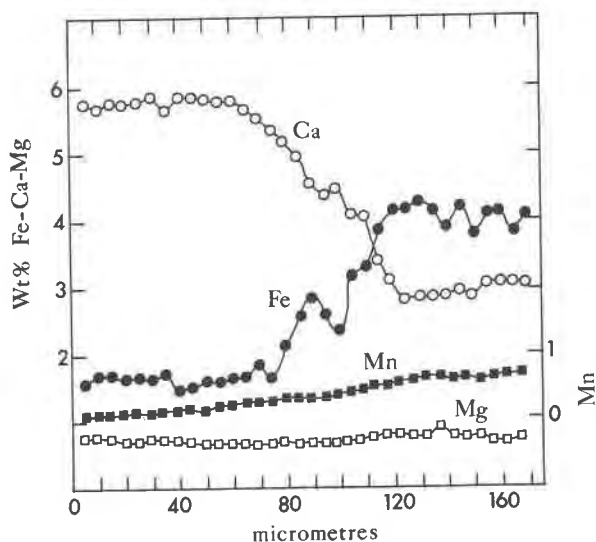


Fig. 5. A detailed traverse of one three-zone garnet showing the compositional changes near the margin (left). In several garnets such as this, the Ca-edge is not a sharp change in Ca concentration but is smooth and more continuous.

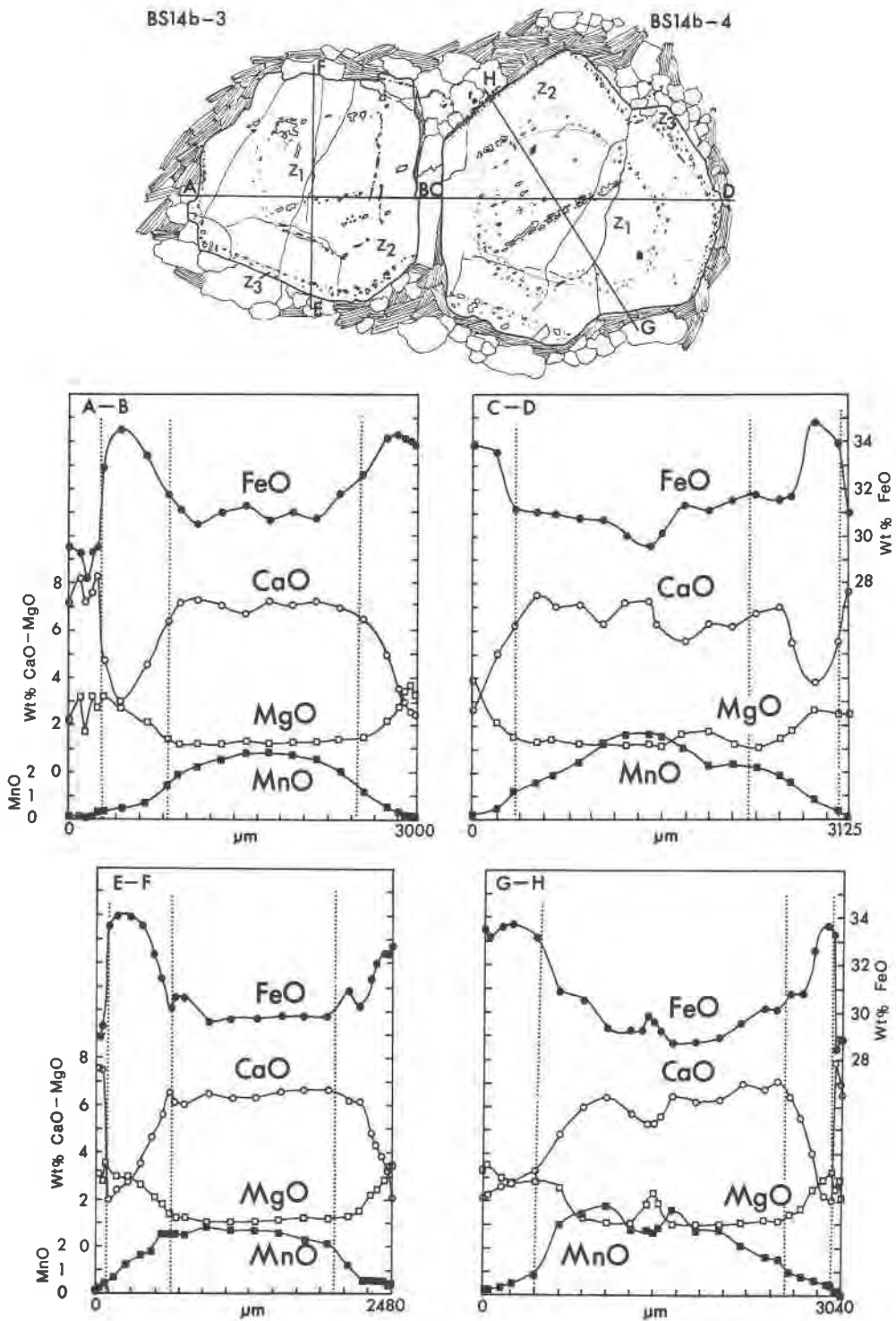


Fig. 6. Two garnets, BS14b-3 and BS14b-4, from the transition zone between semi-pelitic mica-schists in the Morar Pelite. Both garnets have an outer zone (zone 3) which is partially developed, and the porphyroblasts are separated only by several small quartz grains. The outer portions of each traverse contain near-margin compositional fluctuations which correspond with the location of a  $Z_2/Z_3$  boundary.

dency for zone 2 to develop an idioblastic form is maintained.

The marked asymmetry of the Mn and Ca profiles in zone 1 is also unusual. The locus *AB* of points on the Ca-edge on the right-hand side, determined by a series of closely-spaced traverses, is shown in the insert (Fig. 7). Except along the segment *AB*, the Ca-edge, as elsewhere in the garnet, is fixed at the  $Z_2/Z_3$  boundary. The section passes close to the center of the garnet, and both the  $Z_2/Z_3$  boundary and crystal faces are perpendicular to the plane of the section.

The material to the right of the segment *AB* is free of fine graphite and quartz and, furthermore, lacks the laminated structure that is peculiar to zone 3 elsewhere in this and other garnets. Thus, on textural grounds, it is identical with the material in the outer part of zone 2. On the other hand, if the Ca-edge indeed defines the  $Z_2/Z_3$  boundary, it might be argued that the material outside of *AB* should be designated zone 3.

An analogous situation occurs in specimen QBG9b-3 (Fig. 8). Although zones 1 and 2 have textural features similar to those found in other three-zone garnets, the  $Z_1/Z_2$  boundary is abnormal in three respects: (1) there is no accumulation of graphite at or near the boundary (either as laminae or as finely dispersed inclusions in zone 2); (2) there is a discontinuity in the Mn profile (a change of ~3 percent MnO in less than 30  $\mu\text{m}$ ) at the boundary; (3) there is no break of slope in the Ca profile at or near the boundary. A Ca-edge is present at point *A* on the traverse, despite the fact that there is no textural evidence of the growth of zone 3 on the left side of the garnet. Garnets with uniform and non-uniform textural zones are found together in the same rock in similar mineralogical and textural environments. As outlined earlier in this section, there is a simple and unambiguous correlation between textural and chemical zones in most porphyroblasts. The few exceptions such as garnet QBG9b-3, however, require a choice between chemical and textural features to unravel the stages of growth. For example, on purely chemical grounds, the  $Z_1/Z_2$  boundary in QBG9b-3 might be located at point *D* (*i.e.*, at the break of slope in the Ca profile). In a later section, we shall propose that chemical criteria, because they delineate distinct and universal stages in the metamorphic history of each garnet, are probably more reliable. In contrast, textural criteria tend to reflect, to a greater extent, local conditions in the reservoir into which the garnet grew.

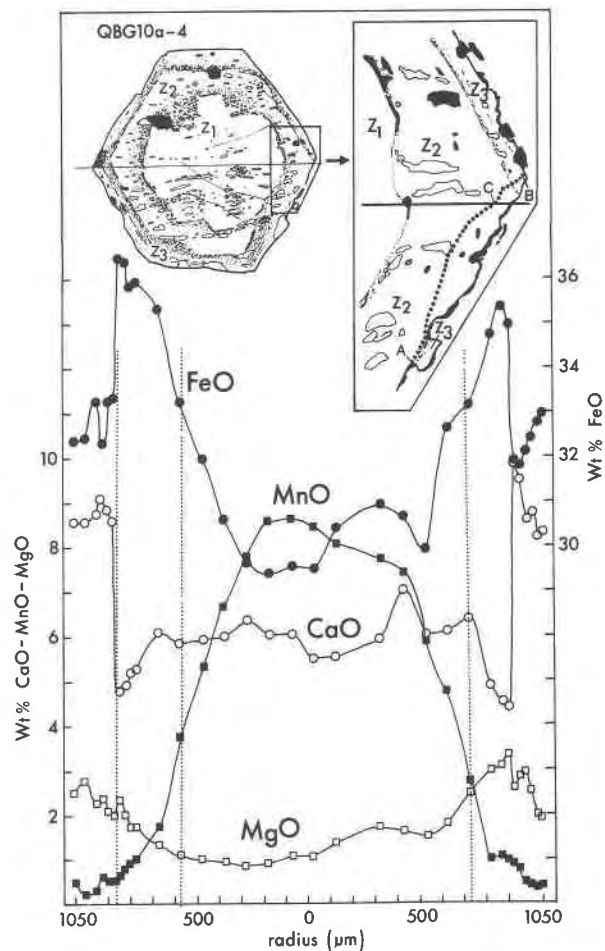


Fig. 7. Sample QBG10a-4 from the garnetiferous mica-schist; note the incomplete development of the outermost textural zone (3). A close-up sketch of the right-hand side of the garnet illustrates the positions of the zone boundaries and the precise location of the microprobe traverse. The locus of points *AB* was determined by analysis of the outer region of the porphyroblast along a short traverse parallel to and on either side of the indicated traverse.

#### Two-zone garnets

Because of their less regular shape and poorly-defined internal and external boundaries, it is more difficult to assess the extent to which profiles measured in garnets from the semi-pelite are distorted by cut effects. Within garnets which contain inner zones of medium size (Fig. 3), small fluctuations in Fe and Ca are antipathetic, whereas Mn and Mg are nearly homogeneous. Analyses of a number of garnets containing inner zones of different size revealed several changes in the nature of these zoning patterns. Where zone 1 in garnet is large (~800  $\mu\text{m}$ ), the Fe profile is

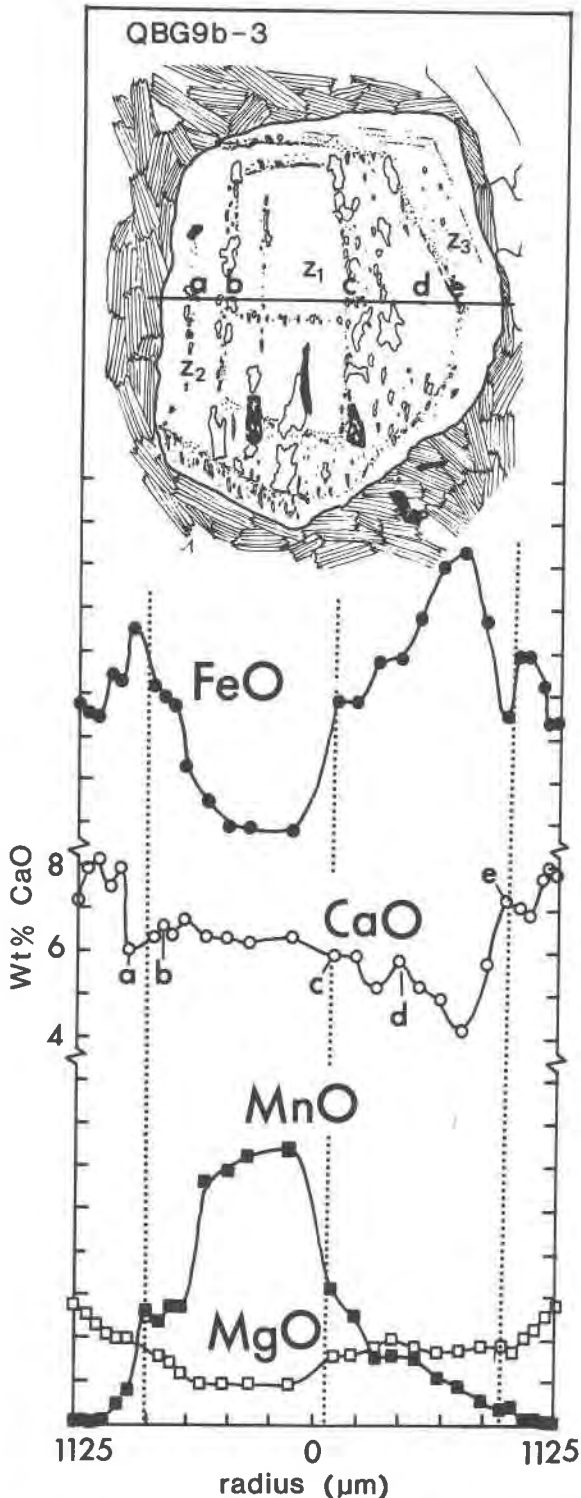


Fig. 8. Sample QBG9b-3 from the garnetiferous mica-schist. The Ca-edge was encountered during analysis at points *A* and *E* along the traverse, yet a textural zone boundary is missing at *A*. Furthermore, *B* and *C* mark positions of the  $Z_1/Z_2$  boundary, but do not correspond with changes in the slope of the Ca profile. The break in slope of the Ca profile normally associated with the  $Z_1/Z_2$  boundary is located in the middle of zone 2 at point *D*.

bowl-shaped and the Ca profile clearly decreases near the  $Z_1/Z_2$  boundary. Trends of Fe and Ca in these garnets are very similar to the Fe–Ca variations typical of zones 1 and 2 in the three-zone garnets.

A Ca-edge is located at the  $Z_1/Z_2$  boundary, and the concentrations of Fe and Ca are nearly constant at this point. Our comparison of a large number of two- and three-zone garnets indicates that the variations of Fe, Mn, and Mg in both two- and three-zone garnets are comparable, outside of the Ca-edge. The Ca variation in the outermost zone of the two sets of garnet, however, is different. In the two-zone garnets, Ca tends to increase rather than decrease.

## Discussion

### *Significance of the Ca variation*

Mn profiles are created by a segregation–depletion process that operates between a garnet and a finite reservoir (Hollister, 1969; Atherton, 1968, 1976). Thus there is a tendency to produce broadly similar profiles independently of the time a garnet nucleated and grew in a metamorphic cycle. At least in principle, the shape and amplitude of the Mn profile should reflect the partitioning conditions that prevailed during nucleation and growth. But we have argued that most, and probably all, of the Mn profiles in three-zone garnets from western Morar have been modified by diffusion (Anderson and Olimpio, 1977). Thus, in practice, the Mn profiles cannot be used with confidence to decipher the growth history of the garnets (see also Woodsworth, 1977; Yardley, 1977). Since the variation of Fe (and Mg) is antipathetic to that of Mn, out to the Ca-edge in two- and three-zone garnets, it is probable that Fe was involved in the same exchange reaction (or reactions) as Mn. Hence, over this region, the Fe profile contains no information that is not derivable from the Mn profile.

Our earlier work suggests that the Ca profile (out to the Ca-edge) is not significantly disturbed by diffusion until the final stages of homogenization (Anderson and Olimpio, 1977). It also appears in western Morar, as elsewhere (Crawford, 1974, 1977), that Ca behaved more or less independently of Fe, Mn, and Mg during segregation of Mn, and was not itself subject to a segregation–depletion process.

### *Conditions of growth in three-zone garnets*

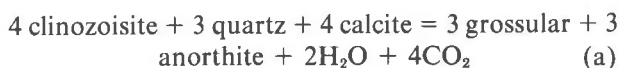
The Ca variation in three-zone garnets may be used to deduce the conditions of growth in the garnetiferous mica-schists. The Ca profile may be split into three segments, each of which seems to represent a



distinct portion of the metamorphic history of the rock: (1) a central plateau of nearly uniform Ca concentration; (2) a region of declining Ca concentration between the central plateau and the Ca-edge; (3) a peripheral region of high Ca content.

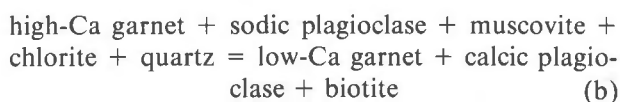
The exact reactions that led to the formation of garnet are difficult to determine, because rocks lower than garnet grade that are not the product of retrogression are not exposed anywhere in the region. It can be concluded, however, that the reactions that led to the formation of segments (1) and (2) of the Ca profile did not include epidote as a reactant. A Ca-rich epidote mineral is present as fine inclusions in three-zone garnets out to the Ca-edge; outside of the Ca-edge, however, these inclusions are very rare or absent (see also McAteer, 1976). This suggests that epidote began to disappear from the matrix of the schists at the time the Ca-edge developed.

McAteer (1976) proposed the reaction



as a source of grossular for the growth of the calcic rims (segment 3) of the garnets. Unlike epidote, calcite is not found as an inclusion in garnet; nor is it present in the matrix of the rock. Nevertheless, its introduction into the above reaction is supported strongly by the chemical arguments advanced by Butler (1965, p. 195). A simple alternate reaction not involving calcite has been derived by Lambert (1958, p. 577).

The equilibrium reaction



put forward by Crawford (1966) may be used to explain the evolution of segments (1) and (2) of the Ca profile. This reaction is consistent with the mineral assemblages of the garnetiferous mica-schists and, in a general way, with what is known of Ca zoning in plagioclase. Lambert (1958, p. 572-573) reported the presence of "...normal (albitic at the margin) ... reversed and oscillatory zoning. ..." in plagioclase but did not discuss the relative abundance or distribution of the different patterns of zoning. Our microprobe data suggest that the predominant pattern is one in which Ca increases from a central homogeneous region towards the rim of the grain. This pattern, combined with the Ca-zoning pattern in segments (1) and (2) of garnet, is compatible with the operation of reaction (b), followed by (a). Reaction (b) also implies that segment (2) was created during

rising temperatures. The prograde disappearance of chlorite, the general increase in anorthite content from core to rim in plagioclase, and the textural evidence in garnet (see below) further support this.

#### *Evolution of textural zoning in three-zone garnets*

The most significant difference between zones 1 and 2 is the abrupt increase in the number of graphite and, to a lesser extent, quartz inclusions in zone 2. The incorporation of material as inclusions, especially finely-divided material, is promoted by higher temperatures (McLean, 1957, p. 239), where the thermodynamic forces driving growth outweigh local equilibria related to interfacial energies. The low density of graphite (and quartz) inclusions in zone 1 indicates that growth may have been sufficiently slow for graphite to diffuse ahead of the growing interface. Conversely, the motion of the interface may have been controlled by the rate at which graphite diffused away. This appears to have been the case where curved laminae of graphite formed along the  $Z_1/Z_2$  boundary.

Unlike zone 1, zone 2 grew in conditions in which any increase in energy associated with the creation of new boundaries between inclusions and host garnet were overwhelmed by the reduction of energy associated with the production of new garnet. A rise in temperature would have provided the optimum conditions for the incorporation of graphite laminae on the  $Z_1/Z_2$  boundary as well as dispersed graphite and quartz inclusions in zone 2.

The most significant difference between zone 2 and zone 3 is the incomplete, often asymmetric development of zone 3. Several pieces of evidence indicate that the rate of growth of garnet changed at the  $Z_2/Z_3$  boundary. That growth may have slowed or ceased temporarily before the addition of zone 3 is suggested by the presence of truncated quartz inclusions and deflected internal fabrics outside of the boundary (e.g. MacQueen and Powell, 1977, Fig. 2; Plate 1), and by the flattening of the Mn profile. Given the presence of very strong concentration gradients and rising temperatures, the possibility that diffusion has modified zoning profiles near the Ca-edge cannot be ignored. If diffusion has modified the profiles, the differences now observed must reflect initial conditions or different periods of exposure to metamorphic conditions.

The non-uniform development of zone 3 might be attributed to the local inhibition of growth by the accumulation of fine particles on the outer rim of zone 2 (McLean, 1957, p. 239). In garnets where parts

of zone 3 are missing, however, there is no obvious accumulation of particulate matter on the rim of the garnet similar to that found along the  $Z_1/Z_2$  boundary. In view of the textural evidence it appears that growth proceeded around and through the particulate matter at this boundary in a manner similar to that at an earlier stage, and at lower temperatures, at the  $Z_1/Z_2$  boundary.

The Ca-edge marks a transition from reaction (b) to reaction (a), and hence reflects a transition from growth in a more or less homogeneous reservoir composed of major minerals (such as chlorite and plagioclase) to growth in a reservoir whose properties are determined primarily by a minor and previously refractory mineral (epidote). The possibility that growth may cease (even during rising temperatures) in circumstances of this kind is discussed by Hollister (1969).

Out to the vicinity of the  $Z_2/Z_3$  boundary, the profiles of Mn, Fe, Ca, and Mg exhibit nearly ideal radial symmetry (in garnets with textural zones of uniform width). Up to that point, intergranular diffusion must have provided a constant supply of material around the rim of the garnet at a rate equal to or in excess of the rate of growth. The order-of-magnitude calculations of Fisher (1977) indicate that intergranular diffusion should replace the rate of interface reactions as the rate-controlling process soon after nucleation.

The operation of intergranular diffusion includes the interplay of (a) the rate of diffusion of ions to the interface, and (b) the effective distance to local sources of these elements. The addition of even a thin mantle of zone 3 would have required the transport of large amounts of material: a layer 100  $\mu\text{m}$  thick on the outside of a garnet (assumed to be spherical) with a diameter of 3000  $\mu\text{m}$  has the same volume as a garnet with a diameter slightly greater than 1400  $\mu\text{m}$ . As the matrix of the rock coarsened, effective path differences for diffusion would have to increase (in part because of the concentration of components into fewer and larger grains) at the same time as concentration gradients decreased.

Atherton (1976) has concluded, from the absence of diffusion halos and other evidence, that the diffusion reservoirs around garnets in regionally metamorphosed rocks must be reasonably large and probably overlap. The radial symmetry of profiles out to the vicinity of the  $Z_2/Z_3$  boundary is consistent with this conclusion, and in many portions of the garnetiferous mica-schists, the uniform development of zone 3 suggests the same conditions were quickly re-

established after the initiation of reaction (a). Elsewhere, however, radial variations in symmetry and the non-uniform growth of zone 3 indicate that the diffusion volumes were localized. Some factors which singly or in combination may have contributed to this localization are: (1) a locally heterogeneous distribution of one of the reactants (*e.g.* epidote) in reaction (a); (2) a limited amount of one of the reactants (Ca-Al); (3) variations in mean path for intergranular diffusion; (4) the mean spacing between garnets.

Factors (2), (3), and (4) may have combined to produce the situation depicted in Figure 6, where two large garnets are located close together. Inter-crystalline deformation took place during the interval growth stopped and recommenced on the  $Z_2/Z_3$  boundary.

#### *Correlation of textural zones and chemical zoning in three-zone garnets*

The precise definition of the  $Z_1/Z_2$  boundary depends primarily on the presence of laminae of graphite. The change of color that takes place across the boundary is generally too subtle and continuous to provide an accurate indicator in the absence of laminae. The accumulation of graphite must have depended on the initial concentration and distribution of carbon in the volume in which the garnet nucleated and grew. The occasional appearance of garnets with two or four textural zones in the garnetiferous mica-schists presumably reflects local variations in the dispersion of graphite in the original sediment.

A simple correlation exists between the textural zones and the features of the Ca profile in particular: (1) the  $Z_1/Z_2$  boundary coincides, within less than 100  $\mu\text{m}$ , with the boundary segments (1) and (2) of the profile; (2) the  $Z_2/Z_3$  boundary coincides with the junction of segments (2) and (3) of the Ca profile.

Discrepancies in this simple pattern always occur in garnets in which one or more of the zones are distorted. One such garnet is QBG9b-3 (Fig. 8). Zone 1 falls entirely within segment 1 of the Ca profile. The discontinuity in the Mn and Fe profiles suggests that zone 1 is a fragment that was mechanically broken away from a larger garnet. After separation, growth recommenced in a reservoir partially depleted in Mn and almost devoid of graphite. This is accounted for if the fragment remained in the reservoir of the original larger garnet among other fragments carrying inclusions or marginal accumulations of graphite.

Growth of segment 1 continued to point D on the right-hand side (Fig. 8), where a break in slope in the Ca profile occurs. Zone 3 is clearly defined by textural

features on the right-hand side of the garnet; the matching of the Ca-edge and the inner boundary of  $Z_3$  is found at point *E*.

Segment 2 of the Ca profile is missing on the left-hand side of the garnet. It appears that growth was stopped at point *A* along a thin band of quartz inclusions (perpendicular to the indicated line of traverse). Moreover, growth probably ceased during the formation of segment 1 of the Ca profile, to begin again only after reaction (b) had displaced reaction (a). Similar examples, to be described in detail elsewhere, of the retardation or inhibition of growth by bands of quartz inclusions are common in three-zone garnets.

The history of growth of garnet QBG10a-4 (Fig. 7) is more difficult to interpret. On the lower and right-hand sides of the garnet, the uneven thickness of zones 2 and 3, combined with the asymmetry of the Mn and Fe profiles, indicates that growth was disturbed over much of the history of the garnet. The formation of high-Ca garnet in the absence of a  $Z_2/Z_3$  boundary is the culmination of this unusual pattern of growth. While the exact causes for the absence of the boundaries and the typical features of zone 3 are not apparent, the existence of the material bounded by the segment *AB* emphasizes the requirements for the coincidence of chemical and textural features: uniform growth in an uniform environment containing a regular distribution of particulate matter.

#### *Correlation of textural and chemical zoning between two- and three-zone garnets*

The zoning profiles of all elements within both types of garnet are similar in several ways: (1) The variations of all elements in zone 1 of the largest two-zone garnets generally compare with those variations observed in zones 1 and 2 in the three-zone garnets; (2) a Ca-edge marks the inner boundary of the outer zones; (3) with the exception of Ca, the variation of all elements in the outer zones are the same. Despite these similarities, it is not easy to match the growth histories of both types of garnet directly. Other chemical and textural characteristics cannot be compared; for example, the Ca profile in most two-zone garnets cannot be matched with the three-segment Ca profile in the three-zone garnets. Moreover, the platy structures used to define the outermost zones in three-zone garnets do not occur within the outer zones of two-zone garnets.

The chemical similarities outlined in (1)–(3) above may be elaborated upon. The point of correlation between two- and three-zone garnets is the Ca-edge.

It appears that zone 2 in two-zone garnets, with its high Ca–Mg and low Fe–Mn concentrations, can be identified with zone 3 in three-zone garnets. In three-zone garnets, there is a simple relationship between the size of the garnets and the shape of the profiles of Mn, Fe, Ca, and Mg in zone 1: larger garnets (3–5 mm) have cores that are almost chemically homogeneous, whereas smaller garnets (1.5–3 mm) are continuously zoned in Mn, Fe, and Mg, and Ca is homogeneous (Anderson and Olimpio, 1977). Furthermore, in larger garnets, there are regular antipathetic fluctuations (up to 1 percent) in the generally flat profiles of Ca and Fe. These properties of the Mn, Fe, and Ca profiles correspond quite closely with those found in zone 1 of a majority of two-zone garnets.

#### *Evolution of textural and chemical zoning in two-zone garnets*

The mineral assemblages of the semi-pelite and garnetiferous mica-schists are similar, although the modal proportions of minerals in each rock type are slightly different. Reactions (a) and (b) may still be invoked to explain the grossular content of two-zone garnets. Fine-grained graphitic dust and other particulate matter is much less abundant in the semi-pelite, and we believe this accounts for the poor delineation of textural zones, as well as the small amounts of graphitic inclusions and laminae, in the two-zone garnets.

We suggested that the flatter profiles of Fe and Mn and the fluctuations in Ca and Fe in the three-zone garnets at the garnet grade of metamorphism are the products of intra-crystalline diffusion (Anderson and Olimpio, 1977). The similarity of profiles indicated that intra-crystalline diffusion may also have been important in two-zone garnets. Alteration by intra-crystalline diffusion may explain why the Ca profile from the core to the Ca-edge in two-zone garnets is normally one flattened segment rather than a combination of two segments, as in the three-zone garnets. If it is assumed that nucleation of garnet began simultaneously in the garnetiferous mica-schists and in the semi-pelites, then homogenization would certainly have proceeded more efficiently in two-zone garnets, since the volume out to the Ca-edge is always much smaller ( $<0.27 \times 10^{-3} \text{ cm}^3$ ) than the corresponding volume in three-zone garnets ( $0.26\text{--}0.9 \times 10^{-3} \text{ cm}^3$ ). These differences are sufficiently large to diminish or negate the effect of any other factors (e.g. initial concentration gradients) that may have influenced the comparative rates of homogenization in the two sets of garnets.

The assumption of synchronous nucleation made above may not be reasonable if the growth rates in two- and three-zone garnets were nearly equal. The smallness of zone 1 in the former means that nucleation may have been delayed, possibly until the temperature rise associated with the development of segment (2) in three-zone garnets. According to Butler (1965), the semi-pelites and garnetiferous mica-schists were derived from sediments that differed chemically, mineralogically, and texturally, and thus may have followed different paths of recrystallization to their current states.

Chemical evidence in the two-zone garnets supports the idea that nucleation of garnet was initiated after garnets began growing in the mica-schists. Allowing for possible cut effects in the garnets from the semi-pelites, certain characteristics of the Ca concentration level in these garnets appear significant: core Ca concentration levels within the two-zone garnets decrease as the radius of zone 1 decreases. Concentration levels in garnets decrease from 7–8 percent CaO in the cores of garnets containing the largest internal zones to 5–6 percent CaO in those garnets having the smallest internal zones. Furthermore the 1–3 percent decrease in Ca corresponds with the amount of Ca decrease across segment 2 of the Ca profile in the three-zone garnets.

Delayed nucleation of two-zoned garnets is not incompatible with the concepts of intra-crystalline diffusion of Mn segregation–depletion. However, additional data are needed in order to determine the role of each process during garnet growth. At higher temperatures, intra-crystalline diffusion within volumes as small as zone 1 may have acted with increased efficiency to alter initial chemical zoning. Segregation–depletion of Mn at higher temperatures is also suggested by the flattened profiles in zone 1.

The innermost zones of two- and three-zone garnets have a minimum diameter, and this, combined with the presence of a Ca-edge in both types of garnet, confirms that nucleation in the semi-pelite ceased at some time during the growth of zone 2 in the mica-schist garnets. The small, almost homogeneous garnets described by McAteer (1976), having high Ca–Mg and low Fe–Mn contents, represents a new stage of nucleation and growth: a stage of higher temperatures which operated during the growth of the outermost zones in the two- and three-zone garnets.

### Summary

The development of broadly similar kinds of chemical zoning of Fe, Mn, Mg, and Ca in garnets from

samples of semi-pelite and garnetiferous mica-schists in western Scotland reflects uniform prograde regional metamorphic conditions during porphyroblast growth. The chemical and textural characteristics of the three-zone garnets from the mica-schists cannot be matched directly to those of two-zone garnets, due to differences in their growth history. These differences are related to: (1) low content of particulate matter in the semi-pelite which was collected along the garnet–matrix interface in quantities sufficient to eventually form only one zone boundary ( $Z_1/Z_2$ ); (2) the possibility that extensive homogenization by diffusion of the cores of semi-pelite garnets occurred, obscuring the early history of growth; (3) the postponement of garnet nucleation in the semi-pelite until sometime prior to the development of the  $Z_1/Z_2$  boundary in the mica-schist garnets. Three growth stages in garnets from the mica-schists are recognized. (1) Growth in steady metamorphic conditions of a spherical core of garnet with a uniform Ca content (zone 1). Growth rates, at least in the later part of this stage, were probably controlled by the rate at which particulate matter expelled by the garnet could migrate ahead of the interface. (2) Growth of a thin zone of progressively less calcic garnet which developed an idioblastic habit (zone 2). Growth during this stage proceeded in a period of rising temperatures. (3) Addition of a thin mantle of calcic garnet which, where uniformly developed, preserved the idioblastic outline (zone 3). Zone 3 in many garnets is incompletely developed, and this, coupled with a progressive loss of radial symmetry in the distribution of Fe, Mn, Mg, and Ca, suggests that very local factors influenced or dominated the growth rate. The most probable factors were: (1) the rates of intergranular diffusion in the matrix surrounding the garnet, and (2) the effective distance to local sources of components such as Ca and Al.

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