

## PROGRESSIVE HOMOGENIZATION OF METAMORPHIC GARNETS, SOUTH MORAR, SCOTLAND: EVIDENCE FOR VOLUME DIFFUSION

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### ABSTRACT

The distribution of Fe, Mn, Ca and Mg has been examined in a suite of optically and texturally zoned garnets from regionally metamorphosed rocks, South Morar, Inverness-shire, Scotland. At the garnet grade of metamorphism, smaller garnets (2-3 mm) are strongly zoned and have Mn-rich cores. Larger garnets from the same rocks (3-4.5 mm) have homogeneous cores with lower concentrations of Mn. With increasing grade across the kyanite and sillimanite zones, optical and textural zones gradually disappear, and garnets of all sizes become progressively more homogeneous. Volume diffusion, during or after growth, provides the simplest explanation for the occurrence of the homogeneous garnets in both situations.

### SOMMAIRE

Nous avons étudié la distribution du Fe, Mn, Ca et Mg dans une série de grenats optiquement et texturalement zonés tirés de roches de métamorphisme régional de South Morar, Inverness-shire, Ecosse. Au grade de métamorphisme du grenat, les grenats plus petits (2-3mm) sont fortement zonés et ont des centres riches en Mn; les grenats plus grossiers (3-4.5 mm) des mêmes roches sont homogènes et ont une concentration plus faible en Mn. Les grenats zonés optiquement et texturalement disparaissent graduellement et les grenats de toutes dimensions deviennent progressivement homogènes avec l'intensité métamorphique croissante en travers de la zone à kyanite et de la zone à sillimanite. La diffusion volumique, durant et après la croissance, nous semble être l'explication la plus simple de la présence de grenats homogènes dans ces deux cas.

(Traduit par la Rédaction)

### INTRODUCTION

Three processes may be assumed to act to varying degrees in the creation or modification of compositional zoning in metamorphic garnets: 1) selective segregation of elements during growth; 2) intergranular diffusion in the matrix enclosing the garnet; 3) volume diffusion within the garnet. All attempts to model the evolution of zoning in garnets have included state-

ments or assumptions concerning the nature and magnitude of these processes. The role of the first process has been examined in some detail in the segregation-depletion models of Hollister (1966), Atherton (1968) and Edmunds & Atherton (1971).

Intergranular diffusion acts to create domains of local equilibrium between nearby garnets and other phases, whereas volume diffusion acts to homogenize individual garnets. The treatments of intergranular and volume diffusion pose similar theoretical problems (Anderson 1976) and their roles are less understood than segregation.

Atherton (1968) and Woodsworth (this issue) have reported examples of increasing homogeneity of garnets at higher metamorphic grades; a further example is presented in this paper. The existence of such garnets may reflect either a change in the nature of segregation and depletion processes at higher grades, or greater effectiveness of volume diffusion at higher temperatures. Several important questions arise if homogenization of segregation zoning occurs. Is there a critical or narrow range of temperature above which volume diffusion begins to modify segregation zoning, or does volume diffusion act, albeit less efficiently, down through the lower grades of metamorphism with unsuspected results?

Evaluating the role of volume diffusion is a difficult task: intuitive notions concerning diffusion, obtained from experience with one- or two-component systems, may be misleading or wrong when applied to diffusion in multicomponent minerals such as garnet. This paper is concerned with a search for evidence of volume diffusion in a suite of garnets from the Moine rocks of the Morar region, Scotland (Fig. 1).

### GEOLOGIC SETTING

The Moine rocks are part of a thick sequence of regionally metamorphosed sediments that were deposited unconformably on older Lewisian gneisses. The Moine rocks in the Morar-Knoydart area have been subject to repeated folding

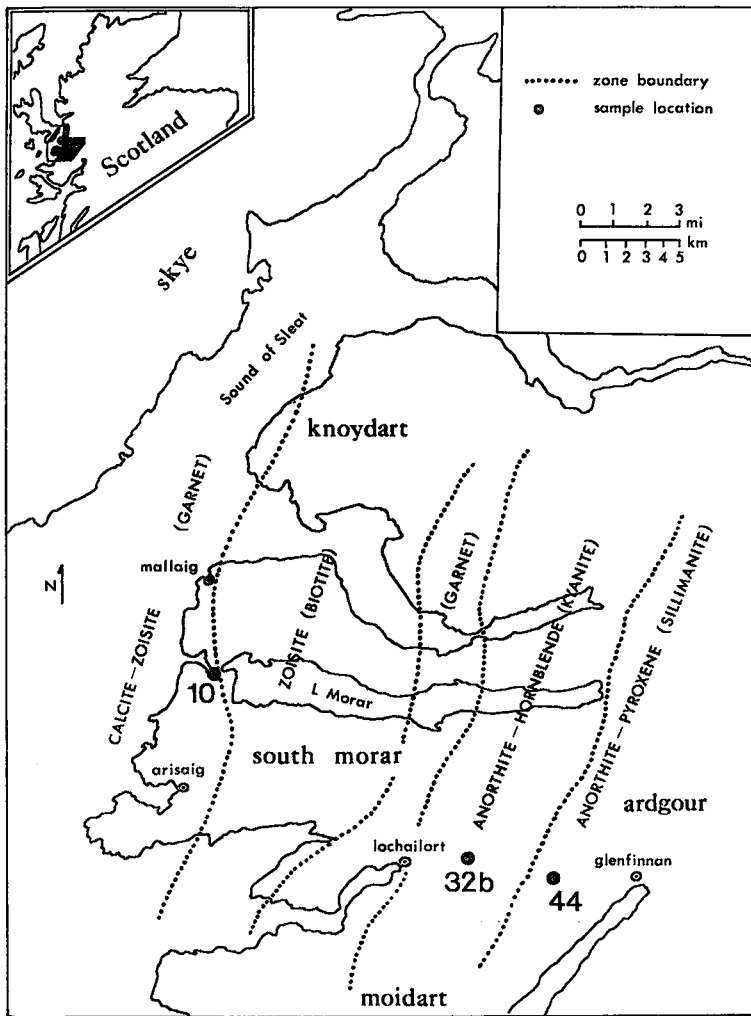


FIG. 1. South Morar, Scotland, showing metamorphic zones (after Kennedy 1949, and, in parentheses, Winchester 1974) and sample locations.

(Poole & Spring 1974; Powell 1974) and two episodes of metamorphism (Lambert 1958-9; Long & Lambert 1963; Powell 1974; Winchester 1974). Brook *et al.* (1976) have recently argued that the first two phases of folding and the first metamorphism ( $M_1$ ) were part of a late Precambrian event ( $\sim 1050$  m.y.), whereas the last two phases of folding and the second metamorphism ( $M_2$ ) were possibly Caledonian ( $\sim 450$  m.y.).

The distribution of metamorphic zones in the Morar-Knoydart region is shown in Figure 1. The work of Lambert (1958, 1958-9) established that the zone of biotite-grade rocks, flanked to the east and west by garnet-grade rocks, represents a region of retrogression in which idioblastic garnets have been pseudomorphed by

biotite-epidote assemblages. In general agreement with Lambert (1958-9) and Winchester (1974), Powell (1974) has proposed that "an early pre- to syntectonic ( $F_2$ ) metamorphism up to at least garnet grade, is represented in all the Moine rocks of the area under discussion, while a later metamorphism reached high grade in the east but only low grade in the west." Garnets in the western garnet zone adjacent to the Sound of Sleat thus grew during  $M_1$  and were only slightly retrogressed (chloritized) during  $M_2$  metamorphism. In contrast, in the biotite zone, garnets produced during the first metamorphism were completely replaced during the second metamorphism.

MacQueen & Powell (1976) have described

the internal fabrics of garnets from the 'Garnetiferous Group' of the Morar Pelite. The material presented here is part of a much broader study by one of the authors (J. C. O.) that aims to relate the zoning to the tectonic and metamorphic history of the region.

#### ANALYTICAL PROCEDURE

Analyses were made for Fe, Mn, Ca, Mg, Ti, Si, and Al (with an ARL-EMX electron microprobe set at 20 kV and a beam current of 0.6 microamps. Analytical procedures, standards, and correction procedures correspond with those described by Sweatman & Long (1969) and Reed (1975). A garnet of known composition was analyzed with each batch of unknowns to check the accuracy of the analyses. Spot checks confirmed the observation of Lambert (1958-9) that only traces of Na and K are present in the garnets. Ti, Si and Al are homogeneously distributed in all of the garnets. The whole-garnet analyses of Lambert (1958-9) show an average ferric oxide content of 1-3%. The totals of the microprobe analyses, with Fe calculated as FeO, are compatible with a low content of ferric iron throughout the garnet.

#### SOUTH MORAR — WESTERN REGION

The garnets from western Morar are the product of the first metamorphism ( $M_1$ ). Because of the presence of rotated inclusion fabrics in most garnets, Powell (1974) concluded that their growth was largely synchronous with the second deformation. Porphyroblastic, from 2-4.5 mm in diameter, the garnets are frequently idioblastic and exhibit only minor chloritization along broken edges and fractures.

In this section, we shall be concerned with a set of idioblastic garnets from a single hand specimen, QBG 10, from a small outcrop of the Garnetiferous unit of the Morar Pelite near the western end of Loch Morar. The features observed in this suite of garnets, however, appear to be typical of those observed in idioblastic garnets from elsewhere in the Morar Pelite and adjacent units in the western garnet zone.

The hand specimen is a quartz-biotite-garnet-plagioclase-muscovite schist that is moderately foliated with no evidence of compositional layering. The garnets almost invariably contain optical zones that are clearly visible in thin section and hand specimens. Three zones are usually present (Fig. 2). All three zones contain inclusions of quartz, magnetite, epidote and a fine dust that may be graphite. The boundary between Zones 1 and 2, although irregular in de-

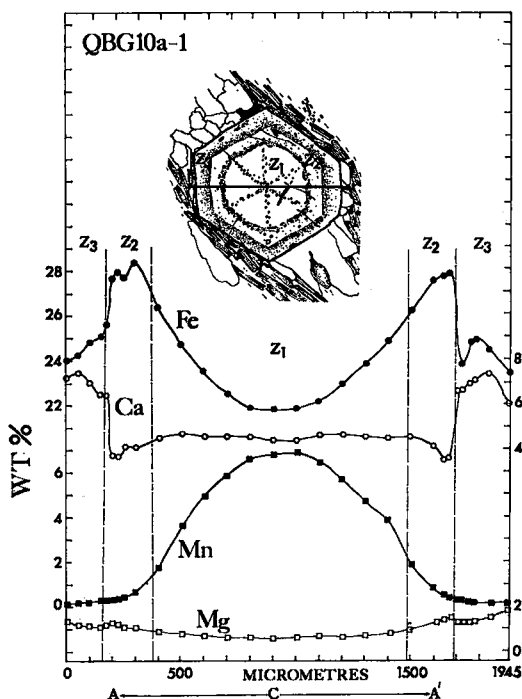


FIG. 2. Compositional profiles of Fe, Mn, Ca and Mg measured with an electron microprobe in an optically zoned garnet from the western garnet zone, South Morar (QBG10a-1). Data corrected for beam current drift, background, counter dead-time and matrix effects (absorption, secondary fluorescence, etc.).

tail, is commonly sub-circular in section. The density of inclusions is very high at the  $Z_1/Z_2$  boundary and decreases outwards across Zone 2. In garnets that are idioblastic, the  $Z_2/Z_3$  boundary is also idioblastic; in some broken garnets this boundary intersects the edge of the grain. Concentrations of dust diminish across Zone 3; inclusions of quartz and epidote are usually more abundant than in Zones 2 or 3. MacQueen & Powell (1977) have illustrated numerous garnets from this area that contain spiral or linear trails of tabular quartz and ilmenite inclusions; radial patterns of inclusions of the kind illustrated in Figure 2 are less common. The internal fabric defined by the inclusions commonly passes without interruption from Zone 1 to Zone 2 and, in a few garnets, into Zone 3. Generally, however, the fabric is either terminated at or bent sharply across the  $Z_2/Z_3$  boundary.

The nature of the compositional variation observed in a particular garnet depends on its diameter. An example of the patterns found in

smaller, idioblastic garnets is given in Figure 2. The concentration of Mn in Zones 1 and 2 is represented by a prominent, continuous dome of the kind predicted by segregation-depletion models. The distribution of Mn is counterbalanced by that of Fe and, to a minor extent, Mg. Ca is homogeneously distributed throughout Zone 1 and the inner part of Zone 2. This pattern of zoning is common to all of the smaller, idioblastic garnets; differences in internal fabrics are not reflected by any significant differences in the zoning.

There is an apparent discontinuity in the profiles of Fe and Ca in the vicinity of the  $Z_2/Z_3$  boundary. In view of the changes in the internal fabric at the  $Z_2/Z_3$  boundary, it is tempting to locate the discontinuity on the boundary. Detailed work, however, suggests that the discontinuity is not necessarily fixed at the  $Z_2/Z_3$  boundary and that, on a finer scale, the profiles in Ca and Fe are continuous with smooth – though very steep – gradients over 50 to 200  $\mu\text{m}$ . Similar changes in Ca (accompanied by changes in Mn rather than Fe) have been noted in the outer parts of garnets by Crawford (1966) and Linthout & Westra (1968), who argued that these changes were due either to reaction between garnet and plagioclase or to an increase of tem-

perature during the later stages of growth. The change in the behavior of Ca in the outer parts of the garnets from the western garnet zone also indicates an event that occurred late in the history of garnet growth. In this section we are only concerned with evolution of the chemical profiles in the region between the steep Fe-Ca gradient (i.e. the region ACA' of Fig. 2).

Larger garnets have cores that are nearly homogeneous with respect to Mn, Ca, Fe, and Mg. In the largest garnets of the suite, however, small, regular fluctuations may be detected in the otherwise homogeneous parts of the profiles. Thus Ca shows a distinct series of primary fluctuations that are symmetric as its concentration decreases to a minimum at the center (heavy line Fig. 3). Superimposed on the primary fluctuations of Ca are secondary maxima and minima that appear to be real (Fig. 3). These fluctuations are matched by similar small-scale fluctuations in Fe and Mg.

The progressive nature of the variation of the Mn profiles with diameter is illustrated in Figure 4: with increasing diameter the region of homogeneity increases and the concentration of Mn at the core decreases. It is important to emphasize that the data are from garnets that have been sectioned within 200  $\mu\text{m}$  of their cores and

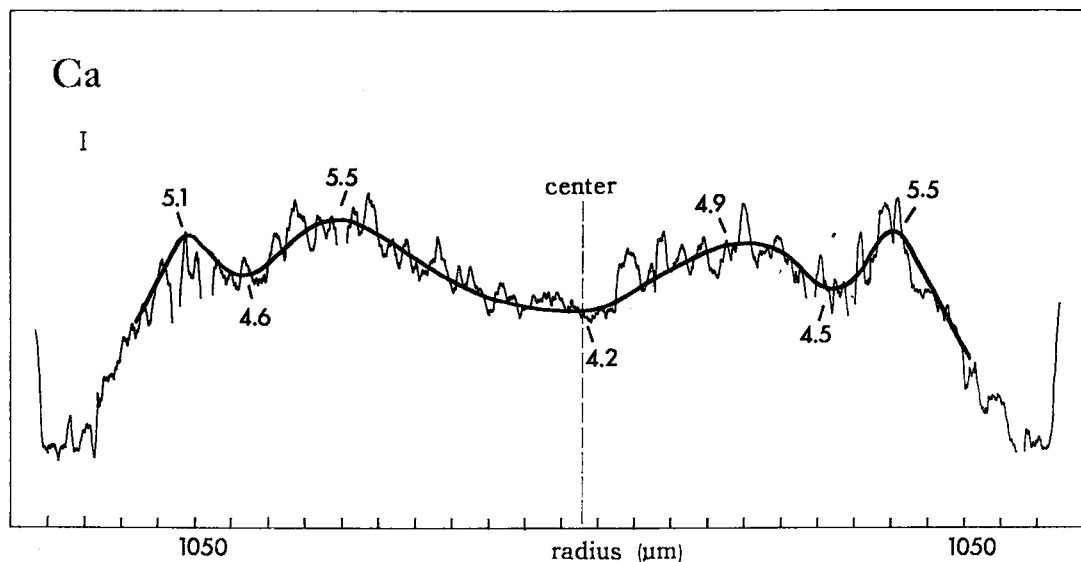


FIG. 3. Chart record (light line) of the intensity of  $\text{CaK}\alpha$  radiation versus distance in one of the largest garnets of sample QBGIO (garnet 4a of Fig. 4). Approximate values of the wt. % Ca, from spot analyses, are shown at a number of points on the heavy line representing the average trend. The bar at upper left gives the size of the maximum fluctuations of intensity obtained with a static probe on the garnet over an interval of five minutes. Many of the larger fluctuations in the chart record (light line) exceed the interval defined by the vertical bar and are systematically reproduced in duplicate traverses. The region covered by the traverse corresponds to the interval between the steep Fe/Ca gradient found in all garnets of the suite, for example ACA' in Figure 2.

thus flattened profiles are not due to a 'cut effect'. Atherton (1968, Fig. 6) reported a series of Mn profiles that bear some resemblance to those of Figure 4. There are, however, several important differences between the two sets of data. The garnets analyzed by Atherton were collected from a suite of rocks spanning the entire garnet zone. With increasing metamorphic grade, the Mn profiles have lower maxima and broader shapes, but there seems to be no simple relationship between the size of the garnets and these two features (e.g. samples 7 and 13, Fig. 6 of Atherton 1968). In contrast, all of the garnets included in Figure 4 are from a single hand specimen in which compositional differences and gradients in temperature, pressure, etc., are assumed to be negligible. We shall now consider the significance of this pattern in terms of growth and diffusion models for garnet zoning.

#### GROWTH MODELS

In order to examine the results expressed in Figure 4 in the light of segregation-depletion models, we shall assume — as other authors commonly have — that diffusion in the garnet is either very restricted or absent (Atherton 1968; Edmunds & Atherton 1971; Kretz 1973). The data of Figure 4 are not consistent with the predictions of Atherton's (1968) segregation-depletion models for nucleation and growth of the garnets during progressive metamorphism — a possibility that is suggested by the comparison of our results with those of Atherton (1968). Nucleation and growth rates increase with rising temperature (Kretz 1973, 1974; Anderson & Buckley 1974); consequently, the largest garnets found in the rock must have nucleated first and grown for the longest period of time. Increasing growth rates and temperature both lower values of the fractionation factor for Mn (Edmunds & Atherton 1971; Kretz 1973), favoring strong fractionation of Mn in garnets nucleated at lower temperatures and less fractionation in garnets formed later at higher temperatures. Thus we might expect the larger garnets to have high concentrations of Mn at the core of the garnet (Hsu 1968) and strongly curved profiles, whereas smaller garnets should exhibit lower, broader profiles. These predictions are the reverse of the relations shown in Figure 4.

The data are also incompatible with growth of the garnets during isothermal metamorphism. If there is no overlap in the reservoirs the garnets draw upon during growth, then all garnets, irrespective of size, should have the same concentration of Mn at the core and roughly the same shape-profiles. Any tendency for reservoirs

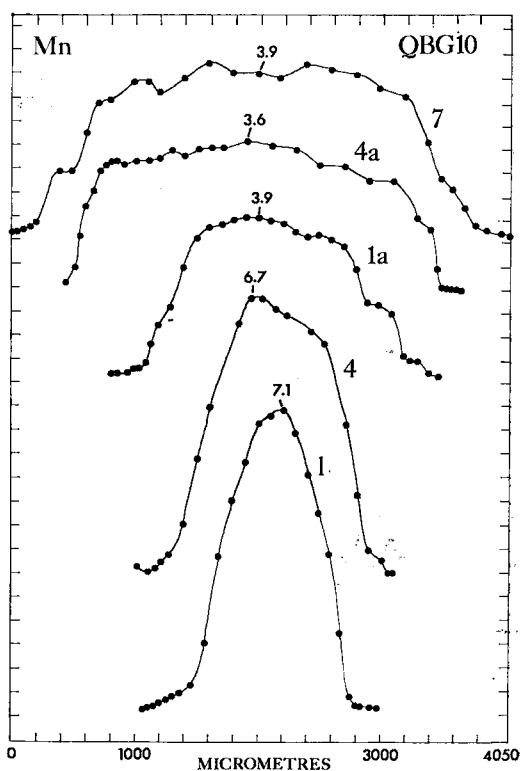


FIG. 4. Mn profiles from a set of garnets of increasing diameter from specimen QBG10. The concentration of Mn (element wt. %) at the center of each garnet is shown on the profiles. Units on the vertical scale are equal to 0.5% Mn.

to overlap would favor lower profiles in the later, smaller garnets. Again, these predictions are contrary to the results obtained in Figure 4.

Nucleation and growth of the garnets in a steadily decreasing temperature would produce profiles compatible with a segregation-depletion process. This model requires that nucleation be delayed until some temperature above the lower stability limit of the garnet is reached and, furthermore, that nucleation and growth proceeded as temperatures fell.

A superficial comparison with the work of Atherton (1968) indicates that considerable overstepping of the lower stability limit of garnet would be necessary. Nucleation of garnets in western Morar would have to have been initiated in conditions equivalent to those of the kyanite isograd in central Perthshire. There is no evidence that overstepping of this magnitude occurred, yet it is not clear if a comparison of this kind has any meaning; too many important factors are unknown, factors, for example, that may have influenced nucleation and the initial

value of the fractionation factor differently in the two regions.

Falling temperature is accompanied by decreasing nucleation and growth rates; in turn, declining growth rates and temperature work together to raise the fractionation factor. The expected profiles match those of Figure 4.

#### DIFFUSION MODELS

The possibility of volume diffusion under the moderate temperatures of the  $M_1$  garnet zone is suggested by a conclusion arrived at later in this paper: during the second metamorphism,  $M_1$  garnets were almost completely homogenized by diffusion at least down to a temperature corresponding to the kyanite isograd. In the following discussion it is assumed that: (a) a segregation-depletion process alone produced the gradients in Mn and Fe and, (b) that volume diffusion acted as garnets grew during progressive or isothermal metamorphism. The question we are concerned with is: could volume diffusion have acted to modify or remove these growth distributions during the later stages of the first metamorphism? The model is based on the supposition that the larger garnets, because of their longer exposure to metamorphic conditions, would be subject to the maximum degree of homogenization by diffusion. Smaller garnets, with a shorter exposure, should exhibit progressively less homogenization.

The relative lengths of time for which the largest and smallest garnets were annealed is an important element of the model. The radius of a garnet provides some measure of the time that it was subjected to metamorphic conditions. During progressive or isothermal metamorphism, the radius of a garnet depends on (a) its time of nucleation, and (b) the form of the growth law (radius as a function of time). If the growth law were linear, the radius of the garnet would have expanded by equal increments per unit of time. Kretz (1973) has deduced, however, that garnets in the Yellowknife region seem to have obeyed a non-linear growth law in which the area — and not the radius — was a linear function of time. In the case of a non-linear growth law of this or some other form (Kretz 1974), decreasing increments of radius would have been added per unit of time. Consequently, a garnet with a radius of 2 mm may have been annealed for (a) twice as long (linear law) or (b) significantly more than twice as long as a garnet of 1 mm radius. Non-linear growth laws would provide particularly favorable circumstances for the progressive homogenization of the larger garnets by diffusion.

From this point on we shall assume that metamorphism takes place in the presence of increasing temperature, but, with only minor modification, all of the arguments presented could be applied to isothermal metamorphism.

An increase in the mobilities (velocity per unit force) of Fe, Mn, Ca and Mg with rising temperature is not sufficient to ensure that a simple path to homogeneity will be the immediate consequence. As is quite evident from Figure 10 of Cooper (1974), Figure 1 of Darken (1951), or Figures 4 and 6 of Kirkaldy *et al.* (1965), the intermediate states produced may appear to be complex. In part, this complexity arises because the ions have different mobilities, but are constrained to move in a cooperative way to maintain electrical neutrality at each point in the crystal. In part, the complexity derives from the interdependence of the chemical gradients that drive diffusion. In the next section we shall briefly sketch the nature of diffusion in garnets with a special concern for the situations depicted in Figures 2, 3, and 4.

#### THE NATURE OF VOLUME DIFFUSION IN GARNETS

In systems or phases of three or more components, each component may diffuse on the gradients of the other components. This effect may enhance, diminish, or reverse the flux of a component on its own gradient (Cooper 1974). The flux of, say,  $\text{Fe}^{2+}$ ,  $J_{\text{Fe}}^0$ , measured with respect to a fixed  $(\text{Al}_2\text{Si}_2\text{O}_{12})^{6-}$  lattice, is for one-dimensional diffusion parallel to  $x$  (Anderson 1976, equation 24):

$$J_{\text{Fe}}^0 = -L_{\text{FeFe}}^0 \left( \frac{\partial \mu_{\text{Al}}}{\partial x} \right) - L_{\text{FeMn}}^0 \left( \frac{\partial \mu_{\text{SP}}}{\partial x} \right) - L_{\text{FeCa}}^0 \left( \frac{\partial \mu_{\text{GR}}}{\partial x} \right) - L_{\text{FeMg}}^0 \left( \frac{\partial \mu_{\text{PY}}}{\partial x} \right) \quad (1)$$

or, generally (for the four ions Fe, Mn, Ca, Mg)

$$J_{\text{Fe}}^0 = - \sum_{k=1}^4 L_{\text{Fe}k}^0 \left( \frac{\partial \mu_{kn}}{\partial x} \right), \quad (i = 1, 2, 3, 4) \quad (2)$$

The  $\mu$ 's in (1) are the chemical potentials of almandine (Al), spessartine (SP), grossular (GR) and pyrope (PY); the subscript  $kn$  in (2) denotes the garnet molecule formed by the combination of the  $k$ -th cation (Fe, Mn, Ca, Mg) with the  $n$ -th component — the anion  $(\text{Al}_2\text{Si}_2\text{O}_{12})^{6-}$ . The  $L_{\text{Fe}k}^0$  are thermodynamic diffusion coefficients, in a lattice-fixed reference frame, that connect the flux of the  $i$ -th ion to the gradient of the molecular component  $kn$ . The definition of the lattice-fixed reference frame (Anderson 1976) requires that (1) distances be measured as the number of unit-cell edges parallel to  $x$ , and (2) concentrations ( $c_{kn}$ ) and chemical potentials be defined in terms of the number of moles of  $kn$  per unit cell.

The diffusion fluxes may also be described by

$$J_i^{\circ} = - \sum_{k=1}^4 D^{\circ}_{ik} (\partial c_{kn} / \partial x), \quad (i = 1, 2, 3, 4) \quad (3)$$

(Onsager 1945), where the  $D^{\circ}_{ik}$  are practical diffusion coefficients in a lattice-fixed frame. Equations 2 and 3 are equally fundamental descriptions of diffusion and contain (through equation 4 below) the same information. Equations similar to (2) usually appear in theoretical and kinetic models because of their evident connection to thermodynamics. The  $D$ 's are coefficients that are commonly used in solving differential equations for concentration versus distance curves. The  $D^{\circ}_{ik}$  and  $L^{\circ}_{ik}$  are related by (Kirkwood *et al.* 1960, equation 26)

$$D^{\circ}_{ik} = \sum_{j=1}^4 L_{ij} \mu_{jk}, \quad (i, k = 1, 2, 3, 4) \quad (4)$$

The lattice-fixed and solvent-fixed reference frames are mathematically identical. Hence, the equations of Kirkwood *et al.* for the solvent-fixed frame may be introduced without modification. The elements of the matrix  $\mu_{jk}$  may be calculated from

$$\begin{aligned} \mu_{jk} &= \frac{\partial \mu_{jn} / \partial c_{kn}}{RT / c_{kn}} [3\delta_{jk} + (c_{kn} / c) \\ &\quad + 3c_{kn} (\partial \ln y_{jn} / \partial c_{kn})] \end{aligned} \quad (5)$$

[Equation 12, Miller (1967) with the conditions - which hold only for garnets - expressed in equations 19 and 20 of Anderson (1976)]. In (5),  $\delta_{jk}$  is the Kronecker delta,  $c$  is the total molarity, and  $y_{jn}$  is the activity coefficient of the  $j$ -th component on a molar concentration scale.

The diffusive flux of a component depends on the magnitude and signs of each of the  $L$  coefficients and each of the chemical potential gradients in (2). In general, the  $L$  coefficients (and the  $D$ 's) will be functions of temperature, load pressure, concentration of every component and, perhaps, oxygen fugacity and time. The on-diagonal coefficients (e.g.  $L^{\circ}_{FeFe}$ ,  $L^{\circ}_{MnMn}$ ) are always positive whereas the off-diagonal coefficients ( $L^{\circ}_{FeMn}$ ,  $L^{\circ}_{FeCa}$ ) may be either positive or negative (de Groot & Mazur 1962; Glandsdorff & Prigogine 1971).

The difficulties of directly measuring the  $D$  coefficients, or solving differential equations involving diffusion coefficients, are proportional to the number of diffusing components in the system. Anderson (1976) has outlined the extreme difficulty, if not the impossibility, of determining the matrix of independent diffusion coefficients in a quaternary system. Ternary and binary systems present progressively less

experimental and computational problems. Recently, procedures for estimating the  $L$  or  $D$  coefficients from simpler quantities have received considerable attention (Kirkaldy 1959; Lane & Kirkaldy 1964; Wendt 1965; Miller 1967; Cooper 1974). If the diffusion coefficients are independent of concentration, the flux equations (3) may be uncoupled with a concomitant gain in simplicity (Gupta & Cooper 1971; Cooper 1974); unfortunately, there is only a slight chance that the  $D$ 's are concentration-independent over the range of gradients found in many garnets (Fig. 2).

As yet, there are no experimental data from which the  $L$  coefficients for garnets might be calculated or estimated. However, experience with the quasi-kinetic model of Lane & Kirkaldy (1964), which provides a means of estimating the  $L$  coefficients from tracer diffusion coefficients, allows some general observations to be made. Relatively large off-diagonal coefficients may be expected if the ions migrating have different valences or significantly different mobilities.

Despite the lack of data concerning the  $L$ 's, there seems to be a strong possibility of proving that garnets may behave as pseudo-binary systems in some common situations. The discussion below of the evidence supporting pseudo-binary behavior is carried through in some detail, in order to stress that this behavior follows primarily from a peculiar configuration of chemical gradients, and not from the sign or magnitude of the  $L$  coefficients. Whether garnets will exhibit pseudo-binary behavior in other situations can only be determined by methods similar to those used here, or by measurement of the  $L$  coefficients.

The region ACA' in Figure 2 is in many ways typical of the pattern of zoning found in garnets from pelitic schists of moderate metamorphic grade. This pattern may be taken as an example of a growth pattern on which diffusion may begin to act (at time  $t=0$ ) as the temperature rises. The possibility that diffusion and growth are synchronous will be discussed later. In the region ACA', the Fe and Mn profiles are mirror images; Ca is nearly homogeneous, decreasing slightly at A and A'. The distribution of Mg may be assumed, for the moment, to be homogeneous without any undue loss of accuracy. This pattern of gradients does not mean that the region ACA' can be automatically treated as a pseudo-binary system. The redistribution of a dilute, initially homogeneous component by diffusion is clearly illustrated in experiments conducted by Darken (1951) and Kirkaldy *et al.* (1963).

To define a lattice-fixed reference frame, the

wt. % scale in Figure (2) must be replaced with a molarity scale ( $C_{kn}$ ) and distances replotted as number of unit-cell edges. The following conditions are then valid: the molar concentration gradients of almandine and spessartine are approximately equal and of opposite sign at each point, or

$$\partial c_{AL}/\partial x \cong -\partial c_{SP}/\partial x \quad (6)$$

and

$$\partial c_{GR}/\partial x \cong 0, \quad (7)$$

and

$$\partial c_{PY}/\partial x \cong 0. \quad (8)$$

In a system of four components, chemical potential and concentration gradients are connected by (Kirkwood *et al.* 1960, equation 23),

$$\partial \mu_{jn}/\partial x = \sum \mu_{jk} (\partial c_{kn}/\partial x), \quad (j = 1,2,3,4) \quad (9)$$

where the matrix  $\mu_{jk}$  is defined by (5). With the assumption that garnet behaves as an ideal solid solution ( $\ln y_{jn} = 0$ ,  $J = 1,2,3,4$ ), expansion of (9), subject to the conditions (6), (7), and (8), may be used to prove (at  $t=0$ )

$$\partial \mu_{GR}/\partial x \cong \partial \mu_{PY}/\partial x \cong 0 \quad (10)$$

and

$$\partial \mu_{SP}/\partial x \cong -(\partial \mu_{AL}/\partial x) (c_{AL}/c_{SP}) \quad (11)$$

The flux equation for Fe at  $t=0$  is from (2), with (10) and (11),

$$J_{Fe}^0 = - [L_{FeFe}^0 - (c_{AL}/c_{SP}) L_{FeMn}^0] \partial \mu_{AL}/\partial x \quad (12)$$

The corresponding equation for Mn is

$$J_{Mn}^0 = - [L_{MnMn}^0 - (c_{SP}/c_{AL}) L_{MnFe}^0] \partial \mu_{SP}/\partial x \quad (13)$$

At the beginning of diffusion, the ratio  $c_{SP}/c_{AL}$  ranges from 0.024 at A (or A') to 0.26 at C; the inverse ratio is 40.8 at A and 3.8 at C. Hence, the term including  $L_{MnFe}^0$  in (13) will generally be very small, even if the coefficient is relatively large; in contrast, the term involving  $L_{FeMn}^0$  in (12) may be significant. Note that the Onsager Reciprocal Relations are satisfied in the lattice-fixed reference frame so that  $L_{FeMn}^0$  is equal to  $L_{MnFe}^0$  (Anderson 1976).

The diffusion of Ca is not precluded by the absence of a chemical potential gradient in grossular; the flux of Ca at  $t=0$  is given by

$$J_{Ca}^0 = - [L_{CaFe}^0 (\partial \mu_{AL}/\partial x) - L_{CaMn}^0] (\partial \mu_{SP}/\partial x) \quad (14)$$

Because of (11), the signs as well as the magnitudes of the  $L$  coefficients are especially important in determining the size of the initial flux of Ca.

Suppose, for the sake of discussion, that Fe is

more mobile than Mn, Ca, or Mg. If the relations in (10) and (11) were exact equalities, the region ACA' would behave as a pseudo-binary system. The flux of Fe is compensated solely by a reverse flux of Mn and its rate of diffusion is partly governed by the mobility of Mn. The compromise rate is expressed formally by the appearance of two  $L$  coefficients in (12). Equations 10 and 11 are not, however, equalities, when concentration and distance units are based on the unit cell, there are small concentration gradients in both grossular and pyrope. The flux of Fe may be compensated by a reverse flux of some combinations of Mn, Ca, or Mg. Equation 12 will then have to be replaced by (1) which contains terms for the coupling of the flux of Fe to the chemical potential gradients of grossular and pyrope.

Because of the complexity of the relationships between chemical potential and concentration gradients expressed in (9), and the coupling of fluxes in (1), diffusion in multi-component systems may produce strange configurations or concentration-distance plots. Waves or damped waved (or parts of thereof) are commonly generated in the solution of the diffusion equations for concentration versus distance in ternary systems (e.g. Sundelof & Sodervi 1963) and have been found in experimental diffusion couples by Kirkaldy *et al.* (1965) and Varshneya & Cooper (1972).

Figures 2 and 3 may be interpreted in terms of a diffusion model in the following way. If Fe and Mn are more mobile than Ca and Mg, pseudo-binary behavior should persist for a considerable time — especially if the coefficients that link the diffusion of Ca and Mg to the gradients and almandine and spessartine (e.g.  $L_{CaFe}^0$  and  $L_{CaMn}^0$ ) are of the same sign. In these circumstances, the models of Anderson & Buckley (1973, 1974) may be used to investigate changes in the profiles of Fe and Mn. Bell-shaped curves, similar to those predicted by segregation-depletion models, appear as transient solutions in the earlier stages of their models. Calculation suggests that subsequent diffusion should lower the height of the growth curve by substantial amounts without changing the shape of the curve by very much (Anderson & Buckley 1973, their Fig. 10). Calculations in their model (C) are performed in spherical coordinate and accurately reflect volume relations in the garnet (which is assumed to be spherical). For a fixed concentration of Mn (moles/unit volume), the total amount of Mn (e.g. total number of moles) contained in a hollow shell of unit thickness near the center of the garnet is much less than the amount contained in a hollow shell of



equal thickness near the rim. On a concentration versus distance plot, which severely distorts volume relations, a transfer of what appears to be a large amount of material from the center produces only small changes in the shape of the profile away from the center. Consequently, although the general shape of the profile is not altered much by diffusion over a considerable interval of time, the height of the profile is significantly diminished. Unless it can be unequivocally demonstrated that diffusion is restricted, any attempt to calculate parameters that depend on the height of the profile (e.g. fractionation factors at the time of nucleation) may be subject to serious errors. A mutual diffusion coefficient of  $10^{-15}$  to  $10^{-16}$   $\text{cm}^2/\text{sec}$  would permit homogenization of a garnet of 2 mm diameter in slightly less than one million years (Anderson & Buckley 1973).

The appearance of primary fluctuations (Fig. 3) may mark the onset of ternary diffusion in the late stages of homogenization. Substantial coupling of the fluxes of Fe and Mn to those of Ca and Mg is more likely as the chemical potential gradients of almandine and spessartine lessen and those of grossular and pyrope become relatively more important. As noted previously, the emergence of fluctuations similar to the primary ones in Figure 3 is a common feature in ternary diffusion and may signify that the flux of Fe is increasingly compensated for by a flux of Ca. It is possible that the secondary fluctuation may also be the result of coupled diffusion.

The combined growth-diffusion model of Anderson & Buckley (1974) above would not be

changed much by simultaneous growth and volume diffusion. The general shape of the Fe and Mn profiles is dictated by partitioning conditions at the moving interface of the garnet; the tendency to create the profiles would not be negated by volume diffusion. The forms of the growth, diffusion, partitioning, and temperature versus time curves are all important in determining the extent to which homogenization proceeds (Anderson & Buckley 1974, Fig. 1).

#### SOUTH MORAR — EASTERN REGION

Compositional profiles flatten and eventually disappear in garnets of all sizes with increasing metamorphic grade to the east of Lochailort (Fig. 1). Even the minor variations of Fe and Ca in garnets from the kyanite zone (Fig. 5) are absent from garnets from the sillimanite zone (Fig. 6). The chemical changes are accompanied by the gradual disappearance of optical zones, internal fabrics, and inclusions.

Powell (1974) and MacQueen (1977) have concluded that garnet began to grow during  $M_1$  before or during the second deformation. The partial preservation of optical zones and internal fabrics leaves little doubt that the garnets observed in the kyanite zone ( $M_2$ ) are metamorphosed  $M_1$  garnets.

The grades of  $M_1$  and  $M_2$  both increased eastward. Consequently, it is difficult to resolve to what extent the chemical changes observed in garnets from eastern Morar should be attributed to the increasing grade of  $M_1$ . Changes in the patterns of zoning and internal fabrics seem to

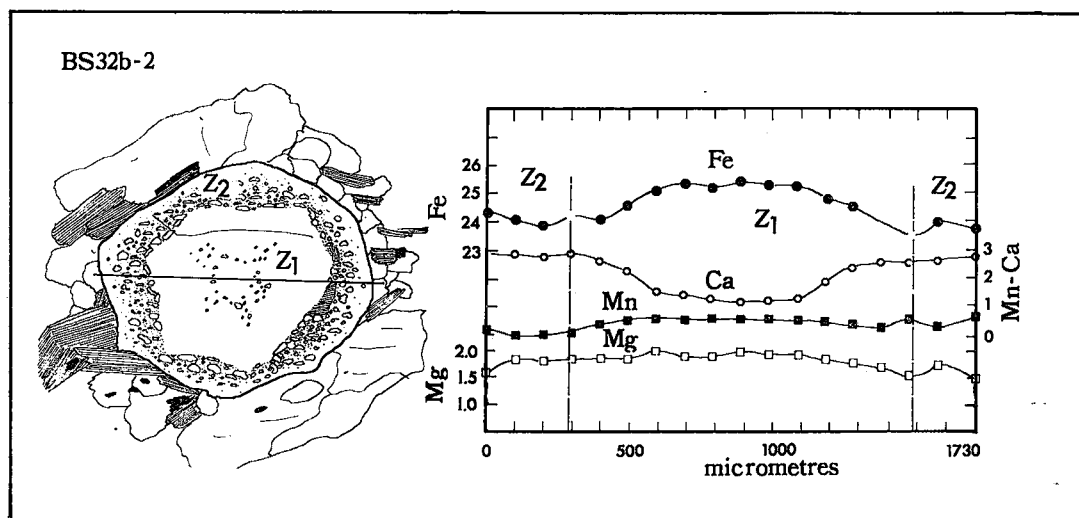


FIG. 5. Compositional profiles of Fe, Mn, Ca and Mg in an optically zoned garnet from the kyanite zone east of Lochailort.

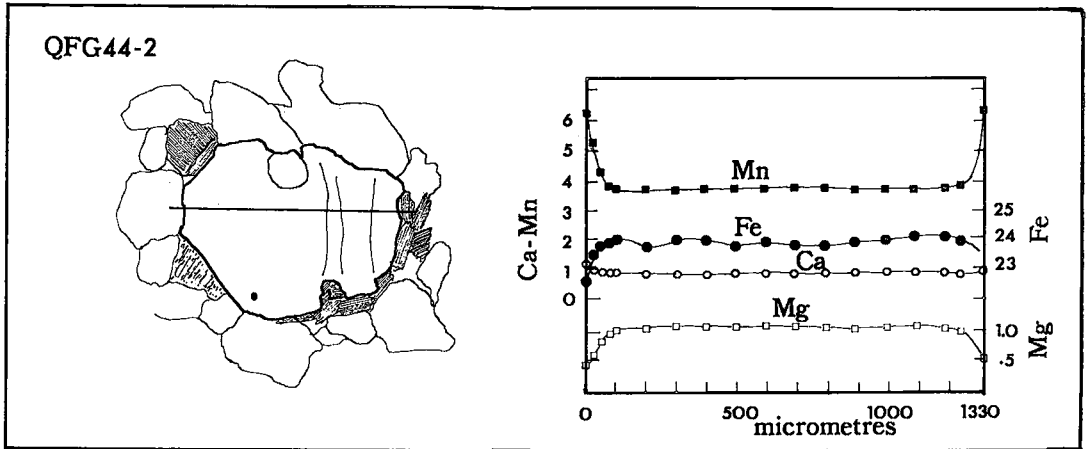


FIG. 6. Compositional profiles of an inclusion-free garnet from the sillimanite zone west of Glenfinnan.

correlate with the disposition of the  $M_2$  zones, but this may reflect an approximate coincidence of the  $M_1$  and  $M_2$  kyanite isograds. What is clear, however, is that volume diffusion has been effective in homogenizing garnets down to the kyanite isograd.

In the outer parts of these high-grade garnets, steep changes in the Fe and Ca profiles do not occur near the  $Z_2/Z_3$  boundary, but are replaced by smaller fluctuations near the rim. If volume diffusion was responsible for removing the steep gradients, then large amounts of material must have migrated across the whole of the garnet.

### CONCLUSIONS

Nearly homogeneous garnets are found in two different situations in the regionally metamorphosed pelites of the South Morar region, Scotland: 1) in the western garnet zone there is a continuous gradation between smaller (2-3 mm), strongly zoned garnets and larger (3-4.5 mm), almost homogeneous garnets; 2) garnets of all sizes exhibit minor departures from homogeneity only at their margins in the kyanite and sillimanite zones. Volume diffusion during or after growth provides the simplest explanation for the occurrence of the homogeneous garnets in both cases.

Strong chemical gradients present in the garnets — established by segregation-depletion processes during growth — created favorable conditions for volume diffusion which led to (a) the progressive homogenization of the interior of the largest (first-nucleated) garnets in the western garnet zone, and (b) uniform homogeniza-

tion of garnets of all sizes within the kyanite and sillimanite zones. An examination of the growth pattern of Mn, Fe, Ca, and Mg zoning suggests that the garnets may have behaved initially as a pseudo-binary system for diffusion; quaternary behavior may have appeared only in the waning stages of homogenization. This conclusion derives from the special configuration of chemical-potential gradients initially present in the Morar garnets, and not from any knowledge of the Onsager  $L$  coefficients in the diffusion equations. The simplification from a quaternary to a pseudo-binary system significantly reduces the experimental and computational problems of analyzing diffusion.

The data collected here do not allow any conclusions to be drawn about the relative magnitudes of the on- and off-diagonal  $L$  coefficients. Thus, there is no reason to believe that binary diffusion will be the rule in garnets; its occurrence in particular situations, however, may be dictated by the nature of the chemical-potential gradients built in by growth processes.

Because of volume relations and the possibility of pseudo-binary diffusion, the preservation of bell-shaped curves in Mn is not sufficient evidence, by itself, to conclude that diffusion was restricted in a particular set of garnets. Binary diffusion would lower the height of the Mn profile without appreciably changing the overall shape of the curve over long periods of time. Conclusions that depend on the height of the profile — for example, the initial value of the fractionation factor for Mn — may be wrong unless it can be shown experimentally that diffusion was indeed restricted in the appropriate metamorphic conditions.

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