

Reaction of Zoning of Garnet

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Abstract. Compositional zoning of garnet in metamorphic or igneous rocks preserves evidence of the equilibration history of the sample and can be interpreted in terms of a growth-fractionation, diffusion-exchange, or diffusion-reaction model. Diffusion zoning is usually assumed to result from exchange reactions between garnet and other phases as the partitioning coefficient varies in response to changing environmental conditions, primarily temperature. However, in many natural environments where garnet grew originally in divariant equilibrium with other phases, changing conditions can promote continuous or “divariant” reactions and consequent compositional shifts of phases that can be much greater in some systems showing these reactions than those related to the small changes of partitioning. Diffusional zoning related to overstepping of these continuous reactions must be related to incongruent reaction and necessitates formulation of a kinetic diffusion-reaction model involving moving phase boundaries as well as solid-state diffusion.

Three samples containing zoned garnets from the metamorphic aureole around the Ronda ultramafic intrusion in southern Spain are used to illustrate two possible models of diffusion-reaction processes. The examples are particularly informative because the reactions are demonstrably irreversible and evidence of the reaction system is preserved. Partitioning data indicates that compositions of product phases are not in equilibrium with the original garnet and do not vary with extent of reaction; therefore, exchange reactions with garnet were not possible and garnet changed composition only by incongruent reaction. After a small amount of reaction, Mg/Fe of the rim composition approaches a value apparently in equilibrium with product phases, but the garnets are zoned inward to the original garnet composition preserved in the interior. Grossularite content is approximately constant and spessartite content variable but small, thus, the rim composition of pyrope or almandine is assumed to be fixed by the external reaction process and is taken as a boundary condition in the following models.

The zoning profile of pyrope or almandine component between the fixed rim and core compositions (assumed to extend to ∞) is described in semi-infinite, half-space models appropriate for large garnets with narrow rims. The first model corresponds to a reaction system in which all garnet com-

positions are metastable (case 1) and zoning depends on the independent variables of the diffusion constant, velocity of the interface between garnet and matrix, and time. The second model, corresponding to systems in which the initial garnet composition is metastable but an equilibrium composition is stable (case 2), depends on the independent variables diffusion constant, time, and a function of reaction compositions. In case 1 the consumption velocity is assumed constant and a steady state zoning profile is reached at large time, whereas, in case 2, the velocity decreases with the concentration gradient and steady state is not possible.

The models were tested using a reaction time estimated from cooling models of the aureole, mass of garnet consumed, determined petrographically, and phase compositions. The two cases are somewhat independent in that different parameters are independent variables. The estimate of the diffusion constant of $10^{-18 \pm 2}$ cm²/sec (assumed to be a mutual or binary coefficient for almandine and pyrope) is considered reasonable for the temperature range of reaction (probably 600–900° C), and the two models are consistent considering the probable error and possible real temperature differences.

It is obvious that details of the metamorphic reaction system must be known to successfully apply diffusion models. Kinetic models, involving consumption or growth of the phase as well as diffusion are probably necessary when dealing with natural rocks. Several possible and interesting complications, such as cross coupling between components, can be investigated if more data were available. Experimental determination of diffusion constants allow natural reaction rates to be estimated by this method. Diffusion zoning is an important consideration that could increase the efficiency of experimentation with chemically recalcitrant phases.

Introduction

Garnet is an outstanding example of a common rock-forming mineral that is often not in equilibrium with other phases as a result of compositional zoning. Definition of equilibrium compositions and modeling of reaction processes are uncertain if zoned garnet is present unless the equilibration behavior of garnet is understood. Diffusion zoning models, presented previously for garnet in meta-pelitic rocks, have assumed simple exchange of components between garnet and the coexisting matrix minerals without molar change by reaction. Many natural examples of zoning, however, may be related to reaction and necessitate the formulation of a kinetic diffusion model involving moving phase boundaries. The natural examples considered here are ideal for this purpose because the original and final equilibrium composition of garnet can be measured and the irreversible reactions taking place can be defined. The purpose of this paper is to present analytical models to describe the formation of diffusional zoning in garnet during reaction in these defined systems.

Minerals that are slow to change composition, as state variables or the bulk composition of the system change, have been called "refractory" by Hollister (1969) and include the phases commonly zoned or characterized by relict persistence in

metamorphic rocks: e.g. plagioclase, staurolite, kyanite, ilmenite, hercynite and garnet. Metastable persistence depends, of course, on diffusion and reaction rates which are dependent in turn upon temperature, composition and abundance of fluids, deformation, etc., and metastable persistence is not expected to be always the rule. Indeed, garnet alters readily to chlorite at low temperatures in hydrous environments. Nevertheless, the common occurrence of garnet in rocks and its wide compositional range and conspicuous zoning make it potentially one of the most useful—or troublesome depending on your point of view—phases for deciphering metamorphic evolution.

It is relevant at this point to consider some previously suggested models of the origin of zoning in garnet and the wealth of information concerning the equilibration *history* of a sample that may be preserved and interpreted. Harte and Henley (1966) suggested and Hollister (1966) detailed a fractionation-depletion model that explains the bell-shaped Mn distribution profiles of common moderate-grade garnets and has been successfully applied by several authors. Chemical isolation of each layer of garnet formed is implicit in the model; the composition of each layer, then, preserves a record of the chemical environment during its formation. A similar argument can be applied for any element; Leake, for example, related the Ca content of garnet crystallizing from adamellite to the activity of Ca in the melt and the crystallization sequence. In addition to preserving a record of the individual chemical activity of an element in the matrix or melt, correspondence of variations can suggest reactions of specific minerals that took place. For instance, Evans and Guidotti (1966) and Hollister (1969) proposed that the increase of Ti as well as Mn toward the rim of some garnets was the result of breakdown of ilmenite, a phase not previously equilibrating with the matrix.

A more general application of zoning to history results from the fact that the composition of garnet crystallizing in a divariant “limiting” assemblage will be only a function of the intensive variables. If sufficient assumptions regarding significant components and the assemblages are made, a record of changing physical and fluid conditions can be interpreted from zoning. Phases or phase compositions indicative of early assemblages and conditions can be preserved inside non-reactive garnets (Evans and Guidotti, 1966; Hess, 1971; Loomis, 1972b). Moreover, such inclusions can be used as geobarometers and the unrecrystallized garnets as indicators of structural motions (Rosenfeld, 1968; Rosenfeld and Chase, 1961). Richardson (1974) is attempting to use zoning related to exchange reactions as a measure of cooling thermal history.

These very useful interpretations of zoning have been based on the assumption that garnet zoning records conditions during growth without any later chemical interaction among growth layers and the matrix. Several writers, however, have interpreted garnet zoning to be a result of diffusion as a crystal reequilibrates with the matrix during changing conditions following original growth. Chinner (1962, p. 330–331) found evidence of marginal zoning in high-grade contact pelites that he ascribed to reaction of the garnet; he states that reaction resulted in “manganese rich, iron-poor rims, up to 10 μm in thickness, that migrated inward as the garnets dwindled ...” The reaction and interpretation are similar in one example described here. Evans and Guidotti (1966), de Béthune *et al.* (1968), Hess (1971), Grant and Weiblen (1971), and Mueller and Schneider (1971) have suggested simple exchange

or diffusion and resorption to explain zoned rims rich in Mn and with varying Mg/Fe. The zoning described by Grant and Weiblen and interpreted to be the result of retrograde metamorphism extends some 400 μm into garnet; diffusion would have been driven by low concentration gradients. Hensen (1971) produced strongly zoned garnet (and cordierite) in an experiment at 1000° C for 305 hrs.

Thus evidence to support both the primary growth model and diffusion model have been published. The importance of diffusion to zoning of garnet under natural conditions is not easily proven by the previous data because the reactions that occurred, or even whether garnet was a reactant or product, is not proven unequivocally. Estimates of temperature, and especially duration of metamorphism, are subject to large uncertainties. The analysis in this paper will attempt to describe the effect of diffusion in garnet in natural rocks in which the reactions occurring are, at least in part, defined.

Anderson and Buckley (1971) applied diffusion models to explain the zoning patterns found in garnet, including the common bell-shaped Mn curves found in low and moderate grade garnets. The theoretical models illustrate the effects of dependence of diffusion coefficients on concentration and effects of limiting diffusion in an initially inhomogeneous matrix around garnet. The assumption of constant surface concentration appears to be justified in the examples of irreversible reaction considered here, but constant volume assumptions are obviously not realistic for reacting phases. Albarede and Bottinga (1972) presented several crystallization models to demonstrate the importance of crystal-liquid interface movement (growth) to the measurement of the trace element partitioning.

Reaction Systems

Garnet grown in equilibrium with other phases will have a fixed composition and molar abundance. If the intensive variables (T, P, μ mobile) change, phase compositions may change by either (or both) exchange reactions or reactions resulting in molar change depending on the reaction system. Pure exchange reactions occur if partition coefficients vary but the number of formula units (molar abundance) of all phases remains fixed. Exchange models of reaction are adequate to describe compositional changes in assemblages, such as those with a variance greater than two, in which phase compositions depend upon the fixed bulk composition of inert components as well as the changing intensive variables; the molar abundance of phases will usually be constrained by mass balance of inert components (barring compositional degeneracy). The exchange model may also be applicable to metastable systems in which failure of nucleation or kinetic factors inhibit potential molar change reactions. Pure exchange can be induced in the laboratory by juxtaposing phases not grown originally in equilibrium.

Changing conditions in common divariant systems can result in compositional shifts by continuous molar change reactions as well as exchange reactions because phase *compositions* are not dependent on the bulk composition but only on the intensive variables. Mass balance constraints do require that the molar abundance of garnet varying composition by continuous reaction must change unless compositional degeneracy of the system exists: the only coexisting phases containing

the varying components in garnet have exactly the same content of all other limiting components (excluding excess and perfectly mobile components). Therefore, the changing molar abundance of garnet during reaction and diffusion must be considered in analytical models, mass balance allows the functional dependence of composition and molar abundance change to be formulated for this system. Overstepping of exchange or continuous molar change reactions results in an irreversible reaction system and may produce zoned phases.

The relative importance of exchange and molar change reactions must be evaluated in each case. For many originally divariant assemblages, a change of state variables sufficient to change partition coefficients will probably also energize molar change reactions. Petrographic evidence may be necessary to define the role of molar change reactions. In the examples discussed here, textural evidence clearly indicates substantial volume change of phases, and the fact that the compositions of product phases do not vary with extent of reaction requires that exchange reactions between reactant garnet and product phases were not effective in a closed system. Zoning of garnet was created by incongruent, irreversible molar change reactions and subsequent reference to "reactions" implies this process.

Garnets considered here are in rocks of pelitic and basic compositions from the inner metamorphic aureole of the Ronda peridotite intrusion, southern Spain (Loomis, 1972a and b). The estimated temperature during reaction was probably in the range 600–900° C, but other conditions changed rapidly during high-grade metamorphism. From analysis of specific reactions, structural development of the aureole, and geophysical models of emplacement, the probable change of variable leading to the reactions was a rapid decrease of total pressure as a result of upward drag of the inner aureole along the margin of the penetrating peridotite intrusion. Regardless of the cause, the only necessary assumption for the arguments of this paper is that the intensive variables change markedly following garnet growth.

Continuous and, in some cases, discontinuous reactions involving previously formed garnet were strongly overstepped by the rapid change of state variables; the phase compositions produced by reaction are not in equilibrium with the reactants as determined from partitioning of Mg and Fe and, thus, the reactions were irreversible. The large difference between the original and final equilibrium composition of garnet resulted in zoning easily measurable by microprobe analysis. Compositional changes of phases with respect to Mg and Fe are much greater than the analytical error. Two types of reaction system can be distinguished.

Reaction System – Case 1

The first type of reaction to be considered may involve the overstepping of discontinuous as well as continuous reactions. The first example is shown in Fig. 1 and will be considered in some detail because the reaction processes are similar in the other examples. The original assemblage was (dashed lines) quartz-K-feldspar – biotite – garnet – sillimante (and kyanite), plagioclase, ilmenite, apatite, pyrrhotite, graphite, and tourmaline. A melt phase may have been present but its composition and distribution are unknown; the reaction of interest can be represented successfully by considering only solid phases. The original assemblage

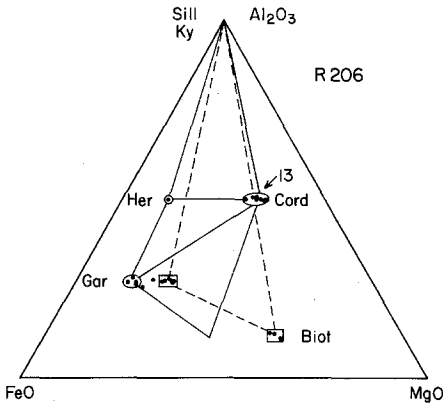
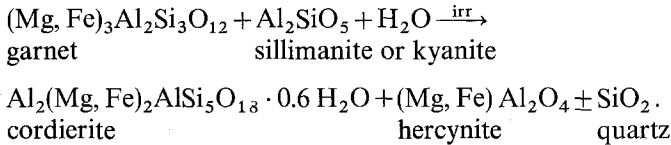


Fig. 1. R-206. Projection from excess phase-components quartz, K-feldspar, and plagioclase. Rectangles: initial assemblage compositions (garnet cores and isolated biotite). Circles: equilibrium compositions of product phases and garnet rims

was unstable with respect to the equilibrium topology shown with solid lines. The reaction (unbalanced) of original garnet was:



The set of phases forming (called “products”) and the set of phases being irreversibly consumed (distinguished as “reactants”), i.e. reactants and products, are not in equilibrium with each other. Continuous reaction leading to divariant compositional shifts, as well as the univariant discontinuous reactions, must have been overstepped to produce the irreversible reaction.

Data for a single thin section are plotted in Fig. 1. Analysis of the irreversible reaction process and behavior of biotite in this sample is elaborated in another paper (Loomis, 1975) and only a summary of the evidence and consideration of the compositional variation of garnet are presented here. The composition of product phases in a thin section was found to be invariant and independent of the varying composition of reactants and varying extent of reaction in different regions; the products are, therefore, probably indicative of final equilibrium values of the state variables during reaction. Rim compositions of reacted garnet (circled in Fig. 1) appear to be in equilibrium with the product phases, and these data allow the equilibrium topology to be outlined (solid lines) in Fig. 1.

Reacted garnet grains are strongly zoned, up to 100 μm from the margin and an unzoned core region is present. The thickness of the rim zoning is independent of the size of the grain; therefore, large grains have a uniform “core” composition for most of their bulk. Comparison of the composition of the unzoned core region from several grains in a section suggests that this composition is invariant. Moreover, biotite inclusions in the core region also have similar compositions and appear

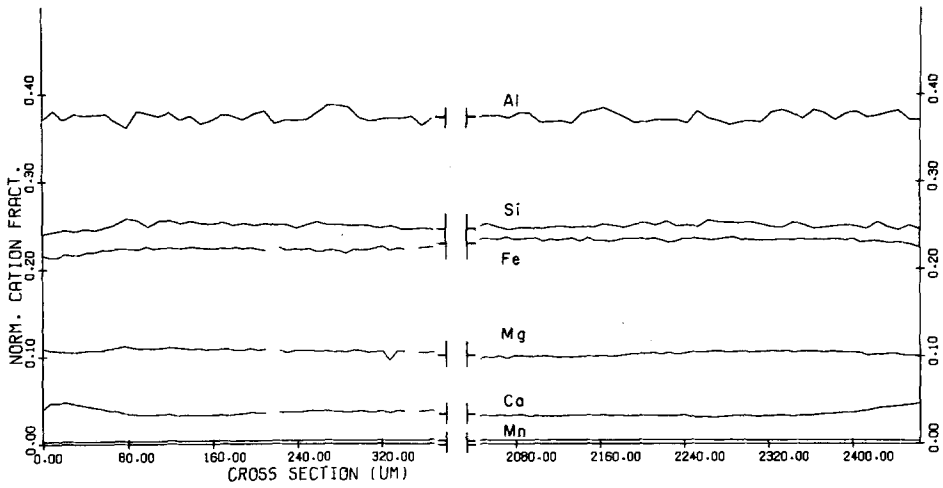
to be in partitioning equilibrium with the adjacent garnet core. It is hypothesized that the garnet core and inclusions preserve evidence of the initial assemblage and phase compositions before reaction began. Additional evidence supporting this hypothesis and the reaction behavior of biotite is available from domain studies and is presented elsewhere (Loomis, 1975). The reaction process is well-defined because the original and equilibrium compositions of the garnet are known.

The progressive development of zoning is illustrated with examples from a single thin section. Garnets from domains in where there is no reaction display little zoning (small variations of Ca) and the Mg/Fe and Mn content is approximately uniform (Fig. 2a). Likewise, core regions in all garnets are unzoned and of this same composition. As reaction begins, narrow zoned rims are produced as demonstrated in Fig. 2b by a garnet from a domain with incipient reaction. Continued reaction results in wider zoning patterns; the small garnet shown on Fig. 2c has reacted extensively on one side but little on the other. Significant reaction resulted in the zoned garnets of Figs. 2d, e, and f. Mn increases toward the margin, but the absolute variation is small and on the order of 2 or 3 mole % spessartite (the initial content of spessartite is only ~1%). Ca is usually unaffected but can show some (inconsistent) variation. By far the major zoning factor is change of Mg/Fe; fortunately, this factor can be related directly to irreversible reaction.

Rim compositions of garnets were measured as a minimum spot total analysis as near the margin as possible. This method obviously becomes less accurate as the zoning gradient increases but was adequate, for well-reacted garnets, to conclude that the rim Mg/Fe rapidly approaches a fixed value soon after reaction begins. I will assume that this fixed rim Mg/Fe exists in all cases considered; it appears to be the value expected for equilibrium with the product phases. If the zoning of grossularite content is negligible, and the zoned but very small spessartite content is neglected, the core and rim concentration of the components pyrope and almandine can be assumed fixed by the initial composition and reaction process and a binary diffusion system modeled.

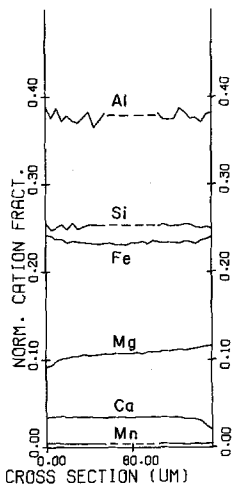
The simplified model of reaction for a pyrope-almandine is as follows. An unzoned garnet of initial composition C_i , where C_i is the initial concentration of the component pyrope or almandine, reacts irreversibly to an equilibrium set of product phases not in partitioning equilibrium with the initial garnet. When reaction begins, the rim composition is immediately fixed at a value C_e in equilibrium with the product phases, and a very steep zoning profile is generated. Garnet and biotite irreversible reaction can occur in separate domains in a thin section and the reactions will be considered independent here (Loomis, 1975). With continued reaction, the width of the zoned rim increases, but the core composition C_i (as long as a core remains) and rim composition C_e remain fixed. Eventually it is suggested that the zoned margin (in a reference frame moving with the grain boundary as garnet is consumed) approaches a constant, or "steady state" profile.

Another reaction of the same type (Sample R118A) resulted from change of conditions great enough that the cordierite-biotite trivariant assemblage became the stable alternative to the initial garnet composition. The actual reactions that took place are complex and also may involve discontinuous ones;



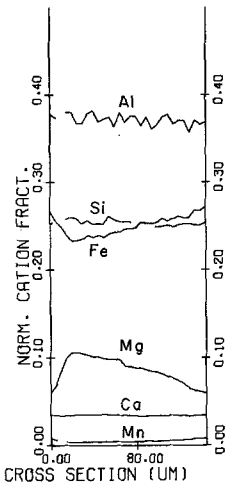
GAR A R206-1

(A)



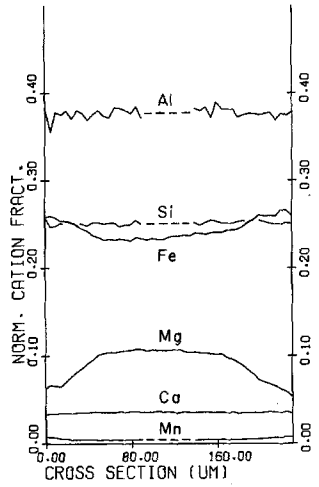
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(B)



GAR D GP 5 R206-1

(C)

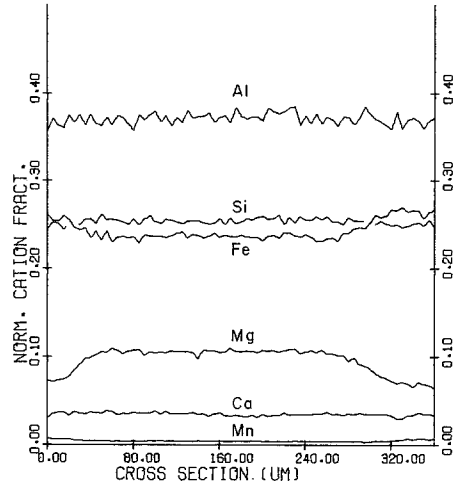


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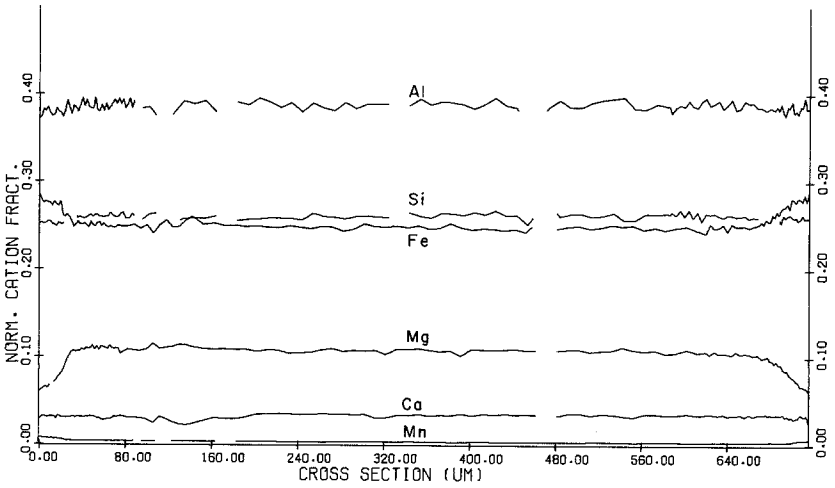
(D)

Fig. 2A-D

Fig. 2A-F. Zoning profiles of garnet grains from different domains within a single thin section of sample R206. Vertical axis, normalized cation fraction, was computed from the counting rate at each *X* measured by assuming a linear relationship between counting rate and molar abundance and normalizing to the observed counting rate and corresponding total analysis (Bence-Albee method) in the core region. The effects of non-linearity (mutual absorption and fluorescence among elements), beam current drift, and background corrections result in small differences between the extrapolated, plotted values and true total analyses. However, the extrapolated molar plots present the sense and approximate magnitude of concentration variation of interest here in a more illustrative way than plots of raw counting rate. (A) abbreviated profile of a large garnet that has undergone no reaction; (B) incipient reaction; (C) extent of reaction at the left less than at the right; (D-F) extensively-reacted garnets



GAR 2 GP 1 R206-1
(E)



(F) GAR F R206-1

Fig. 2E and F

they will be described elsewhere (Loomis, in preparation). Garnet is zoned from an equilibrium rim composition to an unzoned core region of the initial composition, as in the previous example (Fig. 3).

Reaction of garnet in both examples is characterized by the instability of garnet of any composition in the reaction system; that is, garnet as a phase is unstable. In example 1 (R 206) the initial garnet composition and sillimanite are unstable relative to the pair cordierite and hercynite, and the equilibrium composition (rim) of garnet plus sillimanite and cordierite react to hercynite. Example 2 (R 118 A) is similar with the addition that initial garnet is replaced by the pair biotite-cordierite, although the actual reaction is not a direct breakdown of the initial garnet composition but results in zoning.

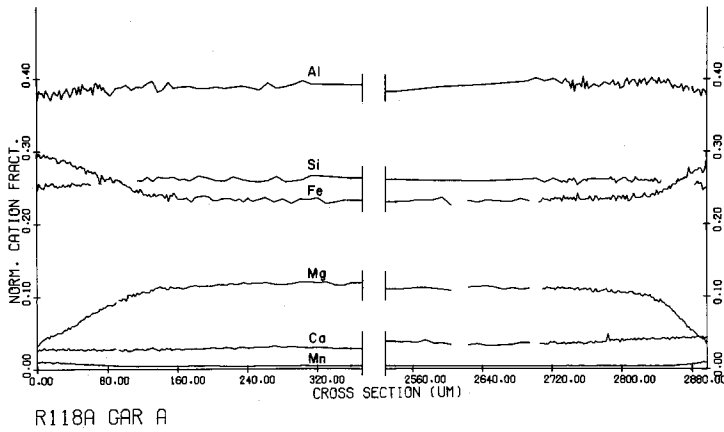


Fig. 3. Zoning profiles of garnet grains in sample R118A (See caption of Fig. 2)

Reaction Model—Case 1

If the pyrope composition of garnet that reacts, C_r , is equal to the initial composition of the homogeneous garnet, C_i , no zoning will appear as garnet is consumed regardless of the efficacy of diffusion. If $C_r > C_i$ the rim of the garnet is depleted in pyrope, as the interface moves inward, and diffusion within the garnet will create a widening zone ahead of the edge. If, however, C_r at any time changes

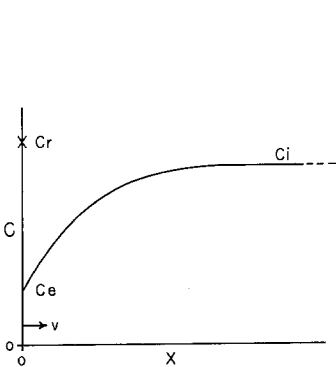


Fig. 4

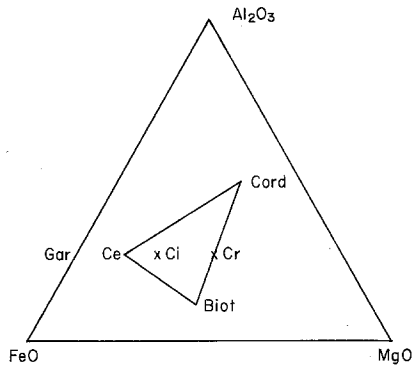


Fig. 5

Fig. 4. Reaction model, Case 1. Variation of the concentration of a component in garnet as a function of the distance from the boundary. Positive x : distance into garnet infinite half-space. Negative x : distance into matrix infinite half-space. v constant velocity of infinite plane boundary between garnet and matrix, and of coordinate system moving with respect to mass points. C concentration of component. C_i initial garnet composition. C_e fixed garnet rim composition for $t > 0$. C_r composition of garnet actually removed by incongruent reaction

Fig. 5. Hypothetical reaction system in projection from K -feldspar, quartz, and plagioclase. C_i initial composition. C_e equilibrium (rim) composition. C_r reacting composition actually subtracted from the garnet phase

to equal C_i , the previously-formed zoning profile will be preserved relative to a reference frame moving inward with the garnet edge. If C_r becomes less than C_i , say equal to the edge composition C_e in these examples, pyrope will accumulate ahead of the moving interface and zoning will steepen.

I will adopt a semi-infinite medium model for simplicity and to enable the use of available analytical solutions. The model is shown in Fig. 4 and is applicable as long as the curvature of the garnet margin is small relative to the width of zoning, and initial garnet is preserved in the core; these conditions are satisfied for samples considered here. The garnet-matrix interface migrates with a velocity v as garnet is consumed by reaction, and the spatial coordinate system is displaced so that the interface remains at $x=0$.

The flux in the x direction of a component across any plane given by x will depend on the concentration gradient, and the rate of movement of the coordinate system tied to the garnet-matrix interface. Assuming D is compositionally independent leads to:

$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2} + v \frac{dC}{dx}. \quad (1)$$

Boundary conditions are assumed as follows:

$$\begin{aligned} x > 0, \quad t = 0 \quad C &= C_i \\ x = 0, \quad t > 0 \quad C &= C_e. \end{aligned}$$

The solution of this transient state problem, assuming v is constant, is given by Carslaw and Jaeger (1959, p. 399):

$$C(x) = C_i + \frac{1}{2}(C_e - C_i) \left\{ \operatorname{erfc} \left(\frac{x+vt}{2\sqrt{Dt}} \right) + \exp \left(\frac{-vx}{D} \right) \operatorname{erfc} \left(\frac{x-vt}{2\sqrt{Dt}} \right) \right\}. \quad (2)$$

As time becomes large, the profile evolves toward "steady state"; the shape of the profile with respect to the moving coordinate system is constant:

$$C(x) = C_i + (C_e - C_i) \exp \left(\frac{-vx}{D} \right). \quad (3)$$

The steady state profile depends only on the ratio of velocity of the garnet-matrix boundary (reaction rate) and the diffusion constant.

The mass balance boundary condition at the surface of the grain ($x=0$), if the edge concentration is maintained at C_e but the reacting composition is C_r , is:

$$C_r v = C_e v + D \left. \frac{dC}{dx} \right|_{x=0} \quad (4)$$

and the surface diffusion flux is

$$D \left. \frac{dC}{dx} \right|_{x=0} = (C_r - C_e)v.$$

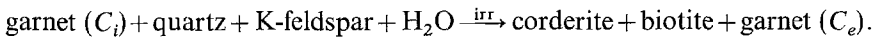
From the steady state solution we find:

$$D \left. \frac{dC}{dx} \right|_{x=0} = (C_i - C_e)v;$$

thus, to remain at steady state the reacting composition must become equal the initial or remaining core composition. Application of this analytical model to natural examples will follow in a later section.

Reaction System – Case 2

The second type of reaction is probably more common and differs from case one in that the equilibrium composition of garnet is stable in the system. A hypothetical example is illustrated in Fig. 5. The hypothetical situation is one that would develop if the aluminum silicate were used up in example one. Assuming garnet reacts irreversibly as in the previous natural examples, we have:



The composition of garnet actually removed from the phase is shown as C_r , because only cordierite and biotite are being produced. By the surface boundary condition (4):

$$v = \frac{D \left. \frac{dC}{dx} \right|_{x=0}}{C_r - C_e}.$$

The compositions C_r and C_e remain constant as reaction proceeds according to the model of irreversible reaction developed previously. Thus, v is proportional to the surface diffusional flux and must continue to decrease as the zoned rim of the garnet widens.

The resulting differential equation for this case is:

$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2} + \frac{D \left. \frac{dC}{dx} \right|_{x=0}}{(C_r - C_e)} \frac{dC}{dx} \quad (5)$$

and is solved by the finite difference methods (Crank, 1956). An average value for v is computed by averaging the velocities of each iteration.

A natural example is provided by an inclusion of basic rock in the Ronda metamorphic aureole, shown in projection in Fig. 6. The garnet core composition

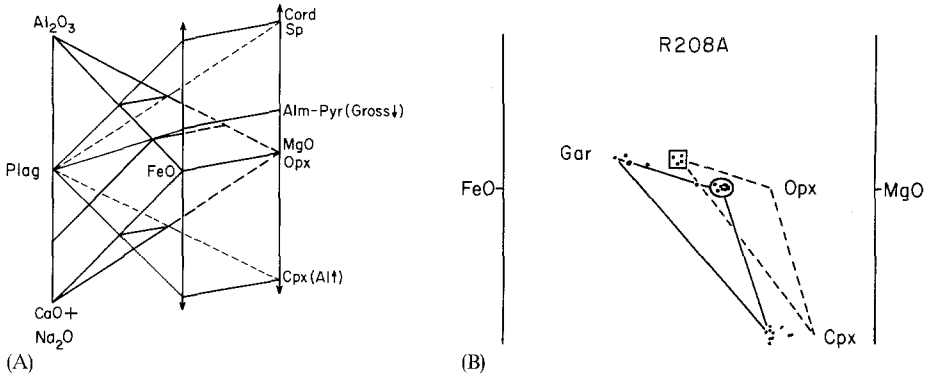


Fig. 6. (A) projection representation used in (B) assuming Na₂O and CaO are isomorphous components; projection is also from quartz. (B) square and dashed lines represent the garnet core composition and other reactant phase compositions predicted from partitioning data; solid lines probable equilibrium product assemblage

(rectangle) and partitioning data enable the initial assemblage to be outlined (dashed lines) and garnet rim values and matrix clinopyroxene suggest approximate compositions in the equilibrium assemblage (solid lines). Steep zoning gradients near the margin are probably responsible for the scatter of “rim” analyses between the true value and the core composition. Zoning profiles are shown in Fig. 7. The reaction was (unbalanced):

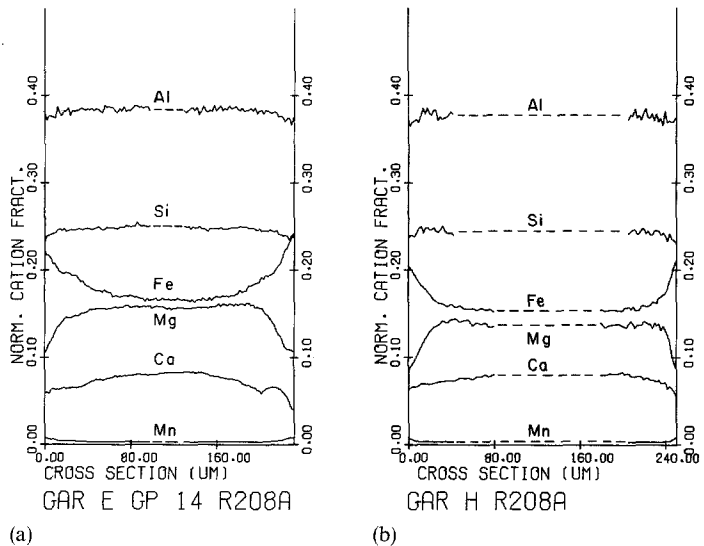
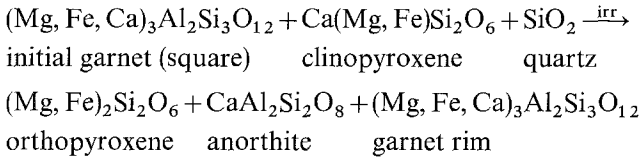


Fig. 7. Zoning profiles of garnet grains in sample R208A (see caption, Fig. 2)

Component Reactions

The overall irreversible reaction of garnet can be described by dividing it into two component reactions, a reversible and an irreversible one. The reversible component reaction represents reaction of a garnet composition in equilibrium with product phases. The irreversible component reaction is the reaction of the initial garnet to form equilibrium garnet plus products. The relative rate of these two component reactions can be used to describe the compositional variation of a reactant as a function of extent of reaction.

The ratio of reversible to irreversible component reaction rates for biotite in example 1 was found to be less than unity (Loomis, 1975). A simple irreversible reaction model in which the reactants were assumed to maintain the initial composition could not be applied; that is, the reversible component reaction was rate limiting as well as the irreversible component. In that case, biotite remained homogenous because internal diffusion was much more rapid than reaction. Therefore, the relative rate of reversible and irreversible component reactions must have been determined by unknown, exterior factors.

When garnet reacts, however, diffusion is a controlling factor. Dividing the reaction into component sections, we have for a component, by mass balance:

$$C_r \frac{dN_r}{dt} = C_i \frac{dN_{ir}}{dt} + C_e \frac{dN_e}{dt},$$

where "ir" stands for irreversible and N is molar abundance of garnet. In one-dimensional space for a molar volume independent of composition, this relation can be written in terms of the velocity components in the x direction ($v - v_r$):

$$C_r v = C_i v_{ir} + C_e v_e. \quad (6)$$

The amounts of garnet reacting reversibly and irreversibly must equal the total reacting:

$$\begin{aligned} dN_r &= dN_{ir} + dN_e, \quad \text{consequently,} \\ v &= v_{ir} + v_e. \end{aligned} \quad (7)$$

Combining 6) and 7), the rate of irreversible reaction can be described as:

$$v_{ir} = \frac{C_r - C_e}{C_i - C_e} v. \quad (8)$$

By comparison of (8) with the surface boundary condition (4), the rate of irreversible reaction is related to the concentration gradient at the surface:

$$v_{ir} = \frac{D \left. \frac{dC}{dx} \right|_{x=0}}{C_i - C_e}.$$

The rate of irreversible reaction is rapid initially but slows during the transient stage as zoning develops. In contrast to the behavior of biotite in example 1, the relative rate of component reactions after the initial instant is determined by diffusion in both cases.

Application of Reaction Models to Natural Data

If we accept the foregoing interpretations of reaction systems, the analytical models can be compared to the data. To match zoning profiles predicted by the models and real data curves would require total analysis data profiles. Collection of total analysis profiles was deemed impractical for the volume of data considered here and the available analytical equipment. Instead, data profiles were characterized by the distance Z from the margin at which C became indistinguishable from C_i . On a plot of counts vs. x for an element, Z is the distance where the curve seems to achieve zero slope and is equivalent to the distance where the error bars on the zoning curve and C_i overlap. The difference between the counts of C and C_i at Z is approximately:

$$\sigma_K \simeq (K C_i)^{\frac{1}{2}} = (B C_i)^{\frac{1}{2}}$$

where K_C is the number of counts collected and B the proportionality constant between counts and concentration. Then the concentration difference between C and C_i will be given by:

$$\sigma_C = \frac{\sigma_K}{B} = \left(\frac{C_i}{B} \right)^{\frac{1}{2}}$$

The value of σ_C for the data used here was about one percent of C_i ; the value of Z computed in the analytical models was the point at which the theoretical concentration curve came within one percent of C_i . Many data profiles can be scanned and a reasonable value for Z estimated. The range of Z encountered may be a result of several factors including non-radial sections of grains (cut not passing through the center), irregular boundaries and diffusion near fractures, and the expected variation with extent of reaction. The complete range of Z values is reported in Table 1 to illustrate the uncertainty, but careful selection of specimen and reaction domains reduces this range.

The primary application of garnet zoning models will probably be to estimate reaction rates if D is known. However, the inverse problem is investigated here

Table 1. Minimum, average, and maximum width of zoning and other data for reacted garnets of natural samples

Sample-Model	Z (μm)	v ($\mu\text{m}/\text{yr}$) $\times 10^4$	D^a (cm^2/sec) $\times 10^{18}$
R118A (1)	140 min	5	9
	180 av	5	13
	200 max	5	15
R206 (1)	40 min	5	2
	65 av	5	3
	100 max	5	6
R208A (2)	20 min	1 ^a	0.2
	40 av	2 ^a	1
	60 max	4 ^a	2

^a Values computed from analytical models.

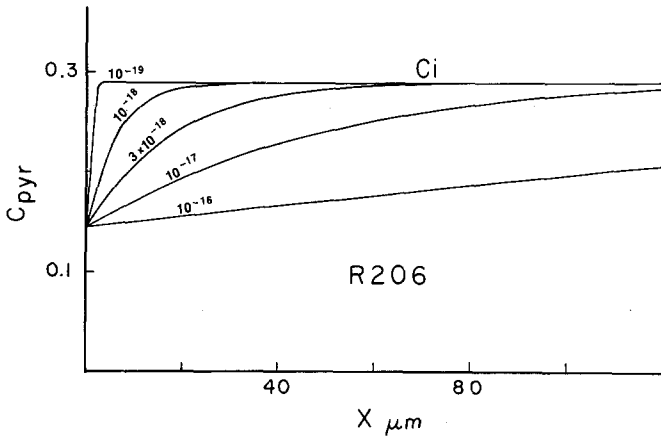


Fig. 8. Pyrope concentration profiles computed by model 1 for various values of D and $v = 5 \times 10^{-4} \mu\text{m}/\text{yr}$, $t = 10^5 \text{ yr}$, $C_e = 0.145$, and $C_i = 0.29$ for sample R206

because unusual evidence of the reaction rate is preserved. The analytical models are tested by estimating values of D , the assumed average mutual diffusion constant for the examples described here, to see if the magnitude is reasonable and the two models consistent.

An approximation of v for each sample is based on a petrographic estimate of the amount of garnet consumed (replaced) coupled with the estimate of 10^5 years as the length of time reaction occurred, derived from cooling models of the metamorphic aureole (Loomis, 1972a, p. 2491). The error of the time estimate is probably less than an order of magnitude, and that of the amount of garnet consumed less than a factor of two. The uncertainty of Z results in some error. Thus, the estimate for D must be considered to reflect well over an order of magnitude of error. Furthermore, the temperature of reaction may have varied between 600–900°C. Obviously, this data is presented to illustrate the applicability of the model to natural processes and the design of controlled experimental work. Knowledge of D as a function of temperature (and composition) would enable reaction rates of various natural processes to be estimated.

Knowledge of v and time enables profiles to be computed using the applicable model and various values of D . Fig. 8 shows some computed profiles for example 1 (R206); a value of $3 \times 10^{-18} \text{ cm}^2/\text{sec}$ for D results in a profile matching the average observed Z of 65 μm (Table 1) for garnets that have undergone extensive reaction. This value for D can then be used to show the expected evolution of zoning through time in Fig. 9; the modeled profile for the estimated time of reaction (10^5 years) is nearly that of steady state at infinite time. In contrast, sample R118A is not at steady state.

Matching solutions for case 2 reactions require more information because v can not be assumed constant. Exact values of C_i and C_e for case 1 solutions have little effect on the width Z of the profile. However, C_r as well as C_i and C_e must be known to correctly compute v during solution of equation 5; *the necessity of understanding the reaction process is obvious*. C_r for sample R208A,

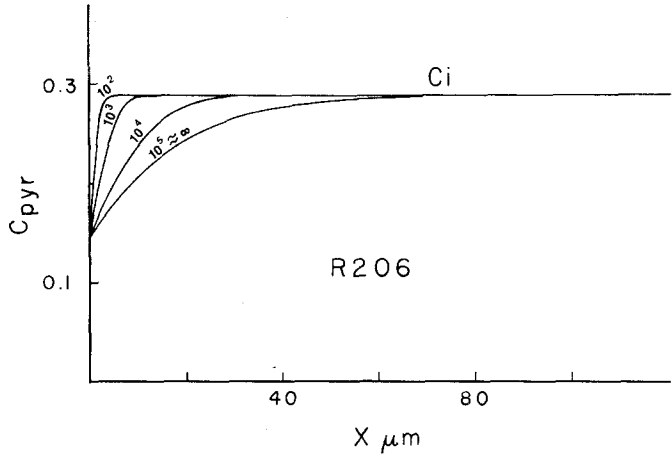


Fig. 9. Pyrope concentration profiles computed by model 1 for various time and $D = 3 \times 10^{-18} \text{ cm}^2/\text{sec}$ and the data of Fig. 8 for sample R206

the composition of garnet actually subtracted, can be assumed to have the $\text{Mg}/\text{Mg} + \text{Fe}$ appropriate for reaction with clinopyroxene to produce the product orthopyroxene (i.e. colinearity with orthopyroxene and clinopyroxene in Fig. 6b). The reaction model is supported by the constant composition of orthopyroxene in R208A and by analogy with the documented irreversible reactions in R206. C_e for pyrope or almandine is estimated from the presumed constant equilibrium rim value of $\text{Mg}/\text{Mg} + \text{Fe}$, assuming that the grossularite content is approximately constant and neglecting the small spessartite variation. Finite difference solutions were computed for several values of D and the estimated reaction time; values of D matching the data and the average computed v are reported in Table 1. The evolution of zoning through time is illustrated in Fig. 10; steady state zoning is not possible in this reaction system.

Data estimated by the methods detailed above for the examples considered here can be compared in Table 1. Values of D computed by the models are lower

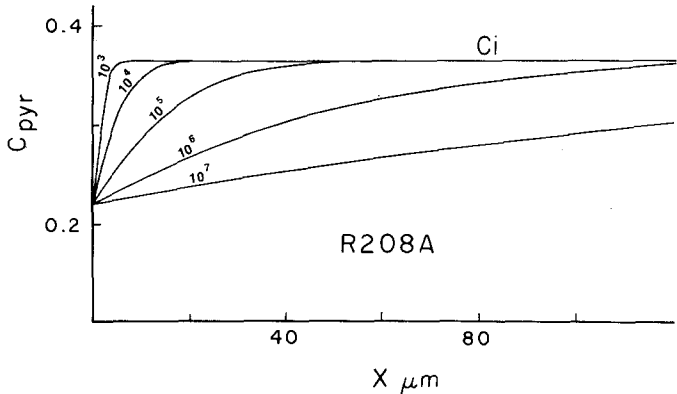


Fig. 10. Pyrope concentration profiles computed by model 2 for various times and $D = 1 \times 10^{-18} \text{ cm}^2/\text{sec}$, $v = 5 \times 10^{-4} \text{ μm/yr}$, $C_e = 0.22$, $C_i = 0.365$, and $C_r = 0.44$ for sample R208A

than expected from the estimate of Anderson and Buckley (1973, p. 88) for the range of conditions averaged here. Possibly some of the difference can be attributed to a shorter time of reaction than used in the model owing to: 1) rapid cooling of the aureole by fluid circulation, or 2) sluggish reaction, as exemplified by domains in sample R 206 in which little or no reaction occurred. If the reaction time is reduced to 10^4 years, the values of D in Table 1 are increased approximately (exactly at steady state) an order of magnitude; thus, if determination of D is considered a result of this work, at least two orders of magnitude error must be acknowledged.

The general agreement among the three examples is within the probable error. The two models are independent in the sense that the input parameters are different. Model 1 incorporates a constant value for v and the result is practically independent (except for the Z value) of compositions. Model 2 requires complete compositional data and the average or integrated v is a computed result. Thus the general agreement of D between the models is probably significant. In addition, the average v computed in Model 2 for sample R 208A is a reasonable value as verified petrographically.

Real differences among the samples are possible because they are from different parts of the aureole. R 208A is slightly closer to the contact (~ 30 m) than R 206 and consequently was hotter, but the temperature range of the different reactions probably varied. A more significant difference is between R 118A and R 206 and is probably real. Smaller values of v were tried in R 118A to bring D into line with the other samples, but the data can not be matched (in 10^5 years) with any value of v for a D of 3×10^{-18} cm²/sec as found for R 206. The compositional shift of the K-feldspar-cordierite-garnet-biotite field was much greater in R 118A than R 206 (the original garnet composition was comparable). The shift is a result of increased T or decreased P_i ; because the *final* equilibrium pressure difference between samples must have been small, the temperature and consequently D of R 118A was probably considerably greater than that of R 206.

Reaction Rates

The foregoing analysis in model 1 assumed the consumption or reaction rate of garnet is constant and, therefore, the reacting composition can be isolated as a variable. The assumption that v is constant is reasonable if the rate of reaction is determined by the rate of solution of a reactant phase in the solution, or "intergranular fluid" in this case. The reactant phase with the slowest dissolution rate will determine the rate of reaction in the system, assuming a system closed to all except volatile components as described here. If the limiting phase is an aluminum silicate, the extent of reaction should have no effect on reaction rate. If garnet or some other ferromagnesian mineral is rate limiting, changing composition could conceivably affect the rate. The problem is compounded by the generation of product phases that adhere and possibly reduce contact of reactants with the solution. The question then becomes what mineralogical factor controls dissolution rate, and are Fe and Mg important in the present examples. Several authors have suggested that diffusion rates of Al are much slower than the other major inert

components in silicates (Anderson and Budkley, 1973, p. 91) and in the "intergranular fluid" of metamorphic rocks (Carmichael, 1969; Fisher, 1973). These observations suggest that dissolution rate may be primarily dependent upon breaking up the Al-Si-O lattice of Al-rich silicates and the ratio Mg/Fe would be expected to have had little effect. The fact that biotite and garnet show similar amounts of reaction when they occur in the same domain also suggests that the dissolution rate of sillimanite or kyanite (the common reactant) was rate limiting.

Consideration of relative reaction and diffusion rates is advantageous in designing experiments involving chemically recalcitrant minerals. Most experiments are designed presently to promote rapid reaction rates in the hope that all possible reactions will reach completion and equilibrium will be achieved. However, completion of all reactions may not be practical at low and moderate metamorphic grades and it would be desirable, therefore, to determine the equilibrium composition of a phase without completely reacting each grain.

An example provides the best explanation of the concept. Let us introduce garnet with other phases into an experimental run to determine if garnet is stable. It is unlikely that the garnet will be of the exact composition to react reversibly and it will react irreversibly with other phases to form the equilibrium product assemblage. If the rate of reaction is rapid relative to internal diffusion, steady state will be reached with generation of a very steep, difficult to detect zoned rim. Thus, garnet will appear to retain the original composition, and the only proof of disequilibrium will be its complete disappearance as a phase with time. Moreover, the composition reacting reversibly (in partitioning equilibrium) can only be found by producing garnet. A more efficient method would be to slow reaction rates, let garnet develop zoning, and measure the equilibrium rim composition directly without the necessity of reacting all the garnet.

Conclusion

The purpose of this paper was to investigate models of diffusional zoning that are applicable to natural situations. Two models were developed and three natural samples used to illustrate the approach. It is obvious that a great deal of information about the specific reaction process must be available before a suitable kinetic model can be formulated and applied. The values of D computed here are meant only to illustrate the model and not replace experimental determination; many idealizations have been introduced as discussed below. A more useful application of zoning models is to use experimentally determined values of D to measure reaction rates of natural reactions at known temperature.

Several simplifications have been used. The constancy of v in model 1 was discussed above. The choice of pyrope and almandine as components instead of Mg^{++} and Fe^{++} is probably justified by the stoichiometric constraints of garnet and the fact that ionic exchange reactions were not allowed in the models because compositions of product phases were found to be fixed. D was assumed to be a mutual or binary coefficient applicable to the Mg and Fe components, an assumption that implies the molar volume of garnet is constant over the composition range. Intrinsic coefficients can be introduced to avoid the volume change problem.

The data are not adequate to accurately evaluate cross coupling coefficients relating the flux of one component to the concentration gradient of another. However, Mg profiles often show an inflexion point near the margin, not usually detectable for Fe, that may be indicative of cross coupling between the Mg and Mn components; Mn is concentrated near the margin in a zone usually narrower than that of Mg and Fe. The effect of Mn and Ca in garnet on the partitioning of Mg and Fe with other phases has been noted by several authors, and Ganguly and Kennedy (1974) have shown that the mixing model, non-ideal interaction parameters between Mg and Ca or Mn are distinctly larger than between Fe and Ca or Mn. It is probable that there is a significant diffusion cross coefficient between Mg and Ca or Mn that will affect the apparent value of D if there is zoning of Ca or Mn in the sample; some zoning is actually present in the samples considered here, especially R208A (Fig. 7). If strong coupling between Mg and Mn is found, modeling of Mn zoning by a pure fractionation (Hollister, 1966) or kinetic fractionation-diffusion process (Albarede and Bottinga, 1972) is complicated by the presence of major element zoning. The importance of major element zoning to trace element distribution, if cross coupling exists, was emphasized by Anderson and Buckley (1973).

An additional uncertainty is related to the variable temperature during diffusion in these samples. Because the dependence of D on temperature is not simple, the meaning of an "average" value of D for a temperature range can not be defined. Richardson and Lasaga (Richardson, 1974) have shown the substantial effect of variable temperature on diffusion profiles generated by exchange reactions. Oxygen fugacity can also affect diffusion of ferrous iron (Buening and Buseck, 1973).

Obviously, problems of great complexity can be proposed and evaluated numerically, but elaborate models can only be theoretical exercises unless sufficient detail of natural reaction systems and compositional zoning of major and trace elements is available, and experimental determination of diffusion parameters is undertaken.

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