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MULTICOMPONENT DIFFUSION IN GARNET:

II. COMPARISON OF MODELS WITH NATURAL DATA

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ABSTRACT. Computational methods developed in part I are used to simulate four sets of diffusion zoning profiles from two samples from the aureole of the Ronda ultramafic intrusion; the necessary reaction and temporal information is available for these samples. Four aluminous components are sufficient to represent the observed compositions, but it is necessary to normalize natural data to insure that average end-point compositions sum to a mole fraction of 1. Binary diffusion and reaction routines for use in the multicomponent model were adapted from previous work.

Sensitivity of computed curves to modeling parameters and ideal intrinsic diffusion coefficients was determined by varying each factor individually. The average composition and temperature selected for computation of D and the solution model are not critical factors. The influence of non-ideal thermodynamic solution is marked, however, and must be used in realistic models. Of the components, only the almandine ideal intrinsic diffusion coefficient (mobility) has a significant effect on profiles of components other than its own in these samples; it should be possible to fit coefficients to excellent data within a factor of 2. The relative magnitude of the pyrope coefficient could not be evaluated adequately; if it is small relative to almandine it can be disregarded in models.

Multicomponent zoning profiles in these natural garnets could be fitted well using these models, and apparent irregularities of measured profiles such as uphill diffusion of grossularite were explained by multicomponent interactions. Cross coefficients are large and can be ignored only if the mole fraction gradients of all but two components are small. The relative magnitude of ideal intrinsic coefficients corresponding to mobilities were determined for high metamorphic temperatures: D^*_{sp} is approximately an order of magnitude less than D^*_{alm} and D^*_{gr} is between D^*_{sp} and D^*_{alm}. It is possible to use these relative magnitudes and the models demonstrated here to model geologic process involving multicomponent diffusion in garnet.

INTRODUCTION

The availability of the electron microprobe for geologic research has made possible the investigation of disequilibrium processes responsible for crystal growth and reequilibration. These disequilibrium processes include long range diffusion between assemblages, short range diffusion around individual crystals, diffusion within a crystal, and crystal interface kinetics. Of these complex phenomena, intragranular diffusion is probably the most tractable, because the transport medium is known, thermodynamic solution models may be available, and compositional gradients can be measured directly with the microprobe in natural rocks.

Compositional zoning of garnet is probably the most abundantly studied disequilibrium phenomenon and is commonly interpreted in terms of the crystallization history of a rock. The emphasis on garnet zoning derives from the facts that diffusion is slow in garnet, and the partitioning of elements between garnet and other phases is widely variable as a function of controlling variables. Most garnets analyzed display zoning of at least three components, and emphasis is often placed on the pattern of minor components that may in part be the result of major component profiles, as stressed in part I. Increasing reliance on zoning of garnet in natural rocks as an indicator of equilibration history necessitates development of more sophisticated models of diffusion than have been applied. It is the purpose of this paper to demonstrate the application of models of garnet zoning that take into account the complexities of multicomponent diffusion and non-ideal solution, yet are simple and flexible enough to be utile.

Models can be computed for any situation for which a binary (interdiffusion) model is available, including numerical solutions. Thus a wide variety of geometries and boundary conditions can be considered by simply replacing one subroutine in the computer program described in part I. An assumption implicit in the model is that diffusion coefficients computed for one composition are adequate, constant approximations to the range of coefficients predicted from compositional dependence; that is, diffusion coefficients can be considered to be compositionally independent. The validity of this assumption is tested in this work.

A great deal of information must be available to model diffusion in garnet, including reaction stoichiometry, interface velocity, reaction duration, temperature, and initial conditions. This information can be approximated for a few samples previously studied from the aureole of the Ronda ultramafic intrusion (Loomis, 1975, 1976, 1977, 1978a). I anticipate that the availability of diffusion models for garnet will encourage the collection of sufficiently detailed compositional and geologic information on other samples to test further the conclusions of this paper.

The objectives of this study are as follows: (1) find the magnitude of interaction between diffusion profiles of components in garnet, (2) test the importance of non-ideal thermodynamic solution, (3) find the relative magnitude of ideal intrinsic coefficients (or mobilities), and (4) test the sensitivity of models to choice of composition and temperature.

MEASURED PROFILES

Garnet zoning profiles are of variable quality, being subject both to the uncertainties of sectioning and those of analytical error and data reduction. Four sets of profiles from two samples were selected from about 30 for comparison with models. Two sets of profiles have large variations of pyrope and almandine only; two others have significant zoning of grossularite. Spot analyses were found to provide reasonably stoichiometric analyses in terms of four components: almandine (alm), pyrope (pyr), spessartite (sp), and grossularite (gr); these components are assumed to total 100 percent in the models.

The mole fraction of each component was computed first by assuming a linear realtionship between counting rate and mole fraction determined at a spot analysis. The effects of non-linearity caused by mutual absorption and fluorescence among elements and beam current drift could result in small differences between extrapolated values and true total analyses. However, these effects are probably less important than statistical error over the small compositional range of zoning.

An additional correction or normalization was necessary to insure that the end points of the profiles summed exactly to a total mole fraction of 1. Estimated end point compositions of the profiles are used as boundary conditions in the models, and the computed model profiles are fixed at those points. Only three profiles are actually computed; the fourth is found by difference from total mole fraction as required by the assumptions of the model. If mole fractions at an end point of the four component profiles do not sum to a mole fraction of 1, the difference is concentrated in the fourth profile. If the difference varies along the profiles, the shape of the fourth profile will be changed, and the others unaffected. In other words, all the uncertainty is concentrated in only one component.

This problem can be alleviated by choosing reasonable end point values of all four profiles and multiplying by a factor to insure a total mole fraction of 1. In effect, this procedure distributes any error over all components in proportion to molar abundance. The set of four profiles was adjusted this way for each garnet by finding the normalizing factor for the edge and interior end points and interpolating the factor in between. The actual factors used in these data range between the worst cases of 0.92 to 1.07.

The normalizing procedure is necessary for all real data. Corrections seem small, but it is impossible to use the fourth profile without them, if the fourth component is one of small mole fraction. With normalization, the choice of fourth (dependent) component is arbitrary. This method also preserves the graphic illustration of the uncertainty of the profiles because the profiles need not be smoothed or fitted with a smooth curve before comparison with the model.

BINARY DIFFUSION MODELS

Justification for assuming that the zoning profiles used for comparison are the result of diffusion is detailed in the papers cited previously. Briefly stated, initially the garnets were unzoned, probably having equilibrated at high temperature, as demonstrated by the unzoned pattern of unreacted grains and central compositional plateaus of reacted ones. Another boundary condition, the rim composition, is assumed to have been instantaneously changed and maintained at new value when reaction started; this assumption is justified by the similarity of all measured rim compositions in a sample regardless of extent of reaction and the probable rapidity of pressure decrease due to the emplacement of the intrusion (the geologic context of the samples is described by Loomis, 1972a and b).

Reaction stoichiometry and velocity are interdependent, if the boundary conditions above apply, as discussed by Loomis (1975). If garnet is reacting by several independent reactions, the reaction stoichiometry is unknown, and the simplest approximation is to assume a constant rate of consumption (or growth) of garnet; reaction stoichiometry will vary with time as a dependent variable. Constant velocity consumption has a simple analytical solution for binary diffusion (Loomis, 1975, p. 295, case 1). If overall reaction of garnet can be approximated by a single balanced reaction, the velocity is variable in time and can be predicted from the diffusion models (p. 296, case 2), although numerical solution is required. These two solutions for a semi-infinite half space geometry are here termed binary models 1 and 2; their derivations are found in the reference cited. Model 2 is applicable to sample R208A (Loomis, 1977), and recent work (Loomis, 1978a) indicated that it is also a good approximation for R118A. Model 1 was used for comparison.

Both models require rim and core compositions and reaction time. Model 1 (constant velocity) requires the velocity to be estimated from the volume of reaction products and time of reaction. Model 2 needs a reaction composition derived from the reaction stoichiometry. Both models assume that the interdiffusion coefficient is independent of composition and time. The second assumption introduces some error, if temperature changes during reaction, but this factor may be minimized in these samples due to rapid change of geologic conditions between initial and final states. At any rate, the effect of temperature change can not be evaluated without more data. Moreover, it should be noted that it is only the differential effect of temperature on diffusion coefficients that might have significant effect on the relative magnitude of mobilities measured by this work.

The actual temperature and time of reaction can be different in each sample or set of profiles. Temperature of reaction depends on position in the aureole and the temperature of the adjacent peridotite. Diffusion coefficients vary up to two orders of magnitude among samples. In addition, the onset of reaction was sporadic within samples, and one crystal, or even one side of a crystal, may have reacted over a longer period of time than another. Consequently, it is acceptable to vary time, but not temperature, to match profiles in one sample. Without knowing temperature and time precisely, we cannot determine the dependence of diffusion coefficients on temperature.

In the four component system used to model these samples, the binary diffusion equation is solved three times for each multicomponent model. An interesting consequence of model 2 is that the predicted velocity of all solutions should agree, if it is to be physically possible. No similar constraint exists for the constant velocity model.

TABLE 1

Compositions of eigencomponents used to compute the curves of figure 1 and curves N of figure 3. Grossularite is the dependent component. Run L118A 52/N of table 2.

Eigencomponent	Almandine	Pyrope	Spessartite
1	−1.301	−1.364	−1.290
2	0.462	0.433	0.467
3	0.502	0.273	0.543

An example of diffusion profiles computed by model 2 for eigencomponents of a garnet in sample R118A (profiles L118A) is shown in figure 1. Note that these curves cannot contain inflexion points or any other unusual features. The compositions of eigencomponents used in this solution are listed in table 1. Obviously, it is not necessary that the transformed boundary conditions have intuitive physical significance, and negative compositions are common. The D matrix corresponding to this solution, using grossularite as the dependent variable and 1 = almandine, 2 = pyrope, 3 = spessartite, is ($\times 10^{-16}$ cm^2/sec):

$$\begin{array}{ccc} 2.28 & 1.47 & 0.615 \\ -0.609 & -0.083 & 0.235 \\ -0.050 & 0.002 & 0.523 \end{array}$$

Obviously, the significance of mobilities or equivalent ideal intrinsic coefficients is more readily apparent than the actual diffusion coefficients used to compute profiles.

UNCOUPLED DIFFUSION MODELS

The first objective of this work is to determine whether cross diffusion coefficients are necessary to analyze diffusion in garnet. Figure 2 shows model curves computed without using cross coefficients. One can attempt to model any given component profile by using the appropriate diffusion equation that satisfies the boundary conditions and varying D and other parameters. Unless the boundary conditions are such that boundary values vary rapidly (they are fixed in these examples), model diffusion curves will generally have the form of those in figures 1 and 2; they are characterized by continuously increasing slopes appropriate to exponential curves. As shown in figure 2, it is not possible to fit the observed curve for grossularite because the slope of the observed profile reverses.

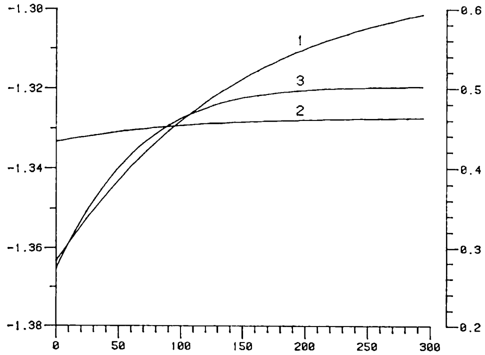

Fig. 1. Zoning profiles of eigencomponents used to compute zoning curves of figure 3. The eigencomponents are listed in table 1. Left ordinate: mole fraction curve 1; right ordinate: mole fraction curves 2 and 3; abscissa: distance into garnet (μm). Run L118A 52/N of table 2.

The additional constraints of mass balance and frame of reference (pt. I, eqs 4 and 5) limit the choice of diffusion coefficients for modeling multicomponent systems. In a binary system, the curve for the second component must be the mirror image of the first (by molar or volume balance arguments), and the same D must be used to model both curves; there are no cross coefficients. Similar restrictions apply to the multicomponent case. Eq 16 (pt. I), requires that the direct (diagonal) coefficients for *all* components be equal for a general choice of composition, if there are no cross coefficients. Then the eigenvectors are equal, and eigencomponents correspond to the initial components. One cannot single out the curve of a particular component and model it without investigating the consequences of using the same coefficient for all other curves. Figure 2 shows model curves for all components computed using the same direct coefficient and without cross coefficients. If the fit for almandine is reasonable, the other curves deviate from the observed curves unacceptably.

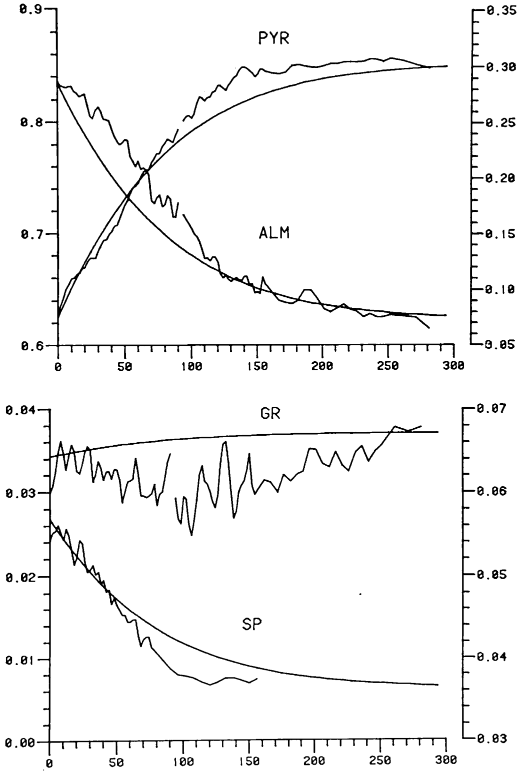

Fig. 2. Microprobe data and model curves computed without cross coefficients for profile set L118A. Left ordinate: mole fraction almandine (alm) or spessartite (sp); right ordinate: mole fraction pyrope (pyr) or grossularite (gr); abscissa: distance into garnet (μm). The same scale is used in figures 3, 5 to 10, and the same axis labels apply in all figures. Irregular line: normalized microprobe data; smooth curve: model curves using $D = 5 \times 10^{-17}$ cm^2/sec for all components.

It is unlikely that the direct coefficients for all components in a multicomponent system can be satisfactorily assumed to be equal.

In fact, cross diffusion coefficients will usually be large, at least in garnet. Figure 3 shows model curves, computed using cross coefficients, that fit the observed curves reasonably well. The diffusion coefficient matrix for these models was listed at the end of the preceding section. The magnitude of some cross coefficients may be an order of magnitude larger than direct coefficients in this example. It is evident that models of diffusion that ignore cross coefficients have been successful approximations *not* because cross coefficients are small.

Cross-coupling of major diffusing components with other components can be ignored only if the mole fraction gradients of the other components are small. For illustration, the diffusion of pyrope and almandine in the current example (fig. 2 and 3, and Loomis, 1975) could

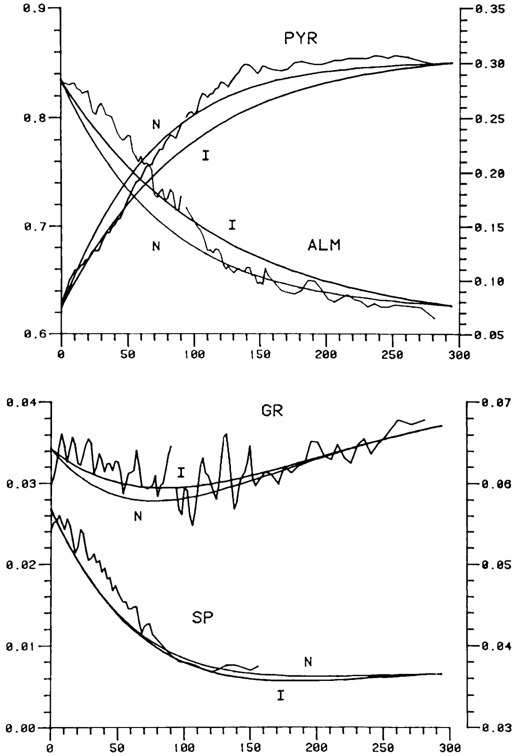

Fig. 3. Microprobe data and computed model curves for profile set L118A. Left ordinate: mole fraction almandine (alm) or spessartite (sp); right ordinate: mole fraction pyrope (pyr) or grossularite (gr); abscissa: distance into garnet (μm). Irregular line: normalized microprobe data; smooth curve N: fitted model curves using nonideal solution model; smooth curve I: model curve computed using same D* as N model but ideal solution. Note that almandine–pyrope and spessartite–grossularite have the same scale. N curve is run L118A 52/N. *D* for the N model is reported in the text, eigencomponent values are in table 1, and eigencomponent curves are shown in figure 1.

be modeled approximately as binary diffusion, because the mole fraction gradients of spessartite and grossularite are small. However, it is not possible to model accurately diffusion of minor components without considering cross coefficients and large gradients of other components. Thus, the diffusion curves of spessartite and grossularite in this example can be simulated only by including the large cross coefficients of the models shown in figure 3.

SENSITIVITY OF SOLUTIONS

Fitting procedure.—In theory, there are four unknown ideal intrinsic coefficients (or mobilities) constrained by the shape of four profiles and the requirement that the computed velocities of solutions using three different eigenvalues and transformed boundary conditions be equal in the variable velocity model. In practice, the following limitations were found and are more fully discussed below: (1) D^*_{pyr} is poorly definable with these data, (2) interface velocities are not readily equated more accurately than a factor of 2 to 3, (3) the complementary nature of pyrope and almandine curves requires that both be fitted by varying essentially only one variable.

Most models were fitted by first setting D^*_{pyr} equal to a fixed value. Then, reasonable values for D^*_{sp} and D^*_{gr} were chosen and D^*_{alm} was varied until reasonable fits for both almandine and pyrope curves were found. Then D^*_{sp} and subsequently D^*_{gr} were found by fitting the spessartite and grossularite curves. Computed velocities varied erratically, and the effect of changing a particular ideal intrinsic coefficient could not be predicted. Moreover, computed velocities depend on the choice of dependent component. As a result, velocities were of little help in the fitting procedure. Justification for this fitting procedure is obvious from the sensitivity analysis discussed below.

Thermodynamic solution.—Figures 3 and 4 show data profiles and curves computed using non-ideal (N) and ideal (I) thermodynamic solution models for garnets representative of the two types of zoning analyzed. Non-ideal models were computed using the mobility model described in part I. A non-ideal model was fitted to the data using the procedure outlined above, then an ideal model was computed using the same ideal intrinsic diffusion coefficients. The figures illustrate the significant effect of the solution model on pyrope and almandine curves.

The difference in figure 3 is the result almost entirely of the interaction parameter between pyrope and almandine (3000 cal), because spessartite and grossularite contents are small, whereas the curves in figure 4 are affected in addition by the differential interaction between almandine-grossularite (1000 cal) and pyrope-grossularite (3800 cal). Hence, the ideal curves are symmetrically displaced from real ones in almandine and pyrope in figure 3, but pyrope is displaced more than almandine in figure 4. The symmetrical solution model of Ganguly and Kennedy (1974) was fitted to natural partitioning and experimental data for compositions up to 25 mole percent grossularite and has been shown to be a valid model for this compositional range by the experimental work of Newton, Charlu, and Kleppa (1977).

The importance of the solution model can be illustrated by fitting the natural data with an ideal-solution model. The ideal model for this example has curves almost identical to the real model, if ideal intrinsic coefficients are multiplied by the following factors: D^*_{alm}: 0.5; D^*_{sp}: 0.9; D^*_{gr}: 0.6 (table 2, run 70I). As discussed below, the values of D^*_{alm} and D^*_{gr} found using real and ideal models are significantly different. Nonideal solution is clearly an important consideration when diffusion, even of only two components, is analyzed in terms of mobilities.

Composition and temperature assumptions.—The effect of the choice of composition at which to compute constant diffusion coefficients is illustrated in figure 5. The normal procedure using an average composition between end points results in the central curves. Models were computed also using a composition displaced three-quarters of the interval between end compositions toward each end, shown as the other two curves in each graph.

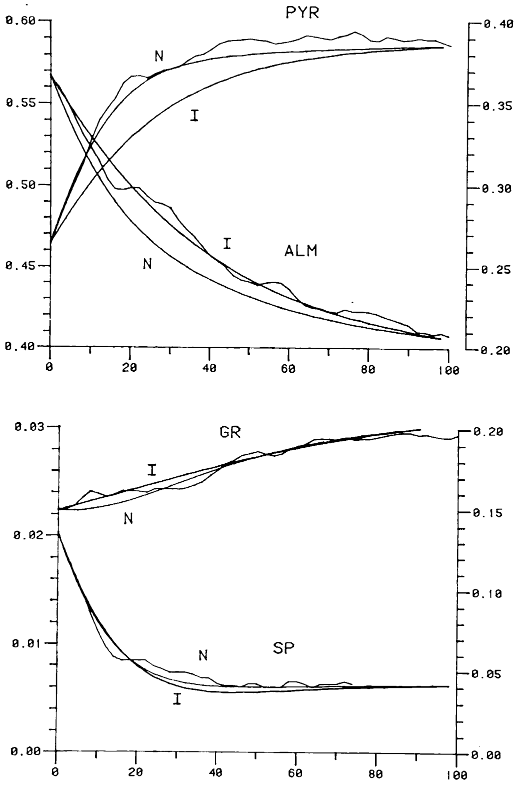

Fig. 4. Data and model zoning curves for profiles L208E. Axis labels as in figure 2. Non-ideal curves were computed in run L208E/22N. Note that almandine, pyrope, and grossularite have the same scale in this figure.

The compositional effect on almandine, pyrope, and grossularite is not significant. The effect on spessartite may require consideration, although note that this graph is vertically exaggerated relative to the others. A curve for spessartite computed taking into account composition change would vary from similarity to the lower curve near the margin to similarity to the upper curve toward the interior. Overall, the curve would resemble that computed using a slightly smaller D^*_{sp} (see fig. 8); the error is demonstrably less than a factor of 2 in this coefficient and little greater than the uncertainty of the data. Interestingly, a similar experiment on garnet L208E (data as in fig. 4) with larger grossularite variation showed almost no effect on any component curve.

A temperature is chosen to compute the solution model but has no direct effect on mobilities in the calculations, that is, D* and temperature are chosen independently. Temperature of calculation for all samples was 975°K, considered to be an average temperature of the range through which reactions occurred; however, as noted above, variation of diffusion coefficients among samples indicates that effective temperature was different. Figure 6 illustrates the fact that temperature variations of ± 100°K have little effect on the models, and choice of temperature is not an important consideration.

Analytical error.—All profiles shown were computed using 50 points in a finite-difference subroutine (model 2). Analytical precision as well as the correct functioning of the program was tested by computing two models using different dependent components. Transformed boundary conditions and eigenvectors depend on the dependent component, but the final computed curves were identical within plotter error. Some

TABLE 2

Ideal intrinsic diffusion coefficients ($\times 10^{17}$ cm^2/sec) and reaction times ($\times 10^{-5}$ yrs) for successful models. N: nonideal thermodynamic solution; I: ideal. Equivalent mobilities can be found by dividing D* by RT, where T is 975°K; the molar mobility corresponding to $D^* = 1 \times 10^{-17}$ cm^2/sec is 1.2×10^{-28} cm/sec dyne.

Profile	Run	D^*_{pyr}	D^*_{alm}	D^*_{sp}	D^*_{gr}	Time
L118A	52/N	0	50	5	15	1
	67/N	5	30	4	5	1
	71/N	7.5	15	2	>100	1
	68/N	10	10	2	>100	1
	70/I	0	25	4.5	9	1
L208E	22/N	0	1	0.1	0.6	1
	38/N	0.1	0.95	0.07	0.7	1
	39/N	0.3	0.7	0.06	0.8	1
	35/N	0.5	0.5	0.05	1	1
R118E	18/N	0	50	8	100	0.5
	19/N	5	20	6	100	0.5
	21/N	7.5	10	5	50	0.5
	22/N	9	9	4	40	0.5
L208H	13/N	0	1	0.03	0.4	0.7
	14/N	0.1	0.9	0.02	0.35	0.7
	15/N	0.5	0.5	0.004	0.6	0.7

binary models required up to 15,000 iterations for coefficients of 10^{-15} cm^2/sec.

Diffusion coefficients.—Sensitivity of models to ideal intrinsic coefficients was tested by using the fitted real model and varying one coefficient by a factor of 2 at a time. The influence of D^*_{alm} on diffusion curves is shown in figure 7. Varying D^*_{alm} by a factor of 2 has a large enough effect on almandine and pyrope curves to affect data fitting; larger variations would also significantly influence spessartite and grossularite. Variation of D^*_{sp} has an obvious effect on the spessartite curve but a detectable effect (not significant) on other curves only for pyrope (fig. 8). Similarly, a factor of two variation of D^*_{gr} has an important influence on the grossularite curve but a detectable impact only on pyrope of the other components (fig. 9).

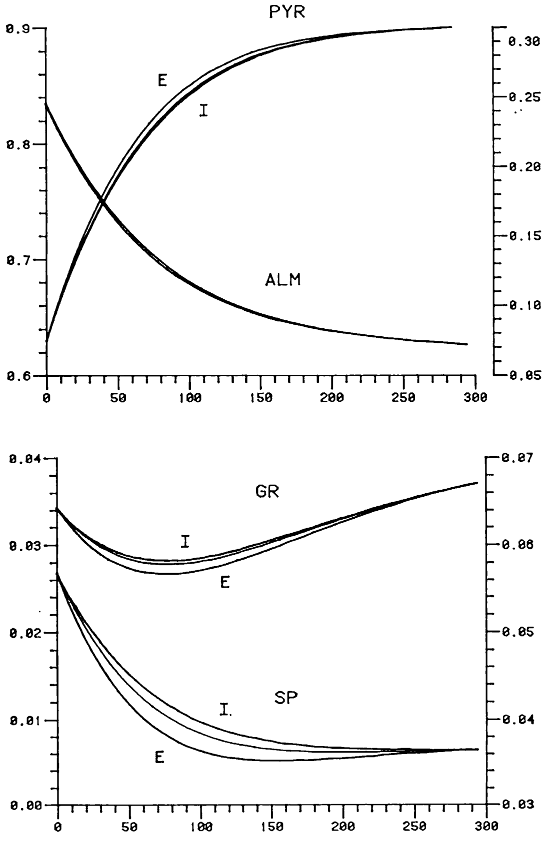

Fig. 5. Profiles computed for different compositions; same coordinates as previous figures. The central curve is the fitted model of figure 3, computed using the average composition. I curves were computed using a composition three-quarters of the difference between end points toward the interior composition; E composition is displaced a similar amount toward edge composition. All profiles are for non-ideal solution.

These experiments indicate that ideal intrinsic coefficients should be able to be fitted to these natural data within a factor of 2. It is necessary to fit almandine first, because it may have a significant influence on the other curves. Large variations of D^*_{sp} or D^*_{gr} could affect the pyrope curve.

Diffusion interaction among components depends on the absolute variation of each component. The same experiments performed on models of the second type of zoning (fig. 4, sample L208E) gave similar results, except that the influence of D^*_{gr} on pyrope was slightly greater. This result is expected, because the magnitude of grossularite zoning is greater in these garnets, and pyrope-grossularite mix least ideally ($W = 3800$ cal). Similarly, greater absolute zoning of spessartite could act to increase the influence of D^*_{sp} on pyrope profiles and vice versa.

The dominant interaction in these garnets is between pyrope and almandine. Interaction is in large part the consequence of mass balance

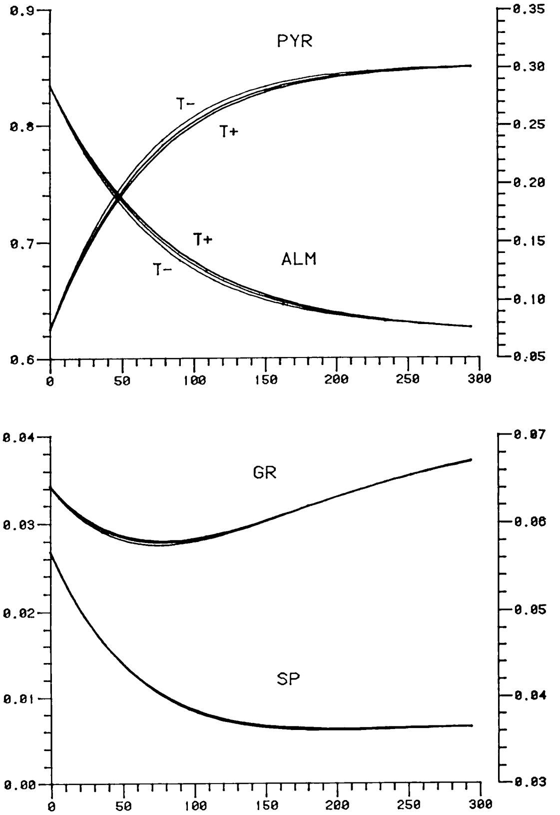

Fig. 6. Computed profiles for the non-ideal solution model based on different temperatures; coordinates as in previous figures. Central curve is the fitted model of figure 3. T+ curves were computed for a temperature 100°K higher (1075°K), and T− curves 100 K lower.

constraints, because partitioning of Fe and Mg between garnet and other phases was affected most by changing conditions, although non-ideal thermodynamic mixing ($W = 3000$) is also a measurable factor. Pyrope and almandine curves resemble mirror images, and changes in one curve are approximately symmetrically reflected in the other (see figs. 3, 4, and 7). Consequently, D^*_{alm} must be determined by fitting both the almandine and pyrope curves simultaneously; in most cases, a compromise value of D^*_{alm} was accepted that maximized the fit of both curves.

Pyrope.—All profiles could be approximated assuming D^*_{pyr} was zero. The pyrope coefficient proved to be the least sensitive parameter and was set to zero in the previous models to avoid using some arbitrary value of indeterminant significance. The magnitude of D^*_{pyr} was increased in a series of models for each garnet, as for other parameters, to test sensitivity. It was found that D^*_{pyr} had a detectable effect on all curves at a magnitude of approx $0.02\ D^*_{alm}$, although a significant

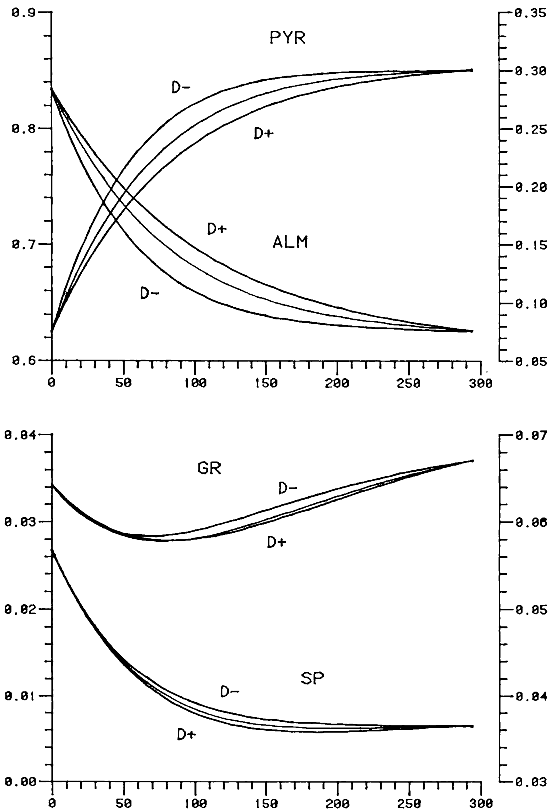

Fig. 7. Profiles computed for different D^*_{alm}; coordinates as in previous figures. Central curve is the fitted model of figure 3. D+ curves were computed for double D^*_{alm} and D− for one-half.

difference in fitting to natural data required values up to 0.1 D^*_{alm}. Thus, the models with D^*_{pyr} equal to zero are appropriate if D^*_{pyr} is more than an order of magnitude smaller than D^*_{alm}. Anderson and Buckley (1974, p. 48) suggest this is the case: "Moreover, at any temperature D^{*m}_{Ca} is about an order of magnitude greater than D^{*m}_{Mg} but is still significantly less than the diffusion coefficients of Fe or Mn" (D^{*m} are tracer diffusion coefficients in the molecular reference frame).

Modeling experiments were conducted to determine if larger values of D^*_{pyr} produced better fits to observed profiles. The effect of raising D^*_{pyr} is illustrated in figure 10. Displacement of the pyrope curve is reflected nearly symmetrically in almandine, having the same effect as changing D^*_{alm}. Spessartite is also displaced, but it is the effect of D^*_{pyr} on grossularite that proved most diagnostic. For models run with small but significant D^*_{pyr}, it was possible to recreate the initial fit by reducing other coefficients, as shown in table 2. The resulting models are so

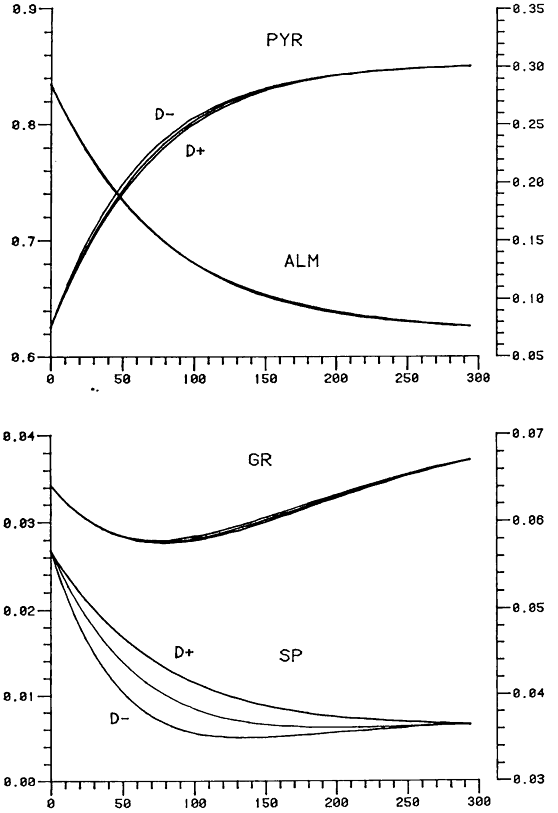

Fig. 8. Profiles computed for different D^*_{sp}; coordinates as in previous figures. Central curve is fitted model of figure 3. D+ curves were computed for double value of D^*_{sp} and D− for one-half.

similar to the initial ones that the relative quality of fit cannot be judged. However, increasing D^*_{pyr} until it is equal to D^*_{alm} usually required very large values of D^*_{gr} greater than D^*_{alm} to fit the grossularite curve (table 2).

These observations are not very restrictive and simply require that D^*_{pyr} be less than D^*_{alm} to avoid unreasonably large values of D^*_{gr}. As noted previously, if mechanistic models predicting the relative rates of diffusion are even approximately correct, D^*_{pyr} can be disregarded. As a practical consideration, it should be noted that the fact that these models are not sensitive to D^*_{pyr} renders this parameter unimportant in the interpretation of natural zoning profiles of garnet in pelitic rock. Determination of the magnitude of D^*_{pyr} will probably await experimental study.

DISCUSSION AND CONCLUSIONS

The foregoing analysis of the sensitivity of models computed according to the methods of part I has demonstrated that the choice of an

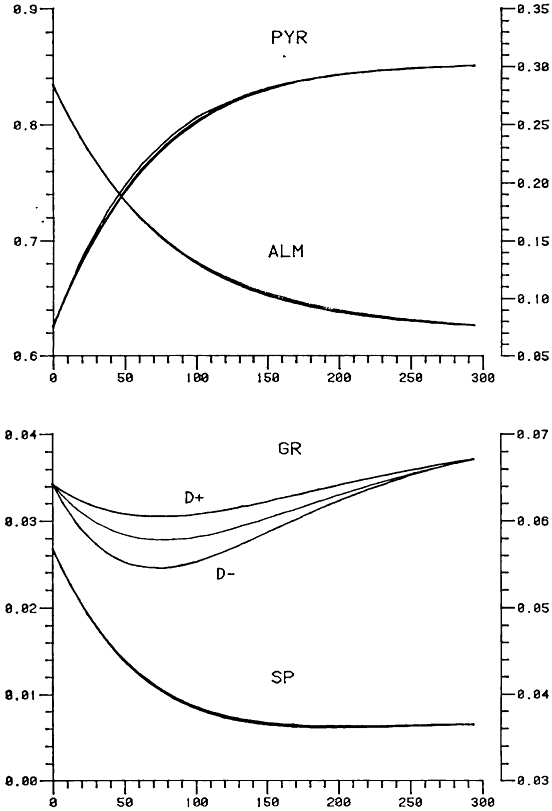

Fig. 9. Profiles computed for different values of D^*_{gr}; coordinates as in previous figures. Central curve is the fitted model of figure 3. D+ curves were computed for double the value of D^*_{gr} and D− for one-half.

average composition and approximate temperature to compute diffusion coefficients is probably sufficiently accurate for most naturally-occurring garnets. Of greater consequence is thermodynamic non-ideal mixing, even if only two components are diffusing. Strong thermodynamic interactions between almandine–pyrope, pyrope–spessartite, and pyrope–grossularite are partly responsible for the shape of diffusion curves, as can be seen in figures 3 and 4.

The reliability of the profiles analyzed was judged to decrease in the following order: L118A, L208E, R118A, L208H. A great deal more precision is necessary to compare absolute magnitudes of several profiles than is necessary simply to discuss trends or to fit binary models. In general, the poorly-known initial and boundary conditions of reaction are the limiting factors in natural samples, and experimentally produced profiles will probably be necessary to derive more accurate results.

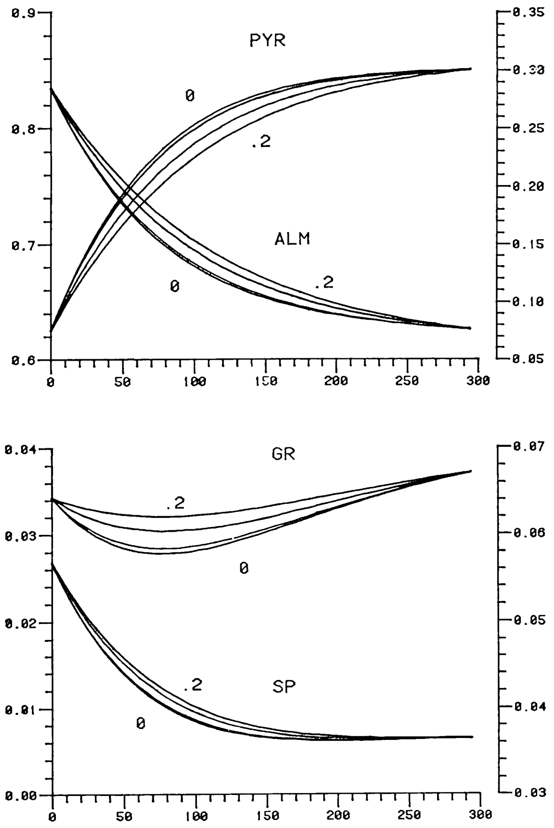

Fig. 10. Profiles computed for different D^*_{pyr}; coordinates as in previous figures. Zero curve is the fitted, non-ideal model of figure 3. Curves successively farther from the zero curve were computed using the following D^*_{pyr} as a fraction of D^*_{alm}: 0.02, 0.1, 0.2.

Profile L118A was assumed to have developed during the full reaction time of 10^5 yrs. Figure 3 demonstrates the overall fit of the curves is good, although the compensatory nature of pyrope and almandine curves required settling for a compromise value of D^*_{alm}. Flattening of these two data curves near the edge could be the result of changing temperature or even irregular movement of the microprobe stepping gears; a similar feature could not be produced in the models. Grossularite data were subject to large statistical error, but the upward concavity of the profile is distinct and is readily matched by the models.

Previous simulation of garnet zoning in this sample relied on a constant velocity model (model 1), because the relative importance of at least three simultaneous reactions had not been evaluated (Loomis, 1975). It has now been determined that only one reaction has a significant effect on garnet profiles (Loomis, 1978a), and it was possible to apply the more accurate model (2) in these calculations. It is interesting to attempt to fit the curves using model 1 and the diffusion coefficients found by model 2 to illustrate the difference between models. It was found for L118A that a constant velocity of 1×10^{-7} cm/yr was a compromise; faster velocities fit almandine and pyrope better, slower fit spessartite and grossularite better. This constant velocity is slower than the average predicted by model 2 by a factor of 3. It can be concluded that accurate determination of reaction boundary conditions and appropriate choice of binary models are prerequisites to interpretation of multicomponent diffusion curves.

It was assumed that profile L208E also developed in 10^5 yrs, because the other sample is much less reliable. Again, a compromise D^*_{alm} was necessary to approximate both almandine and pyrope curves, as shown in figure 4. Spessartite and grossularite fit satisfactorily considering the uncertainty of the data.

R118A curves could be accommodated using the same D^*_{alm} as L118A, if reaction time were shortened by one half to 5×10^4 yrs, an acceptable variation in a sample where some garnets reacted less than others (see Loomis, 1976). All profiles fit as well as in L118A, including grossularite which does *not* have the inflexion point found in L118A. As shown in table 2, however, it was necessary to use a larger value of D^*_{gr} and slightly larger D^*_{sp} than in L118A. The lower reliability of these profiles is due to cracks observed near the garnet edge and uncertainty as to their time of origin. The grossularite profile does appear to have a discontinuity that might be related to a cracking event; it seems to be anomalous (table 2).

The almandine curve of L208H could be matched well using the D^*_{alm} value used in L208E and a shorter reaction time. The pyrope curve is not well enough developed to provide a constraint. Spessartite is less certain than in L208E, and grossularite could only be approximated, because models have a small concavity that cannot be resolved from the measured data.

If reaction time is adjusted so that the same value of D^*_{alm} is applicable to profiles from the same sample, the accordance of other coefficients can be tested. D^*_{sp} is in good agreement between profiles of garnets in sample 118 and is a factor of 3 off between profiles of garnets in sample 208; the uncertainty is within the suggested precision of fitting (factor of 2). D^*_{gr} is consistent in 208 but in poor agreement in 118 owing to the anomalous value required for profile R118A. In view of the uncertainties of sectioning and surface irregularities, these data are reasonably consistent for each sample, except for grossularite in R118A.

The relative magnitude of ideal intrinsic diffusion coefficients is expressed in table 3. As discussed previously, the relative magnitude of D^*_{pyr} cannot be delimited, other than to require that it be less than D^*_{alm}. Two values are given for each ratio in each sample in table 3; the first is for satisfactory models with D^*_{pyr} equal to zero, and the second is for models with D^*_{pyr} equal to 0.1 D^*_{alm} of the first model. These two models represent probable extremes, if D^*_{pyr} is an order of magnitude or more less than D^*_{alm}.

Placing emphasis on the best profiles, L118A and L208E, it may be concluded from table 3 that the mobility of the spessartite component in garnet is about an order of magnitude less than that of almandine. Data for grossularite are less consistent but can probably be interpreted to indicate that the mobility of grossularite is greater than spessartite and less than almandine; a value of a quarter or a half of D^*_{alm} would probably be satisfactory for modeling. Deduced relative magnitudes of coefficients are in general agreement with the predictions of Anderson and Buckley (1974, p. 48), except that grossularite is probably more mobile than spessartite. These ratios must be approximate, because they apply to a range of temperature represented by an absolute change of D^*_{alm} of a factor of 50. More precise coefficients will probably be derived only from analysis of experimental multicomponent profiles.

Overall, it is admissable to conclude that the multicomponent zoning profiles in these natural garnets can be modeled remarkably well considering the uncertainties of measurement and boundary conditions. I believe it is even possible to say that there are spectacular successes, such as the fit of grossularite in figure 3. This is a classic case of "uphill" diffusion, brought about by multicomponent interactions. Several inter-

TABLE 3

Ratios of ideal intrinsic coefficients. Top row shows ratios for models with $D^*_{pyr} = 0$; bottom row is for models with $D^*_{pyr} = 0.1\ D^*_{alm}$ of corresponding top row.

Ratio	L118A	L208E	R118A	L208H
$\frac{D^*_{sp}}{D^*_{alm}}$	0.1	0.1	0.2	0.03
	0.1	0.1	0.3	0.02
$\frac{D^*_{gr}}{D^*_{alm}}$	0.3	0.6	2	0.4
	0.2	0.7	5	0.4

pretations in the literature and my own prejudice were that Ca has a very low mobility in garnet because zoning curves are often irregular. These models demonstrate, however, that the mobility of Ca is probably second only to Fe, and that the irregular curves commonly found are the result of complex thermodynamic and fluid dynamic interactions among components. It is clear that these interactions cannot be intuitatively assessed: interpretation requires application of models of the type used in this work.

It should be possible to evaluate the applicability of diffusion models to explain geologic observations or to simulate geologic processes using these conclusions. Boundary conditions can be incorporated into the solution of an interdiffusion equation, and only rough estimates of temperature and an average composition are necessary to compute multicomponent models. For most situations, it may be possible to set D^*_{pyr} equal to zero. It should then be possible to satisfy the data or model a process by assuming that D^*_{sp} is an order of magnitude less than D^*_{alm}, and that D^*_{gr} is roughly one half of D^*_{alm}. When the temperature dependence of these coefficients has been determined experimentally, it will be possible to model variable temperature processes by iteration using these models.

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