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# MULTICOMPONENT DIFFUSION IN GARNET: I. FORMULATION OF ISOTHERMAL MODELS

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ABSTRACT. Compositional zoning in garnet is an important source of information about the history of a rock, because diffusion is not effective at changing compositions formed at moderate temperature. However, when diffusion must be considered at high temperatures, the complexity of composition of garnet solid solution and interest in the zoning pattern of minor components such as spessartite increase the possible significance of diffusion cross coefficients. The objective of this paper is to review a convenient procedure for computing diffusion profiles in multi-component systems that takes into account cross coefficients.

Theoretical constraints of irreversible thermodynamics and frames of reference limit the number of independent diffusion coefficients. The thermodynamic solution model of Ganguly and Kennedy (1974) is used to constrain the diffusion matrix of garnet. While the mean volume reference frame is a good choice for garnet, the error introduced by using the mean molar reference frame is not significant in view of the uncertainties of data, and this reference frame is used in the model. Transformations of reference frame and dependent component are given so that diffusion coefficients assumed in this and subsequent papers can be compared with other simulations and experiments.

A standard computational procedure using eigenvector analysis that is quite general is outlined and enables one to use mathematical solutions for the binary diffusion model appropriate to the specific diffusion problem. The only limiting approximation is that diffusion coefficients are constant over the compositional range of interest and specific reference frame. This procedure is applied in a subsequent paper to compute models that are compared with zoning profiles from rocks. A FORTRAN IV program that can be adapted to a wide variety of problems involving diffusion in garnet is available.

## GENERAL NOTATION

$A$ — transformation matrix to form conjugate forces (see eq 13 and following).
$B^{rp}_{ij}$ — element of transformation matrix from reference frame p to r.
$C$ — total concentration (moles/cm$^3$).
$C_j$ — concentration of component j.
$D^*_i$ — ideal intrinsic diffusion coefficient, defined by eq 23.
$D'_{ij}$ — uncontracted diffusion coefficient in absolute reference frame.
$D^{r\prime}_{ij}$ — uncontracted diffusion coefficient in reference frame r.
$D^r_{ij}$ — diffusion coefficient for the r reference frame.
${}^nD^r_{ij}$ — diffusion coefficient assuming n to be a dependent component.
$G^{ex}$ — excess Gibbs free energy (in this case, enthalpy) of mixing in aluminous garnets.
$G^r_{ij}$ — see eq 15.
$I$ — identity matrix.
$J_i$ — flux of component i in moles/cm$^2$-sec.
$J^r_i$ — flux of i with respect to mean velocity reference frame r.
$L^r_{ij}$ — phenomenological coefficient corresponding to reference frame r.
$N$ — total moles in system.
$n_j$ — moles of component j.
$n$ — last component (usually 4th).

$q_i$ — mobility of component i.
R — gas constant.
$R$ — matrix with normalized eigenvectors as columns.
T — absolute temperature (°K).
$v^r$ — velocity of reference frame r with respect to absolute (laboratory) coordinates.
$v_i$ — absolute velocity of component i.
$\bar{V}$ — molar volume.
$\bar{V}_i$ — partial molar volume of component i.
$X_i$ — mole fraction of component i.
$\delta_{ij}$ — Kronecker delta ($\delta_{ij}=1$, $i=j$, $\delta_{ij}=0$, $i\neq j$).
$\gamma_i$ — activity coefficient of component i.
$\sigma$ — ' local" entropy production.
$\mu_i$ — chemical potential of component i.

MATHEMATICAL NOTATION

$\widetilde{Z}$ — transpose of matrix $Z$.
$Z^{-1}$ — inverse of matrix $Z$.
$\frac{\partial}{\partial t}$ — "local" derivative at a point fixed in the absolute reference frame.
$\frac{d^r}{dt}$ — substantial derivative at a point moving with flow of reference frame r.
• — dot (inner) vector product.
$\nabla$ — gradient operator.
div — divergence operator ($\nabla \cdot$).

INTRODUCTION

Compositional zoning in garnet crystals is a primary source of information about the history of a rock sample because diffusion is less effective at modifying garnet compositions than it is in most other minerals. In addition, stoichiometric compositional controls of garnet allow a wide range of compositional variation that is related to growth history and is able to record changing conditions of temperature, pressure, and bulk composition of the system.

Garnet composition is a function of all these variables. Growth without reequilibration of earlier-formed garnet can result in depletion effects of inert components, even if partitioning is constant. A change of intensive variables can affect partitioning between garnet and other phases or force compositional change through divariant reactions. Finally, disequilibrium growth may involve the processes of surface kinetics as variables.

In view of the above complications, a great deal of information must be available about a sample to interpret garnet zoning, even if garnet, once formed, becomes chemically inert. In fact, diffusion is an active process at high temperature, and one must add the effects of diffusion within garnet as another variable in the list above. Diffusion will

affect the composition retained by growing garnet in a changing chemical environment, as well as modify previously-crystallized compositions. Evidence of diffusion in natural garnet has been presented (Chinner, 1962; Evans and Guidotti, 1966; de Bethune and others, 1968; Kwak, 1970; Grant and Weiblen, 1971; Hess, 1971; Mueller and Schneider, 1971; Loomis, 1972, 1975; Arkai, Nagy, and Panto, 1975; de Bethune, Laduron, and Bocquet, 1975; Woodsworth, 1977), and some diffusion models considered (Anderson and Buckley, 1973, 1974; Loomis, 1975, 1977; Lasaga, Richardson, and Holland, 1977), but the significance of diffusion cross coefficients has not been evaluated.

While the multicomponent character of garnet composition is an asset, it also complicates analysis of diffusion. If a usually minor component such as spessartite is of interest, then even small cross-coupling with a major diffusing component can be significant, as noted by Anderson and Buckley (1973). In view of the emphasis placed on spessartite in the analysis of garnet zoning, it is worthwhile to consider cross-coupling effects with the major components almandine and pyrope. The necessity of considering cross-coupling when analyzing the diffusion of minor components in garnet is demonstrated in part 2. Thermodynamic mixing models for garnet (Ganguly and Kennedy, 1974) suggest that interaction between pyrope and spessartite may be significant.

The purpose of these papers is to model multicomponent diffusion within garnet using estimated diffusion coefficients and compare the morphology of computed compositional profiles with natural samples to determine the importance of diffusion cross coefficients. Eventually, experimental data will be available and can be evaluated using these models. In view of the applied objective of this review, I will concentrate on parameters that can be measured directly by experiment by comparison of models with natural examples. Transformations are considered to determine what simplifications are appropriate and to enable comparison of experimental (including simulation) results. Mechanistic models of diffusion in garnet have been evaluated critically in the excellent reviews by Anderson and Buckley (1974) and Anderson (1976); these models are not considered here.

Similarly, it is not my intention to review completely the subject of diffusion, many aspects of which are of limited applicability considering the paucity of data available and, particularly, the eventual application to poorly constrained geologic systems. It may be necessary to evaluate many compositionally and directionally dependent parameters to model diffusion fully, but for purposes of predicting reaction rate or grain orientation by recrystallization in heterogeneous rocks under poorly defined T and P conditions, simple approximations are appropriate. An effort is made in this work to justify simplifications without succumbing to the temptation to indulge in details far beyond the present data; the application of an elegant theory to a practical geological problem is a controvertible endeavor. Some simplifying assumptions are made ini-

tially. Garnet is assumed to be in thermal and mechanical equilibrium without temperature or pressure gradients. Crystals are supposed to be isotropic with respect to diffusion. Only aluminous garnets found in pelitic and basic rocks are specifically considered as examples.

While the following analysis is aimed at modeling diffusion in garnet, it is obvious that most of the procedures are generally applicable.

## MULTICOMPONENT DIFFUSION

*Fick's Law.*—Fick's law is of basic importance because compositions and composition gradients are the measured quantities in nature. Allowing for cross-coupling between n components in a substance, Onsager (1945) generalized Fick's law to

$$J_i = -\sum_{j=1}^{n} D'_{ij} \nabla C_j , \tag{1A}$$

where $J_i$ is the flux of component i (moles/cm$^2$-sec), $D'_{ij}$ are diffusion coefficients, and $\nabla C_j$ is the spatial gradient of composition, all measured with respect to an absolute or laboratory reference frame. Composition C is assumed to be concentration (mole/cm$^3$) but could be mass density (g/cm$^3$). It is convenient to formulate the flux eq (1A) in contracted form using a mean velocity reference frame r (de Groot and Mazur, 1962, p. 240) as follows:

$$J^r_i = -\sum_{j=1}^{n-1} D^r_{ij} \nabla C_j . \tag{1B}$$

The flux equations can be operated upon by a continuity equation (substantial derivative of fluid dynamics) to obtain the instantaneous compositional change at a point moving with the mean velocity reference frame (denoted $d^r/dt$)

$$\frac{d^r C_i}{dt} = -\text{div } J^r_i - C_i \text{ div } v^r, \tag{2A}$$

where the operator div is divergence and $v^r$ the velocity of the reference frame r with respect to the absolute or laboratory frame. Eq 2A is analogous to eq 10 in de Groot and Mazur, 1962, p. 13. Eq 2A can also be written in the mean molar reference frame (m)

$$\frac{d^m X_i}{dt} = -\frac{1}{C} \text{ div } J^m_i , \tag{2B}$$

where X is mole fraction and C total concentration or "molar density"; this equation is analogous to eq 13 of de Groot and Mazur, 1962, p. 13. Eq 2B is useful if C is constant, that is, if the partial molar volumes of components over the compositional range of interest are equal. Alterna-

tively, the compositional change at a point fixed with respect to an absolute reference frame is given by

$$\frac{\partial C_i}{\partial t} = \frac{d^r C_i}{dt} - v^r \cdot \nabla C_i . \qquad (2C)$$

These equations can be integrated using boundary conditions appropriate to the problem to find concentrations as functions of time and space. Integration is often not difficult in a binary system (n=2), because mass balance constrains diffusion coefficients to a single matrix element. Problems related to anisotropy, composition dependence, and moving reference frames still complicate analysis. Eqs 2, where referring to a multicomponent system, are difficult to evaluate.

*Components.*—In principle, one can choose any components to describe the system. However, a number of constraints that will relate components exist, and it is easiest to eliminate such dependencies at the outset.

Garnet solid solutions of interest here are described in terms of the components pyrope, almandine, grossularite, and spessartite. Actual diffusion probably involves motion of ions of Mg, Fe, Ca, and Mn, but stoichiometric constraints and local charge balance render fluxes of ions dependent. In addition, the chemical potential of ions cannot be evaluated independently of stoichiometric components. Similarly, oxide components are dependent by stoichiometric constraints of the garnet structure.

Composition of a system is most easily measured in terms of intensive variables. In particular, mineral analyses are usually reported as mole fractions rather than mass fractions or concentrations. It will be convenient to formulate the diffusion equations in terms of mole fractions if possible. Mole fractions of the stoichiometric components are not all independent, being related by mass balance. This remaining dependency will be eliminated below.

*Frames of references.*—Eqs 2 are difficult to solve if the absolute laboratory reference frame is different from the mean velocity reference frame used to define diffusion coefficients. It is most convenient to perform experiments or, in our case, to compute composition profiles in a mean velocity reference frame that closely approximates the absolute reference frame. In other words, it is desirable to find a mean velocity $v^r$ that is approximately zero in the absolute frame of measurement. Diffusion coefficients in any mean velocity reference frame can be related to those used in the chosen frame by transformations discussed below.

The mean volume velocity reference frame is useful for garnet diffusion, because the mean volume velocity of garnet approximately vanishes. Fluxes in the volume frame are

$$J^V_i = C_i (v_i - v^V),$$

where $v_i$ is the absolute velocity of component i, and $v^V$ the mean volume

velocity relative to the absolute frame of reference. The mean volume velocity is found by setting the total flux of volume equal to zero:

$$\bar{V}\, J^v = \sum_{i=1}^{n} \bar{V}_i\, J^v{}_i = 0$$

$$v^v = \sum_{i=1}^{n} C_i \bar{V}_i v_i.$$

$\bar{V}_i$ is the partial molar volume of component i, and $\bar{V}$ the molar volume of garnet of the composition of interest, that is, at the point of interest.

The mean volume velocity $v^v$ vanishes if partial molar volumes are constant, that is, if there is no volume of mixing, as shown by de Groot and Mazur (1962, p. 256). Regression analysis of natural garnets by Novak and Gibbs (1971, p. 817) indicates that the molar volume of garnet can be taken as linearly dependent upon end-member volumes. Then eq 2A is equivalent to 2C and can be integrated using appropriate boundary conditions.

A further simplification may be possible for some problems. Eq 2B is particularly simple if the overall concentration

$$C = \frac{1}{\bar{V}}$$

remains approximately constant. In that case, the mean molar velocity

$$v^m = \sum_{i=1}^{n} X_i\, v_i$$

vanishes, and the mean molar fluxes

$$J^m{}_i = -\sum_{j=1}^{n-1} D^m{}_{ij}\, \nabla C_j$$

become identical with absolute fluxes. Substituting this flux equation into 2B, we have

$$\frac{\partial X_i}{\partial t} = \frac{d^m X_i}{dt} = \operatorname{div} \sum_{j=1}^{n-1} (D^m{}_{ij}\, \nabla X_j), \tag{3}$$

where the mean molar frame (m) and absolute frame are identical. Eq 3 is convenient, because microprobe analyses are reported in mole fraction, and thermodynamic mixing models of garnet usually utilize mole fraction rather than concentration; microprobe zoning profiles can be modeled directly without conversion to concentration.

Eq 3 is applicable, if the mean molar volume is constant during the diffusion process, which, in turn, requires that molar volumes of end-members are identical. The molar volumes (in $cm^3$ at 25°C, normalized to one exchangeable cation) of pyrope (37.9), almandine (38.4), and spessartite (39.4), are probably close enough to be considered equal, especially if the absolute variation of mole fraction of spessartite is small as is commonly the case. Grossularite (41.8) has a slightly larger volume, and approximation (3) is useful, if precise data are available, only for models in which grossularite variation is small. For our purposes, the mean molar reference frame is a reasonable approximation to the mean volume and absolute reference frames, and eq 3 will be used in the examples of part 2.

A different reference frame that would be useful is the lattice-fixed frame, denoted by *l*. Garnet could be considered to comprise the components $Mg^{2+}$, $Fe^{2+}$, $Ca^{2+}$, $Mn^{2+}$, and $Al_2Si_3O_{12}{}^{6-}$, the latter being the "lattice". Fluxes and gradients could be measured with respect to this lattice as the "*l*th" component of reference. The reference velocity, $v_l$, represents motion of the Al–Si–O lattice.

As noted above when the choice of components was considered, stoichiometric requirements constrain some components. In this case, the mole fraction of lattice component $X_l$ must remain constant to maintain stoichiometry, and the gradient of the mole fraction of this component is zero. It is apparent from eq 3 that these conditions are fulfilled in the mean molar reference frame, and the lattice-fixed reference frame is identical to the mean molar reference frame for garnet.

*Independence of diffusion coefficients.*—By analogy with Fick's law (eq 1A), the flux equations in the mean molar velocity reference frame could be written

$$J^m{}_i = -\sum_{j=1}^{n} D^{m\prime}{}_{ij} \nabla C_j .$$

However, both fluxes and concentration gradients are dependent in the mean molar (or other mean velocity) reference frame as reviewed by Brady (1975a). Concentration gradients are dependent by mass balance

$$\sum_{i=1}^{n} \nabla C_i = \nabla C = 0 , \tag{4}$$

and fluxes are related by

$$\sum_{i=1}^{n} J^m{}_i = 0 . \tag{5}$$

Applying (4) to eliminate the nth component as a dependent component, the fluxes of eq 1A can be written in the form (1B)

$$J^{m}_{i} = -\sum_{j=1}^{n-1} (D^{m'}_{ij} - D^{m'}_{in}) \nabla C_j$$
$$= -\sum_{j=1}^{n-1} D^{m}_{ij} \nabla C_j . \qquad (6)$$

Only the $D^{m}_{ij}$ coefficients are independent. In this paper, following de Groot and Mazur (1962, p. 244), diffusion coefficients will be taken as the (n−1) independent coefficients (1B) for (n−1) independent fluxes.

Dependence of fluxes and gradients means that only n−1 components are explicitly considered; one component is chosen as a dependent variable. Thus, the diffusion coefficients reported depend upon the particular component chosen as the dependent variable. In addition, the $(n-1)^2$ independent diffusion coefficients depend upon the choice of reference frame and the compositional parameters used to describe the system. Transformations of diffusion coefficients to other systems using a different dependent component or reference frame are considered below.

*Transformations.*—The diffusion coefficient utilized in these papers refers to the mean molar velocity reference frame and grossularite as the dependent component. It is necessary to present transformations so that the coefficients used in part 2 can be compared with "standard" coefficients reported for the mean volume reference frame or those derived using dependent components other than grossularite. The coefficients can be transformed to a system considering another component as dependent by using equations of molar balance. If diffusion coefficients are based on dependence of component p, coefficients dependent on component n can be found from relations based on eqs 5 and 6:

$$^{n}D^{m}_{ij} = {}^{p}D^{m}_{ij} + {}^{n}D^{m}_{ip} \qquad (7)$$
$$^{p}D^{m}_{ip} = {}^{n}D^{m}_{in} = 0$$
$$^{n}D^{m}_{nj} = -\sum_{i=1}^{n-1} {}^{n}D^{m}_{ij}$$
$$^{p}D^{m}_{pj} = -\sum_{i=1}^{n} {}^{p}D^{m}_{ij} \; (i \neq p),$$

where superscripts p and n refer to the dependent component. These constraints can be solved for the new set of coefficients in terms of the old ones.

Diffusion coefficients measured in one reference frame are not necessarily equivalent in other frames. We have shown that diffusion in aluminous garnets can be evaluated in terms of a mean volume reference

frame and may be approximated by the mean molar reference frame. The error inherent in the use of the mean molar frame can be evaluated by noting the difference in the set of diffusion coefficients in the two frames of reference.

Define a transformation matrix $B^{Vm}$ (after de Groot and Mazur, 1962, p. 243) such that

$$J^V = B^{Vm} J^m \tag{8}$$

for independent fluxes (1B). Elements of matrix $B$ are given by de Groot and Mazur (1962, p. 243):

$$B^{Vm}{}_{ij} = \delta_{ij} + \frac{(\bar{V}_n - \bar{V}_j)}{\bar{V}} X_i. \tag{9}$$

The transformation of the diffusion coefficient matrix is found using matrix equations equivalent to (1B), setting compositional gradients equal, and substituting (8):

$$D^V = B^{Vm} D^m.$$

This transformation is valid for n−1 independent diffusion coefficients defined according to (1B).

One can see by substituting realistic values of molar volumes into eq 9 that transformation from mean molar to mean volume reference frames for garnet results in differences of at most a few percent. Note that transformation, in the general case, does depend on composition. Diffusion coefficients compositionally independent in one reference frame will be compositionally dependent in another. These differences related to frame of reference are not significant in view of other assumptions and the present lack of data. Ignorance of the compositional dependence of diffusion coefficients and the assumption of constant eigenvectors (discussed below) are probably far more important approximations.

## IRREVERSIBLE THERMODYNAMICS FORMULATION

The previous development of diffusion theory is probably sufficient to model diffusion in garnet, if data were available. The theory of irreversible thermodynamics is useful for one reason in this problem: the Onsager reciprocal relations. The theory, excluding the extension to linear phenomenological coefficients, is widely applicable, but the most useful aspect, the assumption that a process can be represented by a set of equations involving only linear terms, is valid for diffusion or only very near equilibrium for chemical reactions (de Groot and Mazur, 1962, p. 206). I will assume that linear phenomenological coefficients can be applied to this problem of diffusion because the energy gradients (forces) are small.

The formalism of multicomponent diffusion has been available for many years and is found in a number of textbooks. The primary reference used here is de Groot and Mazur (1962). Reviews of this subject have appeared in geologic literature in recent years (for example, Fisher, 1973; Anderson and Buckley, 1974; Brady, 1975a,b). Only the basic points applicable to diffusion in garnet are considered here briefly.

*Forces and fluxes.*—The theory can be related to the standard thermodynamic concept of a potential energy function that represents the potential energy available to do work, for example, to drive diffusion. Two assumptions are required (de Groot and Mazur, 1962, p. 20-24) involving the existence of thermodynamic functions and the sources of entropy change at a point.

Using continuity balance equations, these two assumptions can be compared to yield, at uniform T and P:

$$T\sigma = -\sum_{i=1}^{n} J^{r}_{i} \nabla \mu_i, \tag{10}$$

where $\mu_i$ is chemical potential, and $\sigma$ represents the irreversible creation of entropy. The creation of entropy is related to the flow of matter through a potential energy gradient (force).

If the creation of entropy is considered to be the fundamental quantity that measures the progress of an irreversible process, then any choice of flux and force is acceptable as long as the product is $T\sigma$. Forces and fluxes that satisfy this relation can be transformed to new frames of reference using (10) as a constraint. In general, transformation of fluxes from one reference frame to another will require finding new forces, called forces conjugate to the fluxes, such that (10) holds.

Before transformations are considered, the phenomenological coefficients are introduced. The symmetry properties of these coefficients are the primary purpose of introducing the theory. The general assumption is that fluxes are proportional to forces in the system, so that

$$J_i = -\sum_{j=1}^{n} L_{ij} \nabla \mu_j , \tag{11}$$

where $L_{ij}$ are the phenomenological coefficients. As noted above, a linear relationship between forces and fluxes may be valid for diffusion but is probably not valid for heterogeneous reactions.

The usefulness of (11) in our problem is based on the theory that the matrix of phenomenological coefficients, known as the Onsager reciprocal relations (ORR) (Onsager, 1931), is symmetrical. This assumption is valid only if certain conditions are met. Both fluxes and forces in (10) are dependent in any reference frame. As shown by de Groot and Mazur (1962, p. 67-69), if both fluxes and forces are dependent, the ORR are not necessarily valid because the coefficients are not uniquely defined. However, one can choose coefficients so that the ORR are valid by adding appropriate constraints, as detailed by de Groot and Mazur (1962, p. 68-69). Therefore, it is necessary to consider a particular system of fluxes and forces to determine whether ORR are valid.

*Independent fluxes and forces.*—Fluxes are dependent in any frame of reference, as considered above. For the mean molar frame of refer-

ence, eq 5 relates the fluxes. Thermodynamic forces are also dependent by virtue of Gibbs-Duhem relations:

$$\sum_{i=1}^{n} X_i \nabla \mu_i = 0 . \tag{12}$$

Consequently, these fluxes and forces satisfy the requirement (10), but the ORR are not necessarily satisfied.

Using (5) and (12) to eliminate the nth force and flux as dependent, one finds new forces "conjugate" to the independent fluxes so that the entropy production remains invariant:

$$T\sigma = \sum_{i=1}^{n-1} J^m{}_i \overline{X}^m{}_i ,$$

where

$$\overline{X}^m{}_i = - \sum_{j=1}^{n-1} \left( \delta_{ij} + \frac{X_j}{X_n} \right) \nabla \mu_j \tag{13}$$

(de Groot and Mazur, 1962, derive this transformation in general, p. 241). Then the phenomenological relations (11), using independent fluxes and forces become:

$$J^m{}_i = \sum_{j=1}^{n-1} L^m{}_{ij} \overline{X}^m{}_j . \tag{14}$$

In matrix notation, let relation (13) be given as

$$\overline{X}^m = -A^m \nabla \mu$$

and (14) as

$$J^m = L^m \overline{X}^m .$$

If the ORR hold for independent forces and fluxes in one reference frame, they hold in other reference frames. The ORR are assumed to be valid in any reference frame, if fluxes are linear functions of forces, at least fluxes or forces form an independent set, and entropy production remains invariant under reference frame transformation. We will assume that the ORR are valid for independent forces and fluxes in the mean volume and mean molar velocity reference frames for garnet.

*Irreversible thermodynamic constraints on D.*—Thermodynamic forces can be expanded in terms of measurable quantities such as mole fractions:

$$\nabla \mu_i = \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial X_j} \nabla X_j .$$

In matrix notation

$$\nabla\mu = \mu\ \nabla X.$$

Independent forces become

$$\begin{aligned}\bar{X}^m &= -A^m\ \nabla\mu \\ &= -A^m\ \mu\ \nabla X\ .\end{aligned}$$

The product $A^m\ \mu$ is called $G^m$ by de Groot and Mazur (1962, p. 245). They further show that $G^m$ is always symmetrical, although $\mu$ may not be. In this reference frame,

$$\begin{aligned}G^m{}_{ij} &= \sum_{k=1}^{n-1}\left(\delta_{ik} + \frac{X_k}{X_n}\right)\frac{\partial\mu_k}{\partial X_j} \\ &= \frac{\partial\mu_i}{\partial X_j} + \frac{1}{X_n}\sum_{k=1}^{n-1} X_k\frac{\partial\mu_k}{\partial X_j}.\end{aligned}$$

This expression can be simplified by using a Gibbs-Duhem expression at constant T and P:

$$\sum_{k=1}^{n} X_k\frac{\partial\mu_k}{\partial X_j} = 0.$$

Then

$$G^m{}_{ij} = \frac{\partial}{\partial X_j}(\mu_i - \mu_n). \tag{15}$$

Both terms are compositionally dependent, even with ideal solution; therefore $G^m$ is generally compositionally dependent.

The expression for fluxes using diffusion coefficients must be equivalent to the thermodynamic expression. The only restrictions when comparing matrices is that the same component be taken as dependent in both formulations and the same frame of reference be used. Then, using independent fluxes,

$$J^m = -D^m\ \nabla X = -L^m\ G^m\ \nabla X.$$

The comparison yields the relation

$$D^m = L^m\ G^m.$$

If the ORR hold for the independent system and $L^m$ is symmetrical, we have the constraint on the diffusion coefficients that we are after (Onsager, 1945, p. 246; de Groot and Mazur, 1962, p. 246):

$$D^m = G^{m-1}\ \widetilde{D^m}\ G^m\ . \tag{16}$$

The usefulness of relation 16 is apparent from the fact that it constrains the elements of $D$ without explicitly computing $L$. The phenom-

enological coefficients are theoretically useful in this way, even though they must be extremely sensitive to composition if diffusion coefficients are not to vary markedly.

Eq 16 provides three constraints on the nine elements of $D$ in a four component system; thus, only six independent elements must be specified. However, the constraints of (16) are not general but limit only particular elements of the matrix. Specifically, the three diagonal elements and three off-diagonal ones on the same side must be given to solve the remaining three off-diagonal elements. Solution of (16) for a complete $D$ that satisfies the ORR from six input coefficients is one option of the modeling procedure.

It must be noted that $L$, $G$, and $D$ are compositionally dependent (Gupta and Cooper, 1971). However, as the compositional variations of interest become smaller, the assumption of a compositionally independent $D$ becomes justifiable (Cooper, 1974, quoting Sauer). It will be necessary to approximate $D$ as constant for a small compositional range of interest. In view of the uncertainty of the values of diffusion coefficients, especially for garnet, and the small compositional range of interest in most natural rocks, this approximation is probably not too restrictive.

## SOLUTION MODEL

The garnet solution considered here is taken to include four end-member components: pyrope (py), almandine (al), spessartite (sp), and grossularite (gr), formulas normalized to one exchangeable cation. Grossularite is chosen as the "nth" or dependent component in the flux equations.

Chemical potential of component j is calculated from the formula

$$\mu_j = \mu^*_j + RT\ln X_j + RT\ln\gamma_j \tag{17}$$

where $\mu^*_j$ is the molar free energy of the pure end-member with one divalent cation at the T and P of interest, and $\gamma_j$ is the activity coefficient corresponding to the excess free energy of mixing ($G^{ex}$) at T and P. The excess free energy of mixing in N moles of divalent cation in garnet is approximated by a symmetrical solution model by Ganguly and Kennedy (1974, p. 139):

$$\begin{aligned} G^{ex} = {} & \frac{n_{al}\, n_{py}}{N} W_{al\text{-}py} + \frac{n_{al}\, n_{gr}}{N} W_{al\text{-}gr} \\ & + \frac{n_{al}\, n_{sp}}{N} W_{al\text{-}sp} + \frac{n_{py}\, n_{gr}}{N} W_{py\text{-}gr} \\ & + \frac{n_{py}\, n_{sp}}{N} W_{py\text{-}sp} + \frac{n_{gr}\, n_{sp}}{N} W_{gr\text{-}sp}, \end{aligned}$$

where W is an interaction parameter, $n_j$ moles of component j, and N total moles. The activity coefficient for each component is found by differentiating the excess free energy term:

$$RT\ln\gamma_j = \frac{\partial G^{ex}}{\partial n_j} = \frac{\partial G^{ex}}{\partial N}\frac{\partial N}{\partial n_j} + \frac{\partial G^{ex}}{\partial n_j}. \tag{18}$$

Terms of the $G^m$ matrix are found using (15), (17), and mass balance, remembering that $X_n$ is a dependent variable:

$$\begin{aligned} G^m{}_{ij} &= \frac{\partial}{\partial X_j}(\mu_i - \mu_n) \\ &= \frac{\partial \mu_i}{\partial X_j} + \frac{\partial \mu_i}{\partial X_n}\frac{\partial X_n}{\partial X_j} - \frac{\partial \mu_n}{\partial X_j} - \frac{\partial \mu_n}{\partial X_n}\frac{\partial X_n}{\partial X_j} \\ &= \delta_{ij}\frac{RT}{X_j} + \frac{RT}{X_n} + \frac{\partial}{\partial X_j}(RT\ln\gamma_i) \\ &\quad - \frac{\partial}{\partial X_n}(RT\ln\gamma_i) - \frac{\partial}{\partial X_j}(RT\ln\gamma_n). \end{aligned} \tag{19}$$

Applying (19) to the activity coefficient terms found using (18), taking grossularite as the nth component of four, yields:

$$\begin{aligned} G_{al\text{-}al} &= \frac{RT}{X_{al}} + \frac{RT}{X_{gr}} - 2W_{al\text{-}gr} \\ G_{al\text{-}py} &= \frac{RT}{X_{gr}} + W_{al\text{-}py} - W_{al\text{-}gr} - W_{py\text{-}gr} \\ G_{al\text{-}sp} &= \frac{RT}{X_{gr}} + W_{al\text{-}sp} - W_{al\text{-}gr} - W_{sp\text{-}gr} \\ G_{py\text{-}py} &= \frac{RT}{X_{py}} + \frac{RT}{X_{gr}} - 2W_{py\text{-}gr} \\ G_{py\text{-}sp} &= \frac{RT}{X_{gr}} + W_{py\text{-}sp} - W_{py\text{-}gr} - W_{sp\text{-}gr} \\ G_{sp\text{-}sp} &= \frac{RT}{X_{sp}} + \frac{RT}{X_{gr}} - 2W_{sp\text{-}gr}\ . \end{aligned} \tag{20}$$

Other terms can be found from the symmetrical nature of $G^m$. As noted previously, $G^m$ depends on the composition even in the case of ideal solution.

Approximate values of the interaction parameters given by Ganguly and Kennedy (1974, p. 145-146) are as follows (cal):

$$\begin{aligned} W_{al\text{-}py} &= 3000 \\ W_{al\text{-}sp} &= 0 \\ W_{al\text{-}gr} &= 1000 \\ W_{py\text{-}sp} &= 3200 \\ W_{py\text{-}gr} &= 3800 \\ W_{sp\text{-}gr} &= 0\ . \end{aligned}$$

These values are considered to be constant over the range of T and P between the data they used (approx 630°C) and the examples considered here (600°-900°C).

INTRINSIC COEFFICIENTS

The flux of a component can be defined also in terms of mobilities and intrinsic diffusion coefficients. Intrinsic coefficients were introduced by Darken (1948) and Hartley and Crank (1949) in the analysis of binary diffusion. Extension to multicomponent systems has been treated by Cooper (1965) and Carman (1968). The concept is that diffusion of a species takes place as a result of its own chemical potential gradient only, and apparent cross coefficients are the result of the bulk flow of the system to maintain constant volume, concentration, et cetera, depending on the reference frame used.

The flux of a component for the mean molar velocity reference frame is

$$J^m_i = -X_i\, q_i\, \nabla\mu_i + v^m\, X_i, \tag{21}$$

where $q_i$ is the mobility of component i. Applying the mass balance constraints of the mean velocity frame and Gibbs-Duhem equation (eqs 5 and 12), the flux is expressed as

$$J^m_i = -X_i\, q_i\, \nabla\mu_i + X_i \sum_{j=1}^{n-1} X_j(q_j - q_n)\nabla\mu_j\ . \tag{22}$$

Intrinsic diffusion coefficients, or, as used here, *ideal* intrinsic coefficients can be *defined* in terms of mobilities

$$D^*_i = RT\, q_i; \tag{23}$$

ideal intrinsic coefficients are used here instead of mobilities because they have the same units as familiar diffusion coefficients. Then, for *ideal solution*, (21) takes the simple, intuitive form

$$J^m_i = -D^*_i\, \nabla X_i + v^m\, X_i. \tag{24}$$

Expansion of (22) assuming ideal solution, substitution of (23), and comparison with (1B) yields the relationship between measured coefficients used in modeling and ideal intrinsic coefficients

$$D^m_{ij} = \delta_{ij}\, D^*_j + X_i\, (D^*_n - D^*_j).$$

Thus, all nine coefficients in aluminous garnets are specified in terms of four ideal intrinsic coefficients in an ideal system.

Non-ideal solution is treated by expanding (22) using (17). It is still convenient to substitute ideal intrinsic coefficients defined by (23), although the simplicity of (24) no longer holds. Note that "ideal intrinsic coefficients" used here are different from "intrinsic coefficients" used by Carman (1968), and no intrinsic cross coefficients are required. Comparison with (1B) yields the relationship

$$\begin{aligned} D^m_{ij} = {} & \delta_{ij}\, D^*_i + D^*_i\, X_i \left[\frac{\partial \ln\gamma_i}{\partial X_j} - \frac{\partial \ln\gamma_i}{\partial X_n}\right] \\ & -X_i \sum_{k=1}^{n-1} X_k\, (D^*_k - D^*_n) \left[\frac{\delta_{jk}}{X_k} + \frac{\partial \ln\gamma_k}{\partial X_j} - \frac{\partial \ln\gamma_k}{\partial X_n}\right]. \end{aligned} \tag{25}$$

This equation, called the mobility model, is evaluated using (18). Diffusion coefficients for either ideal or non-ideal solution computed this way satisfy the ORR. Most of the modeling of part 2 was accomplished by specifying ideal intrinsic coefficients and computing diffusion coefficients by (25).

## EIGENVECTOR ANALYSIS

The previous sections allow us to test or create the $D$ matrix using thermodynamic constraints. The application of $D$ to an actual problem in diffusion, however, is still complicated by the presence of cross coefficients and the consequent system of coupled partial differential equations in the diffusion equation (2B). A simpler procedure that is quite general and can be used with any solution for binary diffusion is to uncouple the partial differential equations by transforming components.

Diffusion equations have been developed for a specific set of components; in the case of garnet, I have selected pyrope, almandine, spessartite, and grossularite. The composition of garnet can be described just as well using a set of four new components, found by combining the old ones in a linear way. If a new set of components is selected so that the corresponding diffusion coefficient matrix does not have cross terms, the new set of components are "principal" components or eigenvectors in composition space; they form a new set of compositions. For each of these new components, the diffusion equations are independent and can be solved using any model for binary diffusion. After compositional gradients are established using principal components, composition can be transformed back to the original components. The usefulness of this method in analysis of multicomponent diffusion has been emphasized by Gupta and Cooper (1971) and Kirkaldy (1970).

Principal components can be negative or imaginary, but they can be shown always to be real and positive for $D$ as follows (see also, Kirkaldy, Weichert, and Zia-ul-Haq, 1963; Cullinan, 1965). Simplifying notation

$$D = LG,$$

where both $L$ and $G$ are symmetrical and therefore have real eigenvalues (Protter and Morrey, 1964, p. 365). In addition, $L$ must be positive definite, because $\sigma$ is positive (de Groot and Mazur, 1969, p. 39), and eigenvalues of $G$ are also positive, because the second derivative of free energy must be positive for thermodynamic stability of a phase (Prigogine and Defay, 1954; Gupta and Cooper, 1971). Choose a congruent transform of $G$ so that

$$G' = \widetilde{A}\, G\, A = I,$$

where $A$ is the transformation matrix, and $I$ the identity matrix; this is always possible for a symmetric positive definite matrix (de Groot and

Mazur, 1962, p. 108). Transform $D$ by a similarity transform using the same matrix:

$$D' = A^{-1} D A$$

$$= A^{-1} L \widetilde{A}^{-1} .$$

Moreover

$$\widetilde{D'} = A^{-1} \widetilde{L} \widetilde{A}^{-1} .$$

Because $L$ is symmetrical,

$$\widetilde{D'} = D'$$

and $D'$ is symmetrical with positive real eigenvalues. Eigenvalues are preserved under a similarity transform (Protter and Morrey, 1964, p. 361), and therefore $D$ must have positive real eigenvalues even though it is *not* generally symmetric.

The $D$ matrix can be solved for eigenvalues and eigenvectors using standard computational techniques for non-symmetric matrices. The 3 eigenvalues correspond to diagonal diffusion coefficients in $D$ with all cross terms equal to zero for the new set of components. The composition of new components in terms of the old is found using the eigenvectors:

$$X' = R^{-1} X,$$

where $X'$ and $X$ represent, respectively, a composition in terms of the new and old components, and $R$ consists of columns of normalized eigenvectors.

## COMPUTATIONAL PROCEDURE

This brief review of the theory of multicomponent diffusion has been designed to develop the formulas necessary to compute diffusion profiles and compare them with experimental or natural data. The procedure of the computer program is outlined below.

*Thermodynamic solution model.*—Six thermodynamic parameters W for the symmetrical solution model of Ganguly and Kennedy and temperature are specified. Ideal solution is treated by setting W's equal to zero.

*Diffusion coefficients.*—In the completely general case, $\frac{1}{2}n\,(n-1)$ independent constant diffusion coefficients must be assumed for the compositional range of interest. They can be assumed in any mean velocity reference frame and transformed to another using equations equivalent to (9). Again, compositional dependency is introduced by transformation, and its significance can be evaluated. In the case of garnet, I propose to assume coefficients in the mean molar reference frame, and their equivalence in the standard mean velocity frame is given by (9). Little error is introduced by using the convenient mean molar frame instead of the more exact mean volume frame. If a dependent component other than grossularite is desired, the equivalent of my choice of

diffusion coefficients can be found by (7). The remaining elements of $D$ are found by solving eq 16 using the $G$ matrix computed according to (19) or (20) for grossularite as the dependent component. In this way, $D$ will always be compatible with the thermodynamic solution model, and it is not necessary to consider specifically the effect of non-ideal solution.

The alternative method requires assumption of four mobilities or ideal intrinsic coefficients and the validity of the Hartley-Crank model. Diffusion coefficients are computed directly using the solution model from (25) and satisfy automatically the symmetry requirements of $L$ and $G$.

Eigenvalues and eigenvectors of the $D$ matrix are formed using standard algorithms.

*Binary diffusion models.*—A major advantage of the eigenvector method is that any binary diffusion model can be used. Realistic models for geologic situations often involve moving boundaries (reaction) with variable velocities, already difficult to solve. Initial and boundary conditions for the binary model are transformed by the eigenvector for each new component and the model solved using the eigenvalue as a diffusion constant.

The use of the mean molar reference frame is useful because eq 2B or its equivalent can be used with constant C. Then mole fractions can be used directly.

*Final result.*—Computed binary diffusion profiles corresponding to the independently-diffusing components are combined and transformed back to the original components for plotting and comparison with experimental or natural data. Specific examples will be considered in part 2.

A FORTRAN IV computer program following these computational procedures is available from the author.

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REFERENCES

Anderson, D. E., 1976, Diffusion in metamorphic tectonites: lattice-fixed reference frames: Royal Soc. London Philos. Trans., v. A283, p. 241-254.

Anderson, D. E., and Buckley, G. R., 1973, Zoning in garnets-diffusion models: Contr. Mineralogy Petrology, v. 40, p. 87-104.

———— 1974, Modeling of diffusion controlled properties of silicates, *in* Hofmann, A. W., Giletti, B. J., Yoder, H. S., Jr., and Yund, R. A., eds., Geochemical transport and kinetics: Washington, D.C., Carnegie Inst. Washington, p. 15-30.

Arkai, P., Nagy, G., and Panto, Gy., 1975, Types of composition zoning in the garnets of polymetamorphic rocks and their genetic significance: Acad. Sci. Hungarical Acta Geol., v. 19, p. 17-42.

Brady, J. B., 1975a, Reference frames and diffusion coefficients: Am. Jour. Sci., v. 275, p. 954-983.

———— 1975b, Chemical components and diffusion: Am. Jour. Sci., v. 275, p. 1073-1088.

Carman, P. C., 1968, Intrinsic mobilities and independent fluxes in multicomponent isothermal diffusion. I. Simple Darken systems: Jour. Phys. Chemistry, v. 72, p. 1707-1712.

Chinner, G. A., 1962, Almandine in thermal aureoles: Jour. Petrology, v. 3, p. 316-340.

Cooper, A. R., Jr., 1965, Model for multicomponent diffusion: Physics Chemistry Glasses, v. 6, p. 55-61.

———— 1974, Vector space treatment of multicomponent diffusion, *in* Hofmann, A. W., Giletti, B. J., Yoder, H. S., Jr., and Yund, R. A., eds., Geochemical transport and kinetics: Washington, D.C., Carnegie Inst. Washington, p. 15-30.

Cullinan, H. T., Jr., 1965, Analysis of the flux equations of multicomponent diffusion: Industrial and Engineering Chemistry Fundamentals, v. 4, p. 133-139.

Darken, L. S., 1948, Diffusion, mobility and their interrelation through free energy in binary metallic systems: Am. Inst. Mining Metall. Engineers. Trans., v. 175, p. 184-201.

de Bethune, P., Laduron, D., Martin, H., and Theunissin, K., 1968, Grenats zones de la Zone de Mont-Rose (Valle Anzasca, Prov. de Novara, Italie): Bull. Suisse Mineral. Pet., v. 48, p. 437-454.

de Bethune, P., Laduron, D., Bocquet, J., 1975, Diffusion processes in resorbed garnets: Contr. Mineralogy Petrology, v. 50, p. 197-204.

de Groot, S. R., and Mazur, P., 1962, Nonequilibrium thermodynamics: Amsterdam, North Holland Publishing Co., 510 p.

Evans, B. W., and Guidotti, C. V., 1966, The sillimanite-potash feldspar isograd in western Maine, U.S.A.: Contr. Mineralogy Petrology, v. 12, p. 25-62.

Fisher, G. W., 1973, Nonequilibrium thermodynamics as a model for diffusion-controlled metamorphic processes: Am. Jour. Sci., v. 273, p. 897-924.

Ganguly, J., and Kennedy, G. C., 1974, The energetics of natural garnet solid solution I. Mixing of the alumino silicate end-members: Contr. Mineralogy Petrology, v. 48, p. 137-148.

Grant, J. A., and Weiblen, P. W., 1971, Retrograde zoning in garnet near the second sillimanite isograd: Am. Jour. Sci., v. 270, p. 281-296.

Guggenheim, E. A., 1967, Thermodynamics 5th ed.: Amsterdam, North Holland Publishing Co., 390 p.

Gupta, P. K., and Cooper, A. R., Jr., 1971, The (D) matrix for multicomponent diffusion: Physica, v. 54, p. 39-59.

Hartley, G. S., and Crank, J., 1949, Some fundamental definitions and concepts in diffusion processes: Faraday Soc. Trans. v. 45, p. 801-818.

Hess, P. C., 1971, Prograde and retrograde equilibria in garnet–cordierite gneisses in south-central Massachusetts: Contr. Mineralogy Petrology, v. 30, p. 177-195.

Kirkaldy, J. S., 1970, Isothermal diffusion in multicomponent systems: Advances in Materials Research, v. 4, p. 55-100.

Kirkaldy, J. S., Weichert, D., and Zia-Ul-Haq, 1963, Diffusion in multicomponent metallic systems: VI. Some thermodynamic properties of the D matrix and the corresponding solutions of the diffusion equations: Canadian Jour. Physics, v. 41, p. 2166-2173.

Kwak, T. A. P., 1970, An attempt to correlate non-predicted variations of distribution coefficients with mineral grain internal inhomogeneity using a field example studied near Sudbury, Ontario: Contr. Mineralogy Petrology, v. 26, p. 199.

Lasaga, A. C., Richardson, S. M., and Holland, H. D., 1977, The mathematics of cation diffusion and exchange between silicate minerals during retrograde metamorphism, *in* Saxena, S. K. and Bhattacharji, S., eds., Energetics of Geological Processes: New York, Springer-Verlag, p. 353-388.

Loomis, T. P., 1972, Contact metamorphism of pelitic rock by the Ronda ultramafic intrusion, southern Spain: Geol. Soc. America Bull., v. 83, p. 2440-2474.

———— 1975, Reaction zoning of garnet: Contr. Mineralogy Petrology, v. 52, p. 285-305.

———— 1977, Kinetics of a garnet granulite reaction: Contr. Mineralogy Petrology, v. 62, p. 1-22.

———— 1978, Multicomponent diffusion in garnet. II. Comparison of models with natural data: Am. Jour. Sci., p. 1119-1137.

Mueller, G., and Schneider, A., 1971, Chemistry and genesis of garnets in metamorphic rocks: Contr. Mineralogy Petrology, v. 31, p. 178-200.

Novak, G. A., and Gibbs, G. V., 1971, The crystal chemistry of the silicate garnets: Am. Mineralogist, v. 56, p. 791-825.

Onsager, L., 1931, Reciprocal relations in irreversible processes: Physical Review, I: v. 37, p. 405-426; II: v. 38, p. 2265-2279.

———— 1945, Theories and problems of liquid diffusion: New York Acad. Sci. Ann., v. 46, p. 241-265.

Prigogine, I., and Defay, R., 1954, Chemical thermodynamics: London, Longman Group Ltd., 543 p.

Protter, M. H., and Morrey, C. B., Jr., 1964, Modern mathematical analysis: Palo Alto, Addison-Wesley Publishing Co., 790 p.

Skinner, B. J., 1956, Physical properties of end-members of the garnet group: Am. Mineralogist, v. 41, p. 428-436.

Woodsworth, G. J., 1977, Homogenization of zoned garnets from pelitic schists: Canadian Mineralogist, v. 15, p. 230-242.