

## A NOTE ON TRANSFER REACTIONS

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### ABSTRACT

Transfer reactions are those that are expressed by use of the simplified reaction,  $(A,B)^\alpha = (A,B)^\beta$ , in which one or more additional phases of fixed composition may participate. Examples are (Fe,Mg) olivine crystal = (Fe,Mg) olivine melt, and (Fe,Mg) biotite + sillimanite + quartz = (Fe,Mg) garnet + K-feldspar + H<sub>2</sub>O. Thermodynamic equations derived by van Laar relate the composition  $X$  of reactant and product phases to temperature  $T$ . A plot of the equations produces the familiar  $T$ - $X$  loop, which rises with increasing pressure and, for reactions that release H<sub>2</sub>O, falls with decreasing H<sub>2</sub>O activity. Much variation can occur in the relation between volume of product and temperature or time (*i.e.*, the reaction rate) depending on the constants in the relevant van Laar equations and on the initial composition of the reactant phase. Reaction far from equilibrium can give rise to several possibilities for compositional zoning in reactant and product crystals.

*Keywords:* transfer reactions, van Laar equations, reaction rate, fractional crystallization.

### SOMMAIRE

Les réactions de transfert sont celles qui satisfont l'expression  $(A,B)^\alpha = (A,B)^\beta$ ; une ou plusieurs phases additionnelles de composition fixe peuvent y participer. Par exemple, (Fe,Mg) olivine cristalline = (Fe,Mg) liquide de composition d'olivine, ou encore (Fe,Mg) biotite + sillimanite + quartz = (Fe,Mg) grenat + feldspath potassique + H<sub>2</sub>O. Les relations thermodynamiques dérivées par Van Laar décrivent la composition  $X$  des réactifs et des phases produites à la température  $T$ . Une expression graphique des équations donne l'enveloppe  $T$ - $X$  familière, qui augmente avec la pression, et qui s'abaisse, dans le cas de réactions qui produisent de l'eau, avec une diminution dans l'activité de H<sub>2</sub>O. Une grande variation peut exister dans la relation entre volume du produit et la température ou le temps (*c'est-à-dire*, taux de réaction) selon les constantes utilisées dans les équations de van Laar appropriées et la composition initiale des réactifs. Si une réaction est éloignée de sa position d'équilibre, les cristaux des réactifs aussi bien que des phases produites pourraient bien être zonés en composition.

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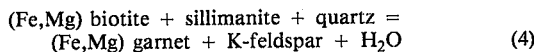
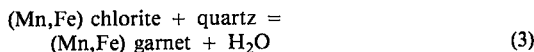
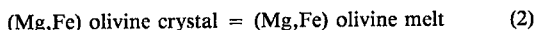
*Mots-clés:* réactions de transfert, équations de van Laar, taux de réaction, cristallisation fractionnée.

### INTRODUCTION

It is now possible to recognize several classes of mineral reactions, ranging from those that occur within crystals to those that involve two or more phases of variable composition. Reactions that consume one phase of variable composition and produce another, as expressed by the simplified reaction,



are referred to as transfer reactions. Normally the A:B ratio is not the same in the two phases (*i.e.*, the equation as written is not balanced), and two mass-balance and energy-balance equations are needed to describe a reaction as it approaches equilibrium. Also, one or more additional phases of fixed or nearly fixed composition may participate in the reaction. Examples of transfer reactions are,



Some natural and experimental data are available on these and other equilibria. For example, Schmid & Wood (1976) have shown that in the Ivrea - Verbano zone of northern Italy, equilibrium (4) is displaced to the right with increasing metamorphic grade, *i.e.*, biotite is consumed, and garnet is produced.

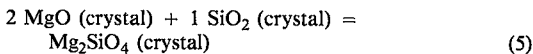
Interphase exchange-reactions form another class of mineral reactions. These occur, for example, when an increase in temperature causes atoms of Mg to migrate from crystals of biotite to crystals of garnet in exchange for an equal number

of Fe atoms. Unlike transfer reactions, exchange reactions do not consume or produce crystals; rather, these only change in composition, and the variance is sufficiently large to permit the composition of the minerals to vary (concurrently) at constant temperature and pressure.

The purpose of this note is a) to propose that the van Laar (1908) equations (which at times have been disregarded) provide the most rigorous thermodynamic description of transfer equilibria, and b) to examine qualitatively some possibilities for variation in reaction rate and in fractional crystallization in solid systems, resulting from the thermodynamic demands that are stated by the van Laar equations. The study is built on some earlier proposals by the writer (Kretz 1973); a more general and different approach to transfer equilibria in assemblages of metamorphic minerals was taken by Thompson (1976) and by Loomis & Nimick (1982).

#### EQUILIBRIUM AND REACTION

Although it is possible to present a definition of equilibrium without referring to a process, a process is always implied. For example, with reference to a system composed of crystalline forsterite ( $\text{Mg}_2\text{SiO}_4$ ), one could say that in the absence of temperature and pressure gradients, equilibrium exists at  $800^\circ\text{C}$ , 1.0 bar when the Mg, Si, and O atoms are arranged as in crystalline forsterite. This implies that the molar Gibbs energy of forsterite is less than that of some other atomic arrangement, *e.g.*,  $2\text{MgO} + 1\text{SiO}_2$ , or  $\text{Mg}_2\text{SiO}_4$  melt, and if these phases were present, a process (reaction) should occur to eliminate them. One can expand, therefore, on the definition of equilibrium (a minimum of Gibbs energy) for the system  $\text{Mg}_2\text{SiO}_4$  by adding that all possible off-equilibrium reactions, *e.g.*,



are displaced toward crystalline forsterite.

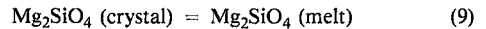
Consider next a system composed of crystalline forsterite and forsterite melt at  $1890^\circ\text{C}$ , 1 bar, *i.e.*, at the melting point. In addition to possible off-equilibrium reactions, an equilibrium reaction can be recognized and defined by observing the changes that occur in response to a small change in temperature. In this case, reaction (6) above becomes the equilibrium reaction. Indeed, crystal-melt equilibria and chemical reactions in general are commonly thought of in terms of a reaction which, on a microscopic scale, is constantly in

progress, moving here to the right and there to the left, at equal mean rates. By defining the equilibrium reaction, we have obtained a mass-balance equation, which leads to the energy-balance equation,

$$G^{\text{Fo(crystal)}} = G^{\text{Fo(melt)}} \quad (7)$$

(where  $G$  stands for molar Gibbs energy) as a requirement for equilibrium.

Consider now a system composed of an olivine crystal and a volume of olivine melt at  $1500^\circ\text{C}$ , 1 bar; the formula for both phases is  $(\text{Mg,Fe})_2\text{SiO}_4$ , or  $(\text{fo,fa})$ , where fo and fa refer to solution components  $\text{Mg}_2\text{SiO}_4$  and  $\text{Fe}_2\text{SiO}_4$ . The experimental results of Bowen & Schairer (1935) have shown that the equilibrium composition of the crystal  $X^c$  at  $1500^\circ\text{C}$  is 0.42, and that of the melt  $X^m$  is 0.75, where  $X = \text{fa}/(\text{fo} + \text{fa}) = \text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+})$ . The equilibrium reaction in this system can be identified by decreasing the temperature slightly and observing the crystallization of olivine, which can be described as the transfer of  $N_{\text{fa}}$  moles of fayalite from melt to crystal, and  $N_{\text{fo}}$  moles of forsterite from melt to crystal. Thus the mass-balance equations for the equilibrium reaction are,



and the energy-balance equations are,

$$\mu_{\text{fa}}^{\text{crystal}} = \mu_{\text{fa}}^{\text{melt}} \quad (10)$$

$$\mu_{\text{fo}}^{\text{crystal}} = \mu_{\text{fo}}^{\text{melt}} \quad (11)$$

where  $\mu$  stands for chemical potential.

Equilibrium requires that both phases be compositionally homogeneous; this condition can be achieved by  $\text{Fe}^{2+}$ -Mg exchange occurring *within* the crystal (between the newly deposited olivine and the crystal's interior) and *within* the melt. It is unnecessary and inappropriate in this case to consider a Mg-Fe exchange reaction *between* the crystal and the melt, a viewpoint adopted by Roeder & Emslie (1970) for olivine and Kudo & Weill (1970) for plagioclase, *i.e.*, the equilibrium reaction is a *transfer* reaction, not a between-phase *exchange* reaction.

#### THE VAN LAAR TRANSFER EQUATIONS

Consider a system composed of phases  $\alpha$  and  $\beta$  formulated as  $(\text{A,B})^\alpha$  and  $(\text{A,B})^\beta$ , where A and B are solution components, and suppose that a reaction relationship exists, as in (2), above. Let  $X$  stand for the mole fraction of B, *i.e.*,  $\text{B}/(\text{A} + \text{B})$ .

The van Laar (1908) equations are derived on the proposition that at equilibrium, the chemical potential of A ( $\mu_A$ ) must be equal in the two phases, and similarly for B, *i.e.*,

$$\mu_A^\alpha = \mu_A^\beta \quad (12)$$

$$\mu_B^\alpha = \mu_B^\beta \quad (13)$$

In the original treatment, component activity and mole fraction were assumed equal. This leads to the following expressions for equilibrium in the system at temperature  $T$ :

$$(1-X^\alpha)/(1-X^\beta) = \exp(\Delta G_A/RT) \quad (14)$$

$$X^\alpha/X^\beta = \exp(\Delta G_B/RT) \quad (15)$$

where  $\Delta G_A$  is the change in molar Gibbs energy for the reaction  $A^\alpha = A^\beta$  at the temperature  $T$ , and similarly for  $\Delta G_B$ . Equations (14) and (15) are now differentiated at constant pressure, followed by an integration and a rearrangement of terms to produce the following two equations:

$$X^\beta = \frac{\exp [(-\Delta H_B/R) (T^{-1}-T_B^{-1})] \{\exp [(-\Delta H_A/R) (T^{-1}-T_A^{-1})]-1\}}{\exp [(-\Delta H_A/R) (T^{-1}-T_A^{-1})] - \exp [(-\Delta H_B/R) (T^{-1}-T_B^{-1})]} \quad (16)$$

$$X^\alpha = \frac{\exp [(-\Delta H_A/R) (T^{-1}-T_A^{-1})] - 1}{\exp [(-\Delta H_A/R) (T^{-1}-T_A^{-1})] - \exp [(-\Delta H_B/R) (T^{-1}-T_B^{-1})]} \quad (17)$$

Here  $\Delta H_A$  is the change in molar enthalpy for the reaction  $A^\alpha = A^\beta$  at temperature  $T$ , and  $T_A$  stands for the equilibrium temperature for this reaction, and similarly for  $\Delta H_B$  and  $T_B$ . After deriving these equations, van Laar (1908) applied them to the plagioclase system (liquidus and solidus). Later, Bowen (1913) showed that they provide a perfect fit to his experimental results for this system, thus presenting evidence for near-ideal behavior of liquid and solid in the plagioclase system at high temperatures.

If the exponential term in equations (16) and (17) that contains  $\Delta H_A$  is referred to as  $\lambda_a$ , and that containing  $\Delta H_B$  is referred to as  $\lambda_b$ , then (16) and (17) may be written:

$$X^\beta = \lambda_b(\lambda_a-1)/(\lambda_a-\lambda_b) \quad (18)$$

$$X^\alpha = (\lambda_a-1)/(\lambda_a-\lambda_b) \quad (19)$$

Thus,

$$X^\beta = \lambda_b X^\alpha \quad (20)$$

Ramberg (1963) pointed out that equations (16) and (17) apply just as well to metamorphic equilibria, such as those described by equations (3) and (4), above; now  $\Delta H$  stands for the change in molar enthalpy for the end-member reactions.

Froese (1973) has emphasized the influence of  $H_2O$  activity in reaction (4). A reduction in  $H_2O$  activity or fugacity causes a shift in the end-member  $P$ - $T$  boundary curves, and a downward displacement of the composition curves. Tracy & Robinson (1988) have explored an alternative approach, which produces a  $\mu(H_2O)$ - $X$  loop at constant temperature and pressure.

The effect of pressure ( $P$ ) on transfer equilibria was considered by Mueller (1963). Proceeding as above, we obtain,

$$X^\beta = \frac{\exp [(-\Delta V_B/RT) (P-P_B)] \{\exp [(-\Delta V_A/RT) (P-P_A)]-1\}}{\exp [(-\Delta V_A/RT) (P-P_A)] - \exp [(-\Delta V_B/RT) (P-P_B)]} \quad (21)$$

$$X^\alpha = \frac{\exp [(-\Delta V_A/RT) (P-P_A)]-1}{\exp [(-\Delta V_A/RT) (P-P_A)] - \exp [(-\Delta V_B/RT) (P-P_B)]} \quad (22)$$

where  $\Delta V_A$  is the change in molar volume for reaction  $A^\alpha = A^\beta$  at temperature  $T$ , and similarly for  $\Delta V_B$ . These equations are analogous to (16) and (17); a plot of  $P$  against  $X$  also produces a loop. An illustration is provided by the olivine - spinel equilibrium at high pressure, which was investigated by Akimoto & Fujisawa (1968).

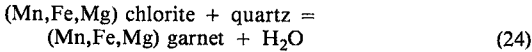
For reactions that involve a vapor (*e.g.*,  $H_2O$ ),  $\Delta V$  in (21) and (22) is a function of pressure, and the equations as written must be modified to take this change into consideration.

The effect of pressure may also be viewed in terms of a displacement of the  $T$ - $X$  loop. In general, an increase in pressure produces an increase in  $T_A$  and  $T_B$ , and an upward displacement of the loop; because  $\Delta H_A$  and  $\Delta H_B$  are not sensitive to pressure, the shape of the  $T$ - $X$  loop will not change greatly with increasing pressure. With regard to the plagioclase system, this expectation was confirmed by Lindsley (1968).

Transfer equilibria may involve two ternary solutions, *i.e.*,

$$(A,B,C)^\alpha = (A,B,C)^\beta \quad (23)$$

An example is,



Composition curves are replaced by composition surfaces, for which equations were obtained by Seltz (1935). At any temperature between the lowest and highest end-member equilibrium temperature, an isothermal plane in the  $X$ - $T$  prism will contain two lines, being intersections with the lower and upper composition-surfaces. Tie lines may then be located from a point on one line to a point on the other, to show different possible compositions of  $\alpha$  and  $\beta$  at equilibrium. These tie lines will not, in general, lie parallel to the sides of the composition triangle. Information on the composition of chlorite and garnet was presented in this form by Albee (1965).

#### ILLUSTRATIONS OF TRANSFER EQUILIBRIUM IN ASSEMBLAGES OF METAMORPHIC MINERALS

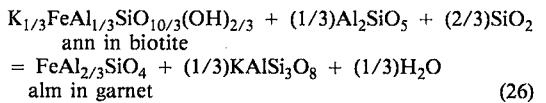
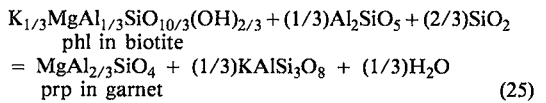
The nature of equations (16) and (17) may be demonstrated by solving and graphing these equations for different values of  $\Delta H_A$ ,  $\Delta H_B$ ,  $T_A$  and  $T_B$ . Consider for example the (Mn,Fe) chlorite - (Mn,Fe) garnet equilibrium [equation (3), above], with  $T_{\text{Mn}} = 678$  K and  $T_{\text{Fe}} = 815$  K at 2.0 kbar, as determined experimentally by Hsu (1968). An arbitrary selection of three sets of values for  $\Delta H_{\text{Mn}}$  and  $\Delta H_{\text{Fe}}$  (a: 60 and 100 kJ, b: 100 and 140 kJ, and c: 140 and 180 kJ) then produces the three

concentration - temperature loops (a,b,c) shown in Figure 1. Numerous solutions of this kind are provided by Reisman (1970, p. 303-310).

In general, for  $\Delta T = T_B - T_A$  between 100 and 500 K and for small values of  $\Delta H$  ( $< 20$  kJ), the gap between the two curves is narrow; larger values of  $\Delta H_A$  or  $\Delta H_B$  or both cause the gap to widen. For small values of  $\Delta T$  ( $\sim 100$  K), both curves may be concave up or down depending on  $\Delta H_A$  and  $\Delta H_B$  (Reisman 1970, p. 309-310).

Oonk (1981) has shown that where mixing in  $\alpha$  or  $\beta$  or both is nonideal, *i.e.*, where activity coefficients enter equations (16) and (17), the concentration curves may contain inflections, and the loop may be quite irregular in shape.

Certain gneisses from the Grenville Province, Canadian Shield, contain biotite, sillimanite, quartz, garnet, and K-feldspar and provide a natural example of the (Fe,Mg) biotite - (Fe,Mg) garnet transfer equilibrium expressed by equation (4), above. The two mass-balance equations are:



The equations define solution components phlogopite (phl) and annite (ann) in biotite (Bt),

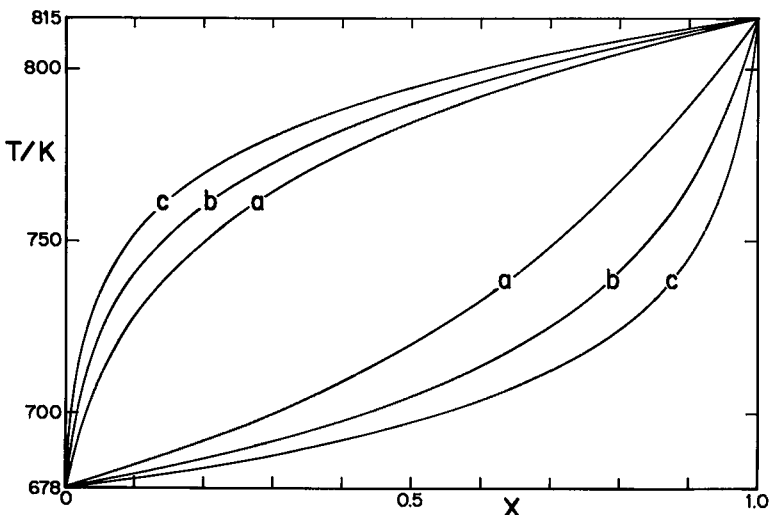


FIG. 1. Illustrative solutions of van Laar equations with prescribed values of temperature ( $T_A$  678 K,  $T_B$  815 K) and with arbitrary enthalpy-of-reaction ( $\Delta H_A$  and  $\Delta H_B$ ) values of 60 and 100 kJ (curves a), 100 and 140 kJ (curves b), and 140 and 180 kJ (curves c).

and pyrope (prp) and almandine (alm) in garnet (Grt) for an idealized model system in which additional components of garnet, biotite, and K-feldspar are disregarded, and H<sub>2</sub>O occurs as a pure vapor. Energy-balance considerations then lead to the van Laar equations (16, 17) in which  $X^{\beta} = X_{\text{prp}} = \text{prp}/(\text{prp} + \text{alm})$ ,  $X^{\alpha} = X_{\text{phl}} = \text{phl}/(\text{phl} + \text{ann})$ , and  $\Delta H_{\text{B}}$  and  $\Delta H_{\text{A}}$  are the enthalpy changes for (25) and (26), respectively.

Enthalpy changes for dehydration reactions do not vary greatly with changes in temperature and pressure, and a numerical estimate for the Mg end-member reaction is obtained from the data compiled by Berman (1988), to give  $\Delta H_{\text{B(T,P)}} \approx \Delta H_{\text{(STP)}} = +38.8$  kJ/mol. Assuming an equal value for  $\Delta H_{\text{A}}$  implies that the heat of formation of annite (which is not well known) is -5190 kJ/mol, which compares with -5160 kJ/mol of KFe<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> as listed by Helgeson *et al.* (1978), and -5150 kJ/mol as listed by Holland & Powell (1989). Thus  $\Delta H_{\text{B}} = \Delta H_{\text{A}} = 39.0$  kJ/mol is assumed.

The end-member equilibrium temperatures are not yet determined experimentally. By assuming values of 860 K for  $T_{\text{Fe}}$  and 1160 K for  $T_{\text{Mg}}$ , the van Laar equations produce the curves shown in Figure 2. These curves provide a satisfactory fit to the natural data, barring one specimen that is

anomalous. By this interpretation, the observed variation in Mg/(Mg + Fe<sup>2+</sup>) of biotite and garnet is attributed to a variation in temperature within the gneissic terrane.

It is not possible to sketch a *P-X* loop for this equilibrium [equations (21) and (22)] because the volume change for the end-member reactions ( $\Delta V$ ) is very small.

An activity of H<sub>2</sub>O less than 1.0 in an assumed vapor or grain-boundary phase does not change the  $\Delta H$  values, but will reduce  $T_{\text{Fe}}$  and  $T_{\text{Mg}}$ , causing the *T-X* curves in Figure 2 to shift downward. The shift can be calculated by use of the modified Clapeyron equation,

$$\frac{d(1/T)}{d \ln f(\text{H}_2\text{O})} = - \frac{R}{\Delta H_{T,i} + \Delta V_{\text{STP}}^{\text{S}}(P)} \quad (27)$$

where  $f$  is fugacity,  $R$  is the gas constant, and  $\Delta V_{\text{STP}}^{\text{S}}$  is the volume change for the solid phases in the end-member reaction. Calculations show that moderate variations in  $f(\text{H}_2\text{O})$  are sufficient to provide an alternative interpretation to the data of Figure 2, namely that the observed variation in Mg/(Mg + Fe<sup>2+</sup>) is the expression of a variation in the activity of H<sub>2</sub>O, not in temperature.

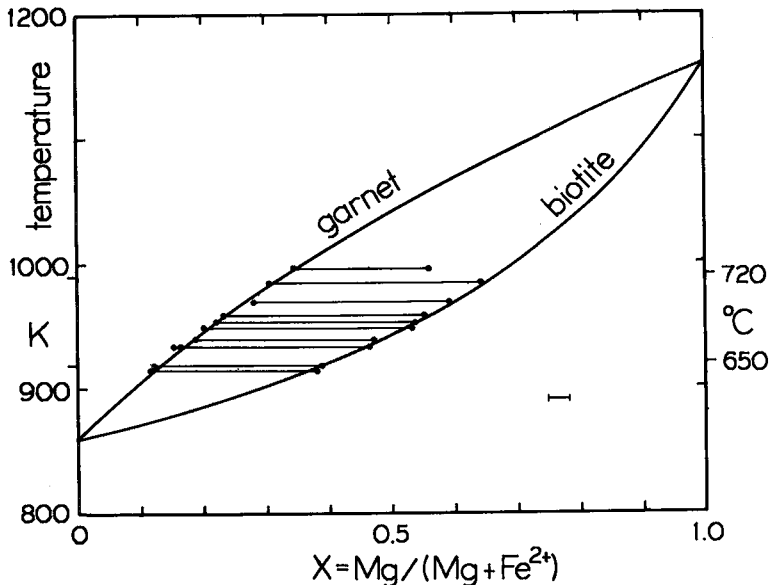


FIG. 2. Mg/(Mg + Fe<sup>2+</sup>) ratios of associated garnet and biotite in Grenville gneisses that also contain sillimanite, quartz, and K-feldspar [transfer equilibrium defined by equations (25) and (26)]. The *T-X* curves represent a particular solution to the van Laar equations. The uppermost garnet - biotite tie line represents an anomalous mineral pair. Analytical error is shown by the error bar. The example is taken from Kretz (1990).

Numerous examples of  $T$ - $X$  relations in metamorphic mineral assemblages were proposed by Thompson (1976), and others. In many cases, the above procedure was not followed in dealing with these equilibria. Thus Thompson (1976) combined one of the two equations (14, 15, above) with a quotient of the kind,

$$\frac{X_B^2}{1-X_B^2} \cdot \frac{1-X_B^2}{X_B^2} \quad (28)$$

which appears in the equation for exchange equilibrium. If the equilibrium reaction is a transfer and not an exchange reaction, as is argued above, then the quotient (28) is not a thermodynamic expression.

Very few experimental data are available on solid-state transfer equilibria. The reaction, (Fe,Mg) biotite + muscovite + quartz = (Fe,Mg) garnet + K-feldspar + H<sub>2</sub>O was investigated by Dahl (1968).

#### REACTION RATES FOR TRANSFER REACTIONS

In general, the rate of a continuous reaction of the kind here considered is expected to depend to a large extent on the rate of change of temperature. Provided that the difference in Gibbs energy between products and reactants remains small, the nature of the van Laar equations will determine, for a given rate of heating, the rate of production of the  $\beta$  phase, *i.e.*, the rate of reaction.

Consider for example a volume of rock in which equilibrium (3), above, is slowly displaced to the right, such that the system is never far from equilibrium, and suppose that the rate of increase of temperature is a known constant. The lever rule may then be used to determine the mass fraction ( $F$ ) of product (garnet) as a function of temperature ( $T$ ), and hence as a function of time. Figures 3a and 3b show  $F$ - $T$  relations for loops *a* and *c* of Figure 1, respectively, and they demonstrate clearly that the  $F$ - $T$  relation depends greatly on the initial composition of the reactant phase. A comparison of Figure 3b with Figure 3a demonstrates further that the  $F$ - $T$  relations also depend on the shape of the composition loop. In particular, curvature in the  $F$ - $T$  plots increases as the composition curves in the loop move apart.

In natural systems, Mn/(Mn + Fe + Mg) in chlorite is much less than in the associated garnet; if  $X$  in Figure 1 is defined as (Fe + Mg)/(Mn + Fe + Mg), curve *c* may represent approximately the  $T$ - $X$  relations in the Mn-Fe-Mg system. Beginning with a Mn-bearing chlorite with (Fe + Mg)/

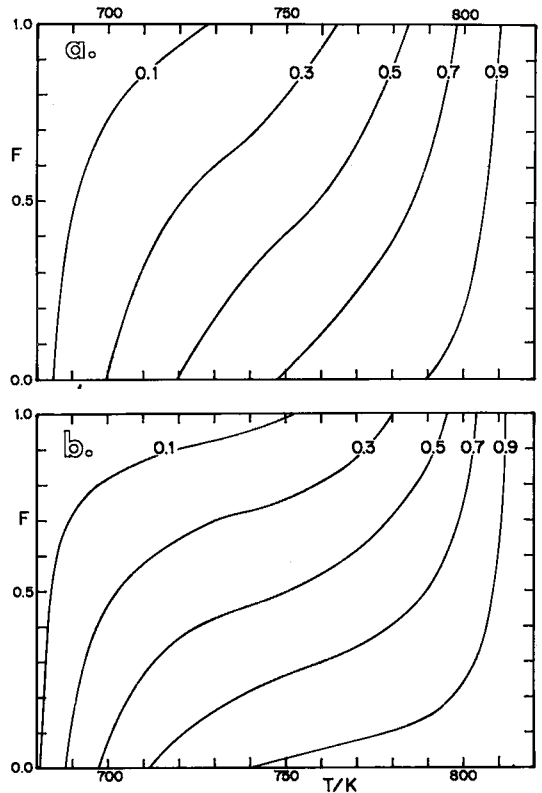
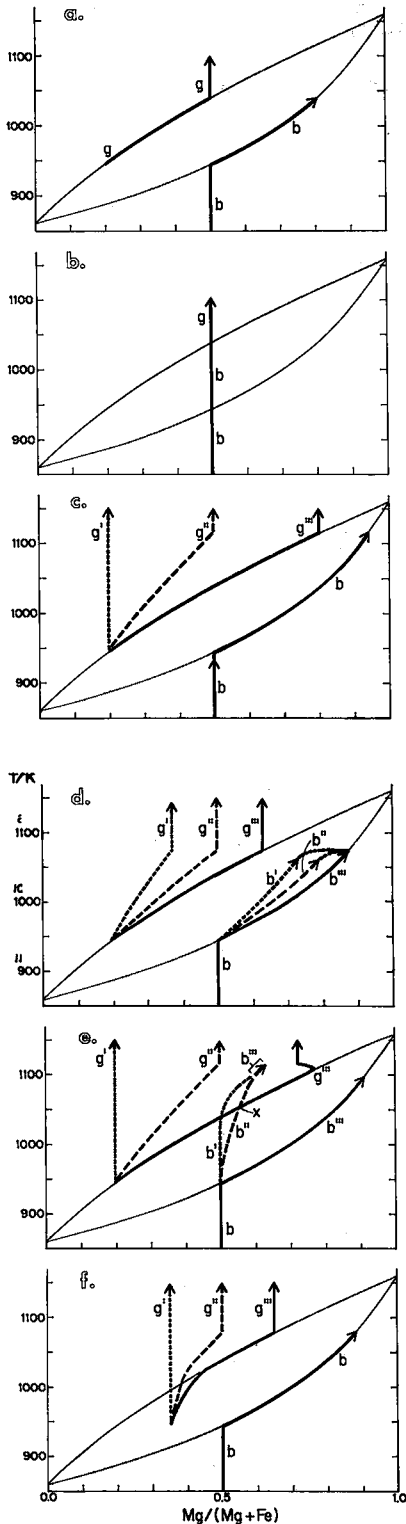


FIG. 3. Fraction of product crystallized ( $F$ ) as a function of temperature ( $T$ ); upper figure (a) is for loop *a* in Figure 1, and lower figure (b) is for loop *c* in Figure 1. Results (obtained by use of the lever rule) are shown for initial compositions  $X$  of the reactant of 0.1, 0.3, 0.5, 0.7 and 0.9.

(Mn + Fe + Mg), equal to 0.9, Figure 3b suggests that a steady increase in temperature should produce a sharp increase in the reaction rate. This is in agreement with conclusions arrived at independently, based on garnet zoning and crystallization distributions (Kretz 1973).

#### FRACTIONAL CRYSTALLIZATION

In van Laar systems, many possibilities exist for fractional reaction and crystallization. With regard to crystallization from a melt, some of these possibilities were defined by Maaløe (1984). With regard to solid-state reactions, the patterns of concentration that develop with temperature and time in reactant and product crystals will depend, for a given van Laar loop, on the rate of increase of temperature relative to the rate of diffusion



within the crystals. Some of these possibilities will now be explored by taking for example the loop shown in Figure 2 and by assuming, in each case, an initial composition for the reactant crystals at  $X = 0.5$ .

Figure 4a shows (only for comparison) composition paths for reactant crystals (denoted b) and product crystals (denoted g) during near-equilibrium reaction. Both reactant and product crystals remain homogeneous throughout, either by Fe-Mg exchange diffusion or by recrystallization in response to deformation.

A rapid rise in temperature could conceivably take the reactant crystals from the lower composition-curve (945 K) to the upper composition-curve (1040 K) before reaction commences (Fig. 4b), causing the product to crystallize with the same Fe:Mg ratio as that of the initial reactant. Reactions of this kind may possibly have occurred locally during rapid heating at igneous contacts or as a result of shock metamorphism.

In the next example (Fig. 4c), the Fe-Mg diffusion coefficient for reactant crystals greatly exceeds that for product crystals, and the rate of heating is such that no diffusion occurs in the product, and complete diffusion occurs in the reactant, *i.e.*, reactant crystals are at all times homogeneous. Also, the rims of reactant and product crystals remain at equilibrium, a condition here referred to as rim equilibrium. There are now three  $X-T$  paths for the product phase, one ( $g'$ ) for the cores of the first-formed crystals, one ( $g'''$ ) for the rim composition of all crystals, and one ( $g''$ ) representing the mean product composition. Path  $g''$  must lie between  $g'$  and  $g'''$ , but the paths  $g'$  and  $g''$  for any particular crystal will depend on the time of nucleation for that crystal. Compared with near-equilibrium reaction (Fig. 4a), the range in temperature of crystallization is extended, and the path for the reactant crystals moves farther to the right. This example is an extension of a model proposed by Hollister (1966) for the formation of zoned crystals of garnet.

In the next possibility (Fig. 4d), diffusion in the product crystals is again prohibited, whereas diffusion in the reactant crystals is somewhat restricted; rim equilibrium is maintained. As the

FIG. 4. Possible concentration ( $X$ ) - temperature ( $T$ ) paths for hypothetical reactions in which reactant crystals (b) yield product crystals (g); the equilibrium van Laar loop is that of Figure 2. The different possibilities include near-equilibrium crystallization (a) and fractional crystallization (b to f). Superscripts refer to compositions in the core of largest crystals ('), at their rim (''), and a mean composition ('') of reactants and products.

reactant crystals are consumed (decrease in size), margins encroach on cores, and hence paths  $b'$  (core composition) and  $b''$  (mean composition) merge with  $b'''$  (rim composition).

Where diffusion in reactant crystals is further restricted (Fig. 4e), path  $b''$  (mean composition of reactant) could conceivably intersect the path for the composition of the product rim ( $g'''$ ) as shown at point X; this would result in a reversal in path  $g'''$ . In this example, rim equilibrium is maintained only to 1100 K, the temperature at which rims of the reactant crystals are consumed, exposing the more Fe-rich interiors. From 1100 to 1115 K, the remaining reactant crystals yield a product with  $Mg/(Mg + Fe)$  lower than that which was deposited at 1100 K, *i.e.*, the final crystals produced will show reverse zoning in their margins. This example provides a possible explanation for garnet crystals that show a reversal in their zoning profiles (Kretz 1973).

The idea that the composition of a product nucleus need not fall on the product composition-curve was considered in relation to metals (as reviewed by Burke 1965), and this behavior is expressed in Figure 4f. The reactant crystals do follow their composition path, and homogeneity within them is maintained. Rim equilibrium is obtained only during the second half of the reaction period, *i.e.*, from 1025 to 1080 K. Evidence for this kind of fractional reaction might be found in garnet populations in which the largest crystals do not all have the same core composition.

The above and other possibilities could in principle be recognized by a detailed examination of mineral assemblages, combined with information on phase relations. It is well known, however, that zoning in crystals is commonly destroyed by diffusion or recrystallization that occur after reaction has ceased. Bodies of rock that escaped deformation and were rapidly cooled soon after reaction ceased are the ones most likely to reveal a record of fractional crystallization.

#### RETROGRADE REACTIONS

The reversal of a transfer reaction could possibly take place in response to a decrease in temperature, a change in pressure, or an increase in  $H_2O$  activity. Thus, in a study of garnet crystals from Massachusetts, Tracy *et al.* (1976) proposed that the enrichment of Fe in the margins of these crystals resulted from a shift of reaction (4), above, to the left during cooling. Another possibility is that during cooling, the van Laar reaction does not reverse and is replaced by an energetically more favorable Fe-Mg exchange reaction involving only biotite and garnet. This almost certainly has

occurred in some rocks where the two minerals are in contact; the evidence was summarized by Tracy (1982).

#### CONCLUSIONS

In reactions of the kind here considered, *e.g.*, (Fe,Mg) biotite + sillimanite + quartz = (Fe,Mg) garnet + K-feldspar +  $H_2O$ , exponential or near-exponential relations between chemical potential and component concentration in the solid solutions lead to complex relations between concentration ( $X$ ) and temperature ( $T$ ), as expressed by the van Laar equations. The equations and the resulting  $T$ - $X$  loops that appear when the equations are plotted are determined principally by temperature and enthalpy changes for the end-member reactions, provided that mixing in the solid solutions is ideal or nearly ideal.

The van Laar equations for a particular reaction, occurring near equilibrium, determine the rate of increase in mass or volume of product in relation to the rate of increase of temperature, and quite different relations (from near-linear to strongly nonlinear) result from differences in the terms that appear in the equations and in the initial composition of the reactant phase.

In general, for crystallization farther from equilibrium (fractional crystallization), solid-state transfer reactions produce compositionally zoned product-crystals, and possibly also reactant crystals. The particular microstructure and microchemical details that are produced in a rock volume depend in part on the nature of the van Laar equations of equilibrium for the transfer reaction, and in part on other controls, including rates of heating, nucleation, and within-crystal diffusion, which also require further study.

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