

Reprint from

# Thermodynamics of Minerals and Melts

Advances in Physical Geochemistry

Volume 1

Edited by R. C. Newton, A. Navrotsky, and B. J. Wood

---

© 1981 Springer-Verlag New York Inc.

Printed in the United States of America. Not for Sale



Springer-Verlag  
New York Heidelberg Berlin

12.

# Calculating Mineral–Melt Equilibria with Stoichiometry, Mass Balance, and Single-Component Distribution Coefficients

C. H. Langmuir\* and G. N. Hanson

## Introduction

Application of phase equilibria is essential to understanding igneous processes. Usually the phase equilibria in systems of interest to petrologists are presented graphically in the form of phase diagrams. Such diagrams are compact representations of data from which the proportions and compositions of phases as functions of temperature and bulk composition can be determined [e.g., Morse (1976)]. These diagrams are strictly applicable, however, only to systems consisting of a small number of components and can be fully presented in two or at most three dimensions. In systems of more components, projections can be used, but the quantitative calculations can no longer be carried out graphically. Since almost all liquids of interest to petrologists have many components, there is a need for methods of numerical calculation which are applicable to both simple and complex systems. One approach to such calculations uses thermodynamic data and is exemplified by the work of Weill *et al.* (1979) and Burnham (1979). At present, thermodynamic data and models are insufficient to allow calculation of phase diagrams for many simple systems of geological interest, much less the complex multicomponent systems in which rocks melt and crystallize. An alternative approach is to use the large and growing body of equilibrium temperature, pressure, and composition data which are available for simple systems as well as rock compositions. One way of processing those data is regression analysis, which supplies lengthy equations to minimize the errors in reproducing the data base [e.g., Weill *et al.* (1979) and Hostetler and Drake (1978)]. A similar method of estimating liquidus temperatures using linear equations is that of Roeder (1975), based on the suggestion of French (1971).

This paper presents an alternative method for calculating phase equilibria using the large, empirical data base which is available. This data base is used to calculate single-component distribution coefficients as a function of temperature, pressure, and composition. These single-component distribution coefficients can then be combined with mass balance and constraints provided by

\*Present address: Lamont Doherty Geological Observatory of Columbia University, Palisades, New York 10964.

the stoichiometry of the solid phases to calculate phase equilibria. The method permits rigorous calculation of the temperatures of occurrence, compositions, and proportions of all phases during melting and crystallization for multi-component systems. The method does not require knowledge of the free energy or enthalpy of mixing or other thermodynamic parameters.

The distribution coefficients used are similar to the single-element distribution coefficients ( $K_d$ 's) used for trace elements in modeling igneous systems. Because it is easier to consider components rather than elements, we use single-component  $K_d$ 's for calculation of phase equilibria.

To demonstrate this method, calculations of phase equilibria are presented for well-known binary systems showing solid solution, eutectic, and peritectic behavior, and for a ternary system showing peritectic behavior. The more important applications of the method are to complex systems not otherwise amenable to quantitative, graphical representation. As an example, calculations are presented for olivine-plagioclase-liquid equilibria in tholeiitic basalts. These calculations are believed to be applicable over a range of compositions and temperature and can be applied to several petrogenetic problems.

For the binary and ternary systems the data for determining the effects of composition and temperature on the distribution coefficients are taken directly from the experimental systems under consideration. This procedure requires accurate chemical compositions for the liquid and solid phases. The distribution coefficients are then combined with mass balance and stoichiometry to calculate the phase equilibria. The relations among composition, temperature, and distribution coefficients are empirical and are usually not simply related to thermodynamic parameters. The relationships are applicable only to the system considered and should not be extrapolated to systems of different composition because small changes in composition in some cases have large effects on the values of the distribution coefficients.

The chemical compositions of the phases are expressed in terms of cation mol%. These are conservative units so that the proportions of phases calculated in a system are independent of the components chosen [see Brady and Stout (1980)]. Cation mol percent is particularly useful because it allows the mole fractions of the components in the phases to be calculated directly from the chemical compositions. Although this paper concerns itself with solid-liquid equilibria, a similar approach should be applicable to solid-solid equilibria as well.

## Single-Component Distribution Coefficients

For any component,  $i$ , distributed between two phases,  $\alpha$  and  $\beta$ , the chemical potentials ( $\mu$ ) in the two phases are related to the activities ( $a$ ) by

$$\mu_{\alpha}^i = \mu_{\alpha}^{i^0} + RT \ln a_{\alpha}^i, \quad (1)$$

$$\mu_{\beta}^i = \mu_{\beta}^{i^0} + RT \ln a_{\beta}^i \quad (2)$$

at equilibrium,  $\mu_\alpha^i = \mu_\beta^i$ , so

$$\log \frac{a_\alpha^i}{a_\beta^i} \equiv \frac{\mu_\beta^i - \mu_\alpha^i}{RT} \quad (3)$$

Since  $a^i = \gamma^i C^i$ , substitution yields [Banno and Matsui (1973)]:

$$\log \frac{C_\alpha^i}{C_\beta^i} \equiv \log K_{d_i}^{\alpha/\beta} = \frac{\mu_\beta^i - \mu_\alpha^i}{RT} - \log \frac{\gamma_\alpha^i}{\gamma_\beta^i}, \quad (4)$$

where  $\gamma$  is the activity coefficient, and  $C_\alpha^i$  is the concentration of element  $i$  in phase  $\alpha$ .

Thus,  $K_d$  can be derived directly from equating the chemical potential of a component in two phases and it describes the equilibrium relationship between the mole fractions of the component in the coexisting phases.

## Mass Balance and $K_d$ 's

The equation for mass balance for any component,  $i$ , in a mineral-melt system is

$$C_0^i = FC_L^i + (1 - F)C_S^i, \quad (5)$$

where subscripts  $L$  and  $S$  indicate concentrations of  $i$  in liquid and solid respectively,  $F$  is the fraction of liquid, and  $C_0^i$  is the concentration of  $i$  in the system considered. This equation also expresses the lever rule used with phase diagrams. For any component,  $i$ , in equilibrium between a phase,  $\alpha$ , and a liquid  $L$ ,

$$K_{d_i}^{\alpha/L} = \frac{C_\alpha^i}{C_L^i} \quad (6)$$

Equation (6) may be substituted into Eq. (5) to yield

$$\frac{C_L^i}{C_0^i} = \frac{1}{K_{d_i}^{\alpha/L}(1 - F) + F} \quad (7)$$

Equation (7) is applicable when there is one solid phase coexisting with the liquid. When there is more than one solid phase, a bulk distribution coefficient,  $D$ , is defined as

$$D = \sum_{\alpha} (X_{\alpha} K_{d_i}^{\alpha/L}) = \frac{C_S^i}{C_L^i}, \quad (8)$$

where  $X_{\alpha}$  is the proportion of phase  $\alpha$  in the solid. Substituting Eq. (8) into Eq. (5) yields the equation that for any given set of conditions and appropriate  $K_d$ 's is valid for determining the distribution of any and all elements involved

in equilibrium melting and crystallization.

$$\frac{C_L}{C_0} = \frac{1}{D(1-F) + F} \quad (9)$$

This equation was derived and applied to the distribution of trace elements by Schilling (1966).

## Stoichiometric Criteria and $K_d$ 's

In addition to the general requirement of mass balance, a crystalline phase must satisfy stoichiometric conditions in order to be stable. The following discussion of stoichiometric constraints relies exclusively on cation mole percent and the Niggli molecular norm [Barth, (1962, p. 65ff)] to represent the abundance of elements, oxides, and components. Use of cation mole percent allows the mole fractions of components in phases to be calculated directly from their chemical compositions.

For each phase the sum of the mole fractions of the components must be one.

$$\sum C_\alpha^i = 1. \quad (10)$$

Site occupancy and charge balance requirements, however, must also be met. In olivine, for example, the octahedral, divalent cation oxides must sum to 66.67 mol%, and tetrahedral quadrivalent cation oxides must sum to 33.33 mol%. For plagioclase, the anorthite plus albite components must sum to 100 mol%, or alternatively, sodium and calcium oxides must sum to 20.00 mol%, silicon and aluminum oxides must sum to 80.00 mol%, and charge balance must be maintained. For more complex phases a series of equations may be necessary to ensure that the requirements of stoichiometry, site occupancy, and charge balance are met. However, it is preferable to work with components which can be expressed as end-member phases, (such as anorthite and albite for plagioclase) because then charge balance and site occupancy are automatically considered.

Stoichiometric considerations can be combined with  $K_d$ 's by combining the definition of  $K_d$  expressed as

$$C_\alpha^i = C_L^i K_d^{\alpha/L} \quad (11)$$

with Eq. (10) to yield

$$\sum C_L^i K_d^{\alpha/L} = 1. \quad (12)$$

Equation (12) specifies the equilibrium condition. A liquid is supersaturated with respect to the solid if the abundance of the species or components in the liquid are high enough so that the sum is greater than 1. For equilibrium to be established, the solid must crystallize, reducing the concentrations and activities of the pertinent components or species in the liquid. Likewise, the liquid is

undersaturated if the sum is less than 1. Only when the stoichiometric criterion is exactly fulfilled, i.e., the sum in Eq. (12) is 1, is there equilibrium between solid and liquid phases.

The stoichiometry of the solid phase provides significant constraints on the relationship of  $K_d$ 's to one another, to exchange reaction distribution coefficients, and to temperature, pressure, and liquid composition. Single-component  $K_d$ 's tend to be dependent on temperature, pressure, and liquid composition. For two similar components, exchange reaction distribution coefficients ( $K_D$ 's), which are ratios of single-component  $K_d$ 's, show less variation because the dependencies of the single-component  $K_d$ 's tend to cancel.

Stoichiometry provides a simple relationship between  $K_d$ 's and  $K_D$ . From Eq. (10), it is apparent that the sum of components which can substitute for one another in the solid phase must be equal to a constant,  $\theta$ , where  $\theta \leq 1$ . If the components have the composition of an end-member phase, such as  $\text{Mg}_2\text{SiO}_4$  and  $\text{Fe}_2\text{SiO}_4$  in olivine, then  $\theta = 1$ . If the components represent a species other than an end-member phase,  $\theta < 1$ ; for  $\text{MgO}$  and  $\text{FeO}$  in olivine, for example,  $\theta = 0.6667$ . For any two components  $A$  and  $B$ , which substitute for one another, an exchange reaction may be written between liquid ( $L$ ) and solid ( $\alpha$ ):

$$A_L + B_\alpha = A_\alpha + B_L \quad (13)$$

from which an exchange reaction distribution coefficient,  $K_D^{A/B}$ , can be defined:

$$K_D^{A/B} = \frac{C_\alpha^A C_L^B}{C_L^A C_\alpha^B} = \frac{K_{d_\alpha}^{\alpha/L}}{K_{d_b}^{\alpha/L}} \quad (14)$$

A separate  $K_D$  can be defined between  $B$  and all substituting elements. Rearrangement of Eq. (14) yields

$$C_\alpha^A = K_D^{A/B} C_L^A K_{d_b}^{\alpha/L} \quad (15)$$

Substitution of equations such as Eq. (15) for all substituting elements into the stoichiometric equation (10) yields

$$K_{d_b}^{\alpha/L} = \frac{\theta}{\sum_{i=A} C_L^B K_D^{i/B}} \quad (16)$$

Thus although the method of calculation presented in this paper uses single-component  $K_d$ 's, Eq. (16) demonstrates that exchange reaction  $K_D$ 's could equally well be used for phases in which solid solution occurs.

Langmuir and Hanson (1980) demonstrated that when  $K_D$  is a constant, i.e., it is independent of temperature, pressure, and composition, Eq. (16) gives the  $K_d$ 's necessary for a liquid to be in equilibrium with a phase even though temperature and pressure are not known.  $K_D$ 's need not be constant for all conditions. Even when  $K_D$  is not constant the stoichiometric requirements of the solid phases cause the values of the  $K_d$ 's to be dependent on one another.

The  $K_d$ 's may be intrinsic to the liquid composition. Thus for a given liquid composition it is sometimes possible to state what the  $K_d$ 's and composition of a solid phase would be, if stable, while not knowing the temperature at which the solid phase would appear.

## Calculating Phase Equilibria

The mass balance equations, stoichiometric equations, and  $K_d$ 's permit the calculation of the distribution of components during melting and crystallization, yielding the identities, compositions, and proportions of the coexisting phases as a function of temperature and pressure. For a given composition, temperature and pressure there are

- (1)  $E$  unknowns for the abundances of  $E$  components in the liquid,
- (2)  $NE$  unknowns for the abundance of  $E$  components in  $N$  solid phases,
- (3)  $N$  unknowns for the proportions of  $N$  solid phases,
- (4) one unknown for the proportion of the liquid phase.

The equations consist of

- (1)  $E$  equations from mass balance, one for each of the  $E$  components in the liquid,
- (2)  $NE$  equations from the  $K_d$ 's since there is a  $K_d$  for each of the  $E$  components between the liquid and each of the  $N$  solid phases,
- (3)  $N$  stoichiometric equations for  $N$  solid phases,
- (4) one equation showing that the sum of all phases must equal 1.

The number of equations equals the number of unknowns, and a unique solution may be calculated.

The above analysis can be used to calculate the compositions and proportions of the solid phases and melts. In order to make these calculations, it is necessary to know the appropriate  $K_d$ 's as a function of temperature, pressure, and composition. For equilibrium crystallization or batch melting the phase proportions and compositions can be determined directly at any temperature. For fractional crystallization, the liquid line of descent is most easily calculated by lowering the temperature from the liquidus to the temperature of interest in small increments, removing the solid phases from the system at each step. Crystallization paths between equilibrium and fractional crystallization can be calculated with larger temperature increments than that for fractional crystallization. More complex crystallization [e.g., O'Hara (1977)] or melting processes [e.g., Langmuir *et al.* (1977)] also require incremental calculations. For the calculation of phase diagrams, it is necessary to find the compositions and temperatures of invariant points, univariant lines, and phase boundaries.

The practicality of this method of calculation obviously depends on how well the values of the  $K_d$ 's are known over the necessary range of temperature,

composition, and pressure.  $K_d$ 's often show systematic variations with liquid composition as well as temperature. Watson (1977), for example, demonstrated that the  $K_d$  for MnO between olivine and liquid varies systematically with temperature and the Si/O ratio of the liquid in the system forsterite–anorthite–albite. Whereas  $K_d$ 's for MgO and FeO between olivine and liquid follow the Arrhenius relationship over a limited compositional range, over a wide range these  $K_d$ 's are also dependent on composition [Roeder and Emslie (1970); Roeder (1974); Longhi *et al.* (1978); Bender *et al.* (1978); Leeman (1978)]. The compositional dependence is often systematic. For example, the distribution of MgO between olivine and liquid in a wide range of low alkali systems can be determined from the formulation of Herzberg (1979).

As long as the dependence of  $K_d$ 's on temperature and composition can be quantitatively expressed, the approach described here is applicable, and phase stabilities, compositions, and proportions can be calculated in multi-component systems. But these calculations are only as accurate as the derived equations describe the temperature and compositional dependence of the single-component  $K_d$ 's. Examples of the calculations are presented below for a binary system showing solid solution (albite–anorthite), a binary eutectic (anorthite–diopside), a binary peritectic (forsterite–silica), a ternary system with peritectic behavior (forsterite–anorthite–silica), and crystallization of a natural basalt melt. The systems are at 1 atm.

The distribution coefficients in these systems are calculated based on the data in each of the experimental systems. The  $K_d$ 's are determined by dividing a given component in the solid by the same component in the liquid. The  $K_d$ 's are applicable not only at the liquidus, but whenever liquid and solid coexist in the system. In systems with ideal solution in both solid and liquid phases and in many other cases the data on a plot of  $\log K_d$  versus  $1/T$  (Arrhenius plot) will be along a straight line [see Eq. (4)]. If there is not such a simple relation, a quantitative representation of the effects of composition on the  $K_d$ 's must be sought. Very often the compositional dependence is systematic. Because the compositional effects are often quite large, the relations given for the  $K_d$ 's are usually applicable only for the system considered and should not be extrapolated to systems with different compositions.

## Binary Solid Solution: Albite–Anorthite

Plagioclase shows essentially ideal solid solution at near-liquidus temperatures in the pure system [Bowen (1913)]. As expected in a system with ideal solution the  $\log K_d$ 's plot along a straight line on the Arrhenius plot (Fig. 1) and give the following relations

$$\log_{10} K_{d_{An}} = \frac{6358}{T} - 3.49, \quad (17)$$

$$\log_{10} K_{d_{Ab}} = \frac{2512}{T} - 1.85. \quad (18)$$



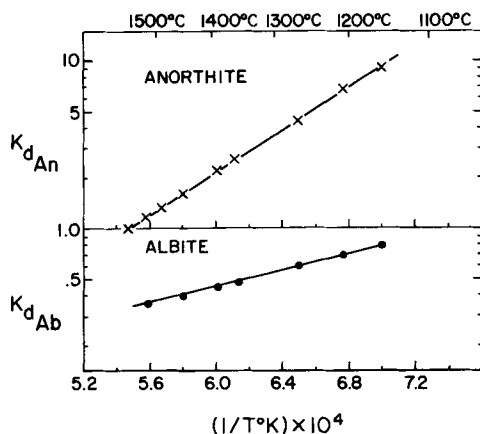


Fig. 1. Arrhenius plot, i.e. inverse temperature plotted against the  $\log_{10}$  of single component distribution coefficients ( $K_d$ 's) for albite and anorthite components in cation mole percent in the binary system [Bowen (1913)].

The stoichiometric equation for plagioclase is

$$K_{d_{An}}^{Pl/L} C_L^{An} + K_{d_{Ab}}^{Pl/L} C_L^{Ab} = 1.0. \quad (19)$$

In this system there are only two components and at equilibrium the melt composition is given by

$$C_L^{An} + C_L^{Ab} = 1. \quad (20)$$

Substituting Eqs. (17)–(19) into Eq. (20) and rearranging yields

$$C_L^{An} = \frac{1 - K_{d_{Ab}}}{K_{d_{An}} - K_{d_{Ab}}} = \frac{1 - 10^{(2512/T) - 1.85}}{10^{(6358/T) - 3.49} - 10^{(2512/T) - 1.85}} \quad (21)$$

which is the equation for the concentration of anorthite component in the liquid on the liquidus as a function of temperature. The concentration of albite in the liquid is then given by Eq. (20). Calculation of the liquidus does not require consideration of mass balance because at the liquidus the system can be considered to be entirely liquid. The calculated liquidus agrees with the experimental determination of the liquidus to within 2°C except at high albite contents, where the calculated liquidus is within 10°C degrees of the experimental.

Calculation of the proportions and compositions of phases below the liquidus, which determines the liquid line of descent, requires mass balance in addition to stoichiometry and  $K_d$ 's. Consider, for example, the problem of determining the compositions and proportions of phases 20°C below the liquidus when the bulk composition is  $C_0^{An} = C_0^{Ab} = 0.5$ . Equation (21) gives a liquidus temperature of 1451°C for a liquid with  $C_L^{An} = 0.5$ . At 1431°C, Eq. (21) gives  $C_L^{An} = 43.2\%$ .  $C_S^{An}$  may then be determined from the  $K_d$  for An at 1431°C given by Eq. (17). The solid plagioclase contains 76.1% anorthite.

Mass balance requires that

$$(1 - F)C_S^{An} + FC_L^{An} = C_0^{An}. \quad (22)$$

Substituting the relevant numbers and solving yields  $F = 0.793$ . Thus 20.7% crystallization has occurred. Fractional crystallization could also be modeled by considering very small temperature increments and considering the calculated melt as the total system for the next increment. Because the values of the  $K_d$ 's can be described accurately as a function of temperature and composition in the pure plagioclase system, it is possible to calculate accurately the temperatures of appearance, compositions, and proportions of the phases.

### Binary Eutectic: Anorthite-Diopside

$K_d$ 's for anorthite and diopside in cation mole percent in the binary system are shown in Fig. 2. The data are from Weill *et al.* (1979). The logs of the  $K_d$ 's are approximately linear when plotted against inverse temperature. The plot for anorthite shows a slight curvature, resulting in deviations from the calculated line by as much as 13°C for some data points. The equations for the  $K_d$ 's are

$$\log_{10} K_{d_{An}}^{An/L} = \frac{3763}{T} - 2.05, \quad (23)$$

$$\log_{10} K_{d_{Di}}^{Di/L} = \frac{4862}{T} - 2.92. \quad (24)$$

Solid solution of Al in the diopside is ignored.

At the eutectic, since both solid phases are stable,

$$K_{d_{An}} C_L^{An} = 1.0, \quad (25)$$

$$K_{d_{Di}} C_L^{Di} = 1.0, \quad (26)$$

$$C_L^{Di} + C_L^{An} = 1.0. \quad (27)$$

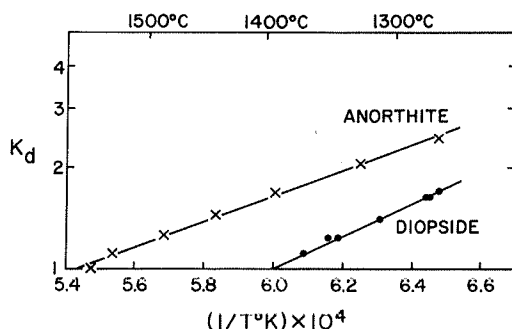


Fig. 2. Arrhenius plot of  $K_d$ 's for anorthite and diopside in cation mole percent from the binary system [Osborne (1942)].

There are then five equations. The unknowns are the two  $K_d$ 's, the two liquid compositions, and  $T$ . Substitution of Eqs. (23) and (24) into Eqs. (25) and (26) and then into Eq. (27) leads to

$$10^{-(3763/T)+2.05} + 10^{-(4862/T)+2.92} = 1.0. \quad (28)$$

The calculated eutectic occurs at 1271°C, with  $C_L^{An} = 0.41$  and  $C_L^{Di} = 0.59$ . The experimental eutectic is 1270°C, with  $C_L^{An} = 0.412$  and  $C_L^{Di} = 0.588$ .

Along the univariant curves in the An–Di binary, one solid phase is stable. This leads to four equations and five unknowns, which is appropriate for univariant conditions.

### Binary Peritectic: Forsterite–Silica

The mathematical derivation for a binary peritectic is the same as that for a eutectic. In the system forsterite–silica,  $K_d$ 's for forsterite and enstatite were obtained from the experimental data (Fig. 3) and yield

$$\log_{10} K_{d_{Fo}}^{Fo/L} = \frac{1614}{T} - 0.7452, \quad (29)$$

$$\log_{10} K_{d_{En}}^{En/L} = \frac{11406}{T} - 6.223. \quad (30)$$

These equations put all of the MgO in the melt into enstatite or forsterite components. Thus a liquid with 50 cation mol% MgO and 50 cation mol% SiO<sub>2</sub> would contain 100% enstatite, or 75% forsterite plus 25% silica.

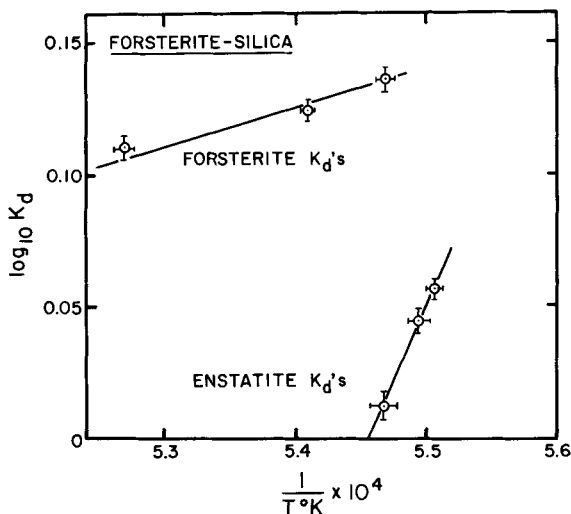


Fig. 3. Arrhenius plot of  $K_d$ 's for forsterite and enstatite components from the binary system forsterite–silica [Bowen and Andersen (1914)]. The forsterite component in the liquid was calculated by putting all MgO in forsterite. The enstatite component in the liquid was calculated by putting all MgO into enstatite.

At the peritectic, both forsterite and enstatite are stable, so

$$K_{d_{\text{Fo}}}^{\text{Fo}/L} C_L^{\text{Fo}} = 1, \quad (31)$$

$$K_{d_{\text{En}}}^{\text{En}/L} C_L^{\text{En}} = 1. \quad (32)$$

Substituting from Eqs. (29) and (30) and solving yields a calculated peritectic temperature of 1556°C and calculated compositions of

$$C_L^{\text{Fo}} = 72.9\%, \quad C_L^{\text{SiO}_2} = 27.1\%.$$

These compare with experimental values of 1556°C and compositions of

$$C_L^{\text{Fo}} = 73.1\%, \quad C_L^{\text{SiO}_2} = 26.9\%.$$

Whether peritectic-eutectic or eutectic-eutectic behavior is exhibited in the Fo-SiO<sub>2</sub> system can be expressed by the relative values of the  $K_d$ 's for Fo and En. For peritectic behavior, when  $C_L^{\text{En}} = 1.00$  ( $C_L^{\text{Fo}} = 0.75$ ),  $K_d^{\text{En}}$  must be less than 1, while  $K_d^{\text{Fo}}$  must equal 1.33. In contrast, for a Fo-En eutectic, when  $C_L^{\text{En}} = 1.00$ ,  $K_d^{\text{En}}$  must equal 1, while  $K_d^{\text{Fo}}$  must be less than 1.33. Thus when peritectic behavior changes to eutectic behavior with increased pressure, the  $K_d$ 's for En must increase relative to those for Fo.

## Multicomponent Invariant Points

The approach used for the binary eutectic and peritectic applies for invariant points involving any number of phases and components. Consider a system at constant pressure in which  $n$  components in the liquid are  $i, j, \dots$ . At an invariant point,  $N$  solids are stable, and there are  $N$  stoichiometric equations of the form

$$\sum K_d C_L^i = 1. \quad (33)$$

The  $K_d$ 's for each component in each phase must be known, so there are  $Nn$  equations describing the variations of the  $K_d$ 's with temperature and liquid composition. Also, for any liquid composition, the sum of all components in the liquid must be 1.0. As long as  $N = n$ , the unknowns include  $(Nn)$   $K_d$ 's, the abundances of the  $n$  components in the liquid, and  $T$ . The number of equations equals the number of unknowns, and the isobaric invariant composition and temperature are thus specified. Because there is a single solution, the system is invariant. If pressure were a variable, there would be an additional unknown and the system would be univariant.

Along every isobaric univariant curve in the system,  $N - 1$  solid phases are stable. Then there are the same number of unknowns as for the invariant point, but one less stoichiometric equation. The solution is a line, i.e., there is one degree of freedom, and the system is univariant. An analogous development applies for any number of degrees of freedom, in correspondence with the phase rule.

## Anorthite–Forsterite–Silica

All of the examples discussed thus far have been relatively simple systems where  $\log K_d$  varies linearly with inverse temperature. But in many systems the dependence of the  $K_d$ 's on composition must be determined. As an example of how to treat a more complex system, calculation of the liquidus fields for forsterite, anorthite, and enstatite and the associated cotectics and ternary peritectic in the forsterite–anorthite–silica system will be presented. Figure 4 shows  $K_d$ 's for forsterite as a function of inverse temperature. Except for the  $K_d$ 's on the binary joins, the  $K_d$ 's in the ternary system can be approximated by

$$\log_{10} K_{d_{\text{Fo}}}^{\text{Ol/L}} = \frac{3925}{T} - 2.002. \quad (34)$$

The  $K_d$ 's for enstatite show a fair correlation on the Arrhenius plot but some experimental points differ by as much as  $30^\circ$  from a least-squares line through the data. There is, however, a systematic dependence of the  $K_d$ 's on the  $\text{SiO}_2$  content of the liquid, so that the temperatures and compositional dependence of the  $K_d$ 's can be approximated by the following equations:

$$\log_{10} K_{d_{\text{En}}}^{\text{En/L}} = \frac{A}{T} + B, \quad (35)$$

$$A = 8790 C_L^{\text{SiO}_2} + 2195, \quad (36)$$

$$B = 4.73 C_L^{\text{SiO}_2} - 1.202. \quad (37)$$

These equations recover temperatures to within  $14^\circ\text{C}$ . Data are shown in Fig. 5(a).

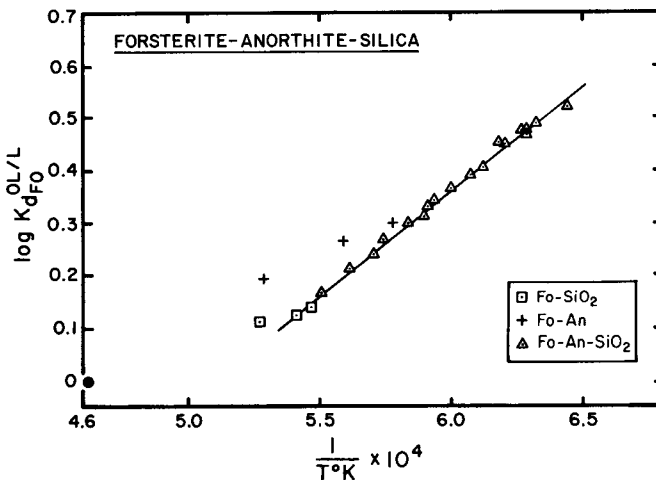


Fig. 4.  $K_d$ 's for forsterite in cation mole percent from the ternary system anorthite–forsterite–silica [Andersen (1915)]. The solid dot is for melting of pure forsterite. Note that the  $K_d$ 's for the two binaries (Fo–SiO<sub>2</sub>, Fo–An) do not lie on the same line as the  $K_d$ 's from the ternary.

The anorthite liquidus surface exhibits a more complex dependence on temperature and composition. The following equations recover temperatures for all ternary experimental compositions to within 8°C.

$$K_d^{\text{An}/L} = \alpha \left[ 1.06 - \left( \frac{1.03 C_L^{\text{Fo}}}{C_L^{\text{Fo}} + C_L^{\text{SiO}_2}} \right) \right] \left[ 10^{(4363/T) - 2.395} - 10^{(2099/T - 1.152)} \right] + 10^{(2099/T) - 1.152} \quad (38)$$

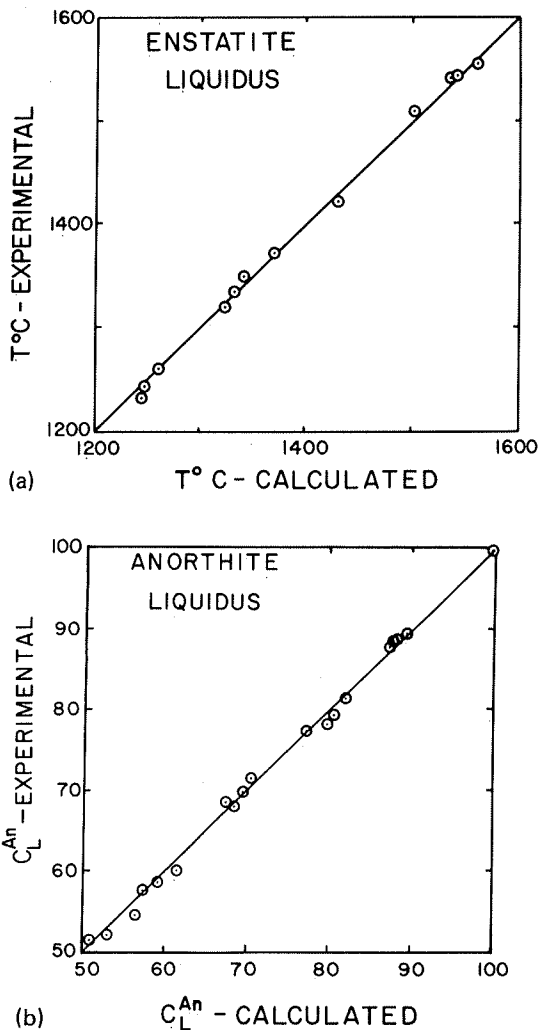


Fig. 5. (a) Comparison of experimental temperatures [Andersen (1915)] with calculated temperatures for the enstatite liquidus surface in the system forsterite-anorthite-silica. (b) Comparison of experimental [Andersen (1915)] and calculated ternary compositions for the anorthite liquidus surface in the system forsterite-anorthite-silica. The maximum difference of less than 2 cation mol% anorthite corresponds to a maximum temperature difference of 10°C.

When  $C_L^{\text{An}}/C_L^{\text{SiO}_2} > 5$ ,  $\alpha = 1$ . When it is less than 5,

$$\alpha^2 = \frac{C_L^{\text{An}}/C_L^{\text{SiO}_2} - 4 \left[ C_L^{\text{Fo}} / (C_L^{\text{Fo}} + C_L^{\text{SiO}_2}) \right] + 0.54}{6}. \quad (39)$$

When the cation ratio of  $C_L^{\text{An}}/C_L^{\text{SiO}_2} \geq 5$  (i.e.,  $\text{CaAl}_2\text{Si}_2\text{O}_8$  molecules are more abundant than  $\text{SiO}_2$  molecules), the liquidus surface is quite simple, changing smoothly from the forsterite to silica join. The exponential terms in Eq. (38) give the relative distance between lines appropriate for the An–Fo and An– $\text{SiO}_2$  joins on Arrhenius plots, and the first term shows that the change is simply related to the Fo/ $\text{SiO}_2$  ratio of the liquid. Once  $C_L^{\text{An}}/C_L^{\text{SiO}_2} < 5$  (or the molecular ratio of  $\text{CaAl}_2\text{Si}_2\text{O}_8/\text{SiO}_2 < 1$ ), however, the  $K_d$ 's show a dependence on the An/ $\text{SiO}_2$  ratio of the liquid as well as the Fo/ $\text{SiO}_2$  ratio. The regular covariation of  $K_d$ 's with simple compositional parameters potentially gives insight into the structure of silicate liquids. A comparison of calculated points with experimental data is given in Fig. 5(b). Equation (39) does not give  $\alpha = 1$  when  $C_L^{\text{An}}/C_L^{\text{SiO}_2} = 5$ . So the isotherms have been interpolated across the  $C_L^{\text{An}}/C_L^{\text{SiO}_2} = 5$  boundary in Fig. 6.

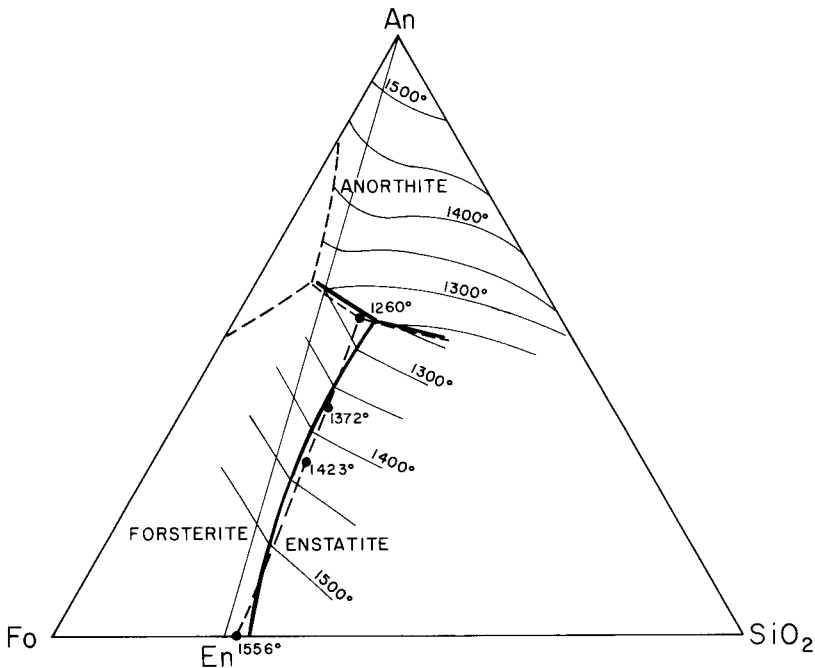


Fig. 6. Calculated portions of the phase diagram for the system forsterite–anorthite–silica in cation mole percent. Solid lines are calculated isotherms and cotectics. Dashed lines are cotectics drawn between experimental data points. Experimental temperatures for the four experimental points on the forsterite–enstatite cotectic are printed in small numerals. The calculated and experimental temperatures agree to better than  $10^\circ\text{C}$  except for two points in the enstatite field. Experimental data are from Andersen (1915).

Liquidus surfaces are plotted in Fig. 6, where they are compared with experimental data points and cotectics. The Fo-An and An-En calculated cotectics are very close to the experimental cotectics. The calculated Fo-En cotectic shows an opposite curvature to that of the experimental cotectic causing the calculated ternary peritectic to differ from the experimental point by 2.5 mol% SiO<sub>2</sub> which is the maximum deviation from the experimental data. The equations for the  $K_d$ 's could also be used to calculate melting paths and liquid lines of descent for both equilibrium and fractional crystallization.

## Olivine Saturation in Basaltic Magmas

The olivine-enstatite-liquid equilibrium in both the Fo-SiO<sub>2</sub> binary and the An-Fo-SiO<sub>2</sub> ternary can be quantitatively modeled without explicit consideration of silica activity. The effect of silica is taken into account by the dependence of the  $K_d$ 's on liquid composition and temperature. It is thus feasible to model olivine-liquid equilibria considering  $K_d$ 's for forsterite and fayalite components alone when all MgO and FeO are calculated as forsterite and fayalite. In practice, this means that olivine-liquid equilibria can be modeled using  $K_d$ 's for MgO and FeO without explicit consideration of silica, as shown by Roeder and Emslie (1970).

The stoichiometric criterion provides a simple way of looking at the olivine saturation surface and also permits evaluation of the probable effects of other components on the stability of a phase. Because Roeder and Emslie (1970) used MgO and FeO for their olivine saturation surface, we will also use MgO and FeO, though to be more rigorous these components should be given as forsterite and fayalite. For olivine,

$$C_{Ol}^{MgO} + C_{Ol}^{FeO} = 0.6667. \quad (40)$$

From the definition of  $K_d$ ,

$$C_{Ol}^{FeO} = C_L^{FeO} K_{d_{FeO}}^{Ol/L}, \quad (41)$$

$$C_{Ol}^{MgO} = C_L^{MgO} K_{d_{MgO}}^{Ol/L}. \quad (42)$$

Substituting Eqs. (41) and (42) into Eq. (40) gives

$$C_L^{MgO} K_{d_{MgO}}^{Ol/L} + C_L^{FeO} K_{d_{FeO}}^{Ol/L} = 0.6667. \quad (43)$$

Equation (43) defines the olivine saturation surface as long as the  $K_d$ 's for orthopyroxene or pigeonite components are sufficiently low so that pyroxene does not replace olivine as the stable phase. If Eq. (43) sums to less than 66.67 cation mol% the liquid is undersaturated with respect to olivine and olivine is not stable. If it sums to exactly 66.67 mol%, the liquid composition is at the olivine saturation surface. If it sums to greater than 66.67 mol%, the liquid is supersaturated with respect to olivine.

The stoichiometric criterion for equilibrium provides a simple mathematical formulation for the olivine saturation surface when the  $K_d$ 's for MgO and FeO are dependent only on temperature [see, for example, Roeder and



Emslie (1970)]

$$\log_{10} K_{d_{\text{MgO}}}^{\text{Ol/L}} = \frac{A_1}{T} - B_1, \quad (44)$$

$$\log_{10} K_{d_{\text{FeO}}}^{\text{Ol/L}} = \frac{A_2}{T} - B_2. \quad (45)$$

Substituting Eqs. (44) and (45) into Eq. (43) gives

$$C_L^{\text{MgO}} 10^{(A_1/T) - B_1} + C_L^{\text{FeO}} 10^{(A_2/T) - B_2} = 0.6667. \quad (46)$$

At constant  $T$ , Eq. (46) is a straight line on a plot of MgO versus FeO. If there were no compositional dependence of the  $K_d$ 's, this would be the equation for the olivine saturation surface as a function of temperature and the abundances of MgO and FeO in the liquid.

Figure 7 shows the olivine saturation surface for tholeiitic basalt liquids using  $K_d$ 's from Roeder and Emslie (1970) converted to cation mole percent.

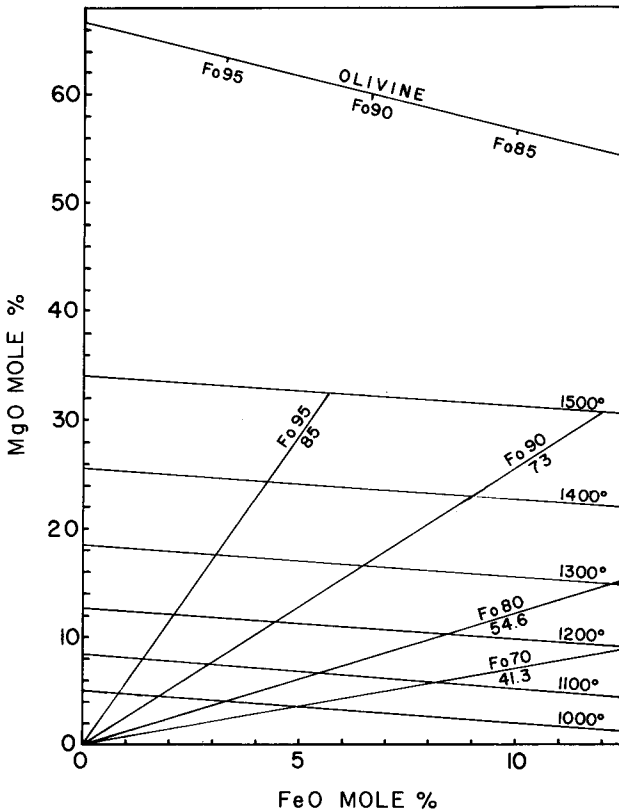


Fig. 7. Olivine saturation surface on a plot of MgO vs. FeO in cation mole percent using the data of Roeder and Emslie (1970). Temperatures are in degrees C. The Fo compositions above the lines radiating from the origin are the olivine compositions which coexist with liquid compositions along the line. Numbers below the line are the MgO/(MgO + FeO) ratios or Mg numbers for those liquids.

The saturation surface yields the temperature of appearance and composition of olivine crystallizing from any liquid for which the  $K_d$ 's are appropriate. Roeder and Emslie (1970) and Hanson and Langmuir (1978) discuss applications of such a saturation surface.

## Effects of Minor Components

As a further example of the utility of the stoichiometric criterion for equilibrium, consider the addition of MnO or NiO to a liquid in equilibrium with olivine. Equation (43) then becomes

$$C_{\text{Ol}}^{\text{MgO}} K_{d_{\text{MgO}}}^{\text{Ol/L}} + C_{\text{Ol}}^{\text{FeO}} K_{d_{\text{FeO}}}^{\text{Ol/L}} + \sum (C_{\text{Ol}}^i K_{d_i}^{\text{Ol/L}}) = 0.6667, \quad (47)$$

where the first and second terms represent the major components MgO and FeO and the summation in the third term represents the addition of minor components. Data from basalts demonstrate that the  $K_d$  for NiO between olivine and liquid is higher than that for MnO [Irving (1978)]. As either of these components are added to a liquid in equilibrium with olivine, the liquid will become supersaturated with respect to olivine as shown by the incremental addition of the third term in Eq. (47). Because NiO has a higher  $K_d$  than MnO, addition of NiO to the melt will stabilize olivine more than will the addition of MnO. For a  $K_d$  of about 10, 0.1% NiO<sub>2</sub> in the melt allows olivine to be in equilibrium when FeO and MgO in olivine sum to only 65.67. This is approximately equivalent to a 4°C increase in the temperature of olivine appearance. If the  $K_d$  for MnO at the same temperature is about 3, then 0.33% MnO would have to be present in the liquid to have the same effect as 0.1% NiO.

If a component which does not enter olivine (i.e.,  $K_d = 0$ ) is added to an olivine saturated liquid in near ideal solution, the concentrations of MgO and FeO in the liquid are decreased, so higher  $K_d$ 's are required for the liquid to be saturated with olivine. This would require lowering the temperature because the  $K_d$ 's increase as the temperature decreases.

## Liquid Lines of Descent for Basaltic Magmas

In order to show the potential of this approach to more complex systems we calculate the phase stabilities, compositions, and proportions in a basalt system which has been studied experimentally at 1 atm by Bender *et al.* (1978). Few published experiments give sufficient data for comparison with calculated liquid lines of descent. A common deficiency is the lack of internally consistent results because of problems of maintaining bulk composition. Bender *et al.* (1978) present data on the experimental crystallization of an ocean ridge basalt from the FAMOUS area which show consistent changes in the chemical composition of the liquid with decreasing temperature. They were also very successful in maintaining bulk composition. They report olivine

(Fo 89.5) as the liquidus phase at 1268°C, joined by plagioclase (An 89) at 1235°C. The lowest temperature for which data are reported is 1208°C, at which the olivine is Fo 84 and the plagioclase An 79–80. Pyroxene does not appear until lower temperatures.

For the conditions of this set of experiments, there are 11 unknowns for a given temperature: the abundance of MgO and FeO (or forsterite and fayalite components) in olivine and liquid, the abundances of anorthite and albite components in plagioclase and liquid and the proportions of olivine, plagioclase, and liquid. The 11 equations are the two stoichiometric equations for olivine and plagioclase.

$$C_L^{\text{MgO}} K_{d_{\text{MgO}}}^{\text{Ol/L}} + C_L^{\text{FeO}} K_{d_{\text{FeO}}}^{\text{Ol/L}} = 0.6667, \quad (48)$$

$$C_L^{\text{An}} K_{d_{\text{An}}}^{\text{Pl/L}} + C_L^{\text{Ab}} K_{d_{\text{Ab}}}^{\text{Pl/L}} = 1, \quad (49)$$

four mass balance equations of the form

$$\frac{C_L^i}{C_0^i} = \frac{1}{D^i(1-F) + F}, \quad (50)$$

where  $C_0^i$  is the abundance of the component in the initial liquid; four equations for the  $K_d$ 's for the four components; and an equation stating that the proportions of olivine, plagioclase, and liquid must sum to one. For any temperature and liquid composition, the  $K_d$ 's can be calculated and substituted into Eqs. (48) and (49), so the system is reduced to six equations and six unknowns.

Solution of this system of equations is readily accomplished by rewriting the  $D^i$ 's in Eq. (50) as  $\sum(XK_d)$ , and then substituting the mass balance equations into the stoichiometric equations. Each stoichiometric equation can then be manipulated algebraically to polynomials of the form

$$L_1 F^2 + L_2 F + L_3 = 0, \quad (51)$$

where  $L_1$ ,  $L_2$ , and  $L_3$  are of the form

$$L_i = A_1 x^2 + A_2 x + A_3, \quad (52)$$

where  $x$  is the proportion of olivine in the solid and  $(1-x)$  is the proportion of plagioclase. The coefficients in equations such as Eq. (52) consist of  $C_0$ 's and  $K_d$ 's, and thus are constants for any temperature and liquid composition. These constants change, of course, as crystallization proceeds.<sup>1</sup>

Bender *et al.* (1978) report  $K_d$ 's for MgO and FeO between olivine and liquid, and those have been converted to cation mole percent and used.  $K_d$ 's for anorthite and albite were derived using a wider set of experiments on

<sup>1</sup>Systems of equations such as Eqs. (51) and (52) can be solved easily with a computer. A copy of the computer program is available from the senior author on request. The program carries out either equilibrium or fractional crystallization of olivine and plagioclase from liquid compositions. It is not applicable if phases other than plagioclase or olivine are crystallizing. The only necessary inputs into the program are the initial liquid composition and equations for the  $K_d$ 's. Liquidus temperatures, phase proportions, phase compositions, and hence the liquid line of descent are all output from the calculations.

Table 1. Comparison of experimentally determined and calculated temperatures of appearance and compositions for crystallization of olivine and plagioclase from FAMOUS glass 527-1-1. Experimental data are from Bender *et al.* (1978). Calculations were carried out using  $K_d$ 's based on the data of Bender *et al.* (1978).

	Experimental	Calculated
OLIVINE		
Temperature	1268	1268
Composition	Fo 89.5	Fo 89.5
PLAGIOCLASE		
Temperature	1235	1223
Composition	An 89	An 82

oceanic basalts [Bender *et al.* (1978); Walker *et al.* (1979)] and the general formulation for plagioclase  $K_d$ 's presented in Langmuir (1980) and Langmuir and Hanson (in preparation).

Table 1 compares the calculated and experimental temperatures and compositions of the first olivine and plagioclase to appear. The experiments and the calculations agree well for the temperature of olivine appearance and the composition of the olivine. The calculations predict plagioclase appearance 10°C below the experimentally determined temperature, and predict a plagioclase composition of An 82–84, in contrast with the reported plagioclase composition of An 89. Several lines of evidence suggest that the calculated plagioclase composition may actually be closer to the equilibrium value. Bender *et al.* (1978) report that the first plagioclases to crystallize were very small and difficult to analyze and their analyses are not stoichiometric. They were also unable to obtain plagioclase analyses in several experimental charges at temperatures just below the first appearance of plagioclase. Finally, if the first plagioclase were indeed An 89, then the plagioclase analyzed at lower temperatures should also be more anorthitic, but for lower temperatures the calculated and experimental compositions agree very well.

Figure 8 compares the liquid line of descent for equilibrium crystallization from the experiments and the calculations. The agreement demonstrates the appropriateness of the  $K_d$ 's and the internal consistency of the experiments. For basalts of similar composition, the  $K_d$ 's should allow calculation of olivine-plagioclase-liquid equilibria. For example, Fig. 9 shows liquid lines of descent for basalts for five different MgO, FeO, An, and Ab compositions. Liquids with lower An/Ab ratios crystallize olivine alone over a larger temperature interval than those with higher An/Ab ratios and similar abundances of total plagioclase, MgO, and FeO.

The use of  $K_d$ 's based on the experiments themselves illustrates the applicability of this method of calculation to complex silicate liquids. Quantitative calculations of liquid lines of descent for such liquids are generally not possible with phase diagrams because of the large number of components. The

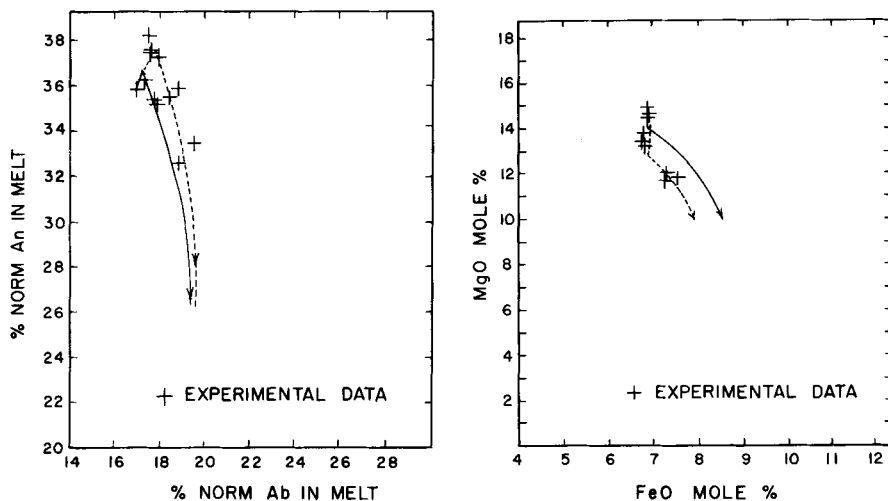


Fig. 8. Comparison of calculated liquid lines of descent for FAMOUS basalt 527-1-1 with experimentally determined compositions [Bender *et al.* (1978)]. Two sets of  $K_d$ 's are used. The dashed line was calculated using  $K_d$ 's from the experiments of Bender *et al.* (1978). The solid line was calculated using  $K_d$ 's for plagioclase from Langmuir (1980), which may be applicable to compositions ranging from tholeiitic basalt to dacite.

overall utility of the method clearly depends on developing equations for  $K_d$ 's which are appropriate over relatively wide ranges in composition. Such equations for  $K_d$ 's for plagioclase are presented in Langmuir (1980) and Langmuir and Hanson (in preparation). These equations were derived from experiments reported in the literature on compositions ranging from basalt to dacite, but no compositions corresponding to ocean ridge basalt were included in the data base. We can determine how well these  $K_d$ 's apply to an ocean ridge basalt composition by using them to calculate the liquid line of descent for this FAMOUS basalt. The results are shown in Fig. 8. The calculated liquid line of descent is very similar to the experimental liquid line of descent, even though the  $K_d$ 's were derived independently. The development of general relations for other minerals would allow calculation of liquid lines of descent for a broad range of geologically important liquid compositions.

The present ability to calculate olivine-plagioclase-liquid equilibria accurately has several immediate applications. One of the most fruitful methods of analyzing mineral/melt equilibria has been the projection of the liquid compositions onto ternary diagrams [see, e.g., O'Hara (1976)]. In such projections the variations in the MgO/FeO and An/Ab ratios are generally ignored resulting in cotectic fields rather than cotectic lines. The method described here makes it possible to quantify the effects of varying the MgO/FeO and An/Ab ratios on the temperatures and positions of olivine-plagioclase cotectics on such projections. Table 2 shows the effects of varying only the An/Ab ratio of the normative plagioclase in the melt on the temperature and MgO

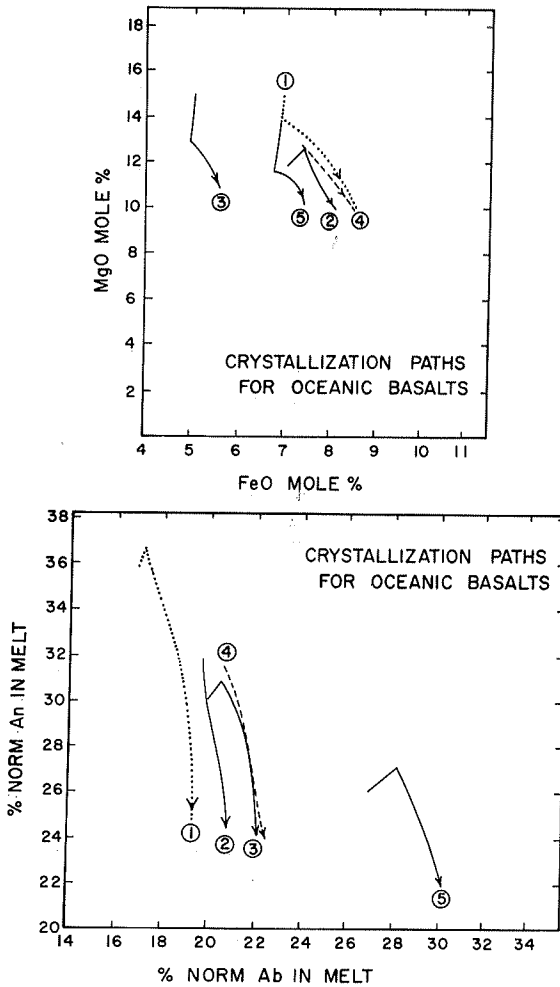


Fig. 9. The effects of composition on the liquid lines of descent. Numbers represent the same compositions in both plots. Compositions 1, 3, and 5 crystallize olivine followed by olivine + plagioclase. Composition 2 crystallizes plagioclase followed by olivine + plagioclase. Composition 4 crystallizes olivine + plagioclase. The order of appearance of the phases reflects the relative amounts of MgO, FeO, An, and Ab in the liquid.

and FeO content of the liquid when the olivine-plagioclase cotectic is reached. All of these liquids initially have olivine alone on the liquidus. As the composition of the first plagioclase varies from An 86 to An 68, the temperature at which the cotectic is reached decreases by over  $60^{\circ}\text{C}$  and the plagioclase/olivine ratio at the cotectic changes more than 25%.

The ability to calculate liquid lines of descent is also important for evaluating crystallization processes in magma chambers. For example, although fractional crystallization is frequently considered to occur in magma cham-

Table 2. The effect of changing the An/Ab ratio in a basalt liquid on the temperature ( $T_{cot}$ ) and composition of the phases on the first intersection of the olivine-plagioclase cotectic on cooling. All liquids contain the same initial amount of normative plagioclase, MgO and FeO.  $C_L^{Fo}$ ,  $C_{Plag}^{An}$ , etc. are the abundances of the various components in the phases, and  $F$  is the fraction of liquid remaining where the cotectic is first reached in cation mole percent.

Initial Conditions									
$C_0^{MgO} = 15.0$									
$C_0^{FeO} = 6.43$									
$C_0^{Ab} + C_0^{An} = 53.5$									
$\frac{C_0^{An}}{C_0^{Ab}}$	$T_{cot}$	$C_L^{MgO}$	$C_L^{FeO}$	$C_L^{An}$	$C_L^{Ab}$	$F$	$C_{OL}^{Fo}$	$C_{Plag}^{An}$	$\frac{C_L^{An} + C_L^{Ab}}{C_L^{MgO} + C_L^{FeO}}$
0.726	1475	11.7	6.25	23.9	33.5	0.92	86	68	3.20
1.378	1511	13.4	6.39	31.9	23.4	0.96	87	78	2.79
2.690	1537	14.6	6.49	38.9	14.7	0.98	88	86	2.54

bers, the conditions under which many experiments occur is equilibrium crystallization. The modeling method allows  $K_d$ 's to be taken from the equilibrium experiments to calculate fractional liquid lines of descent. Figure 10 compares a liquid line of descent for fractional crystallization with the liquid line of descent for equilibrium crystallization of the same composition. When the extent of crystallization becomes large, the two lines of descent differ considerably from one another.

These calculations are also applicable to complex crystallization processes such as might occur in periodically refilled magma chambers. The abundances of major elements in a liquid derived by hundreds of cycles of replenishment

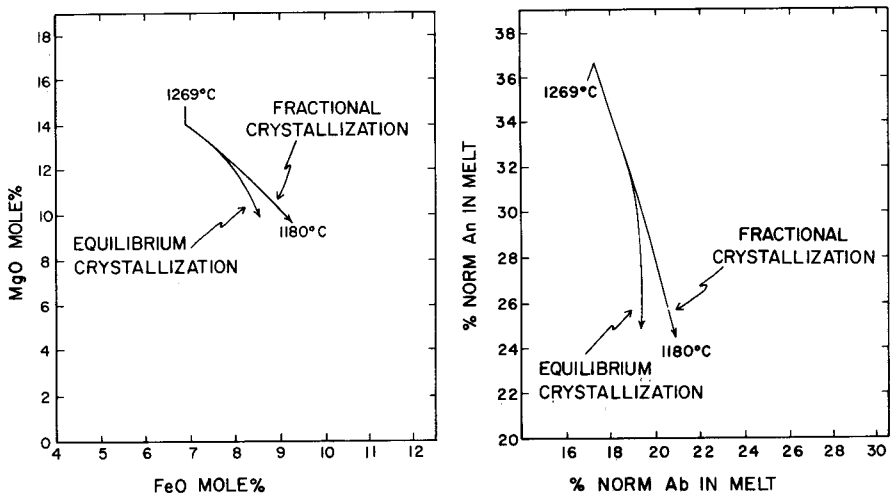


Fig. 10. Liquid lines of descent for fractional and equilibrium crystallization of the same liquid composition.

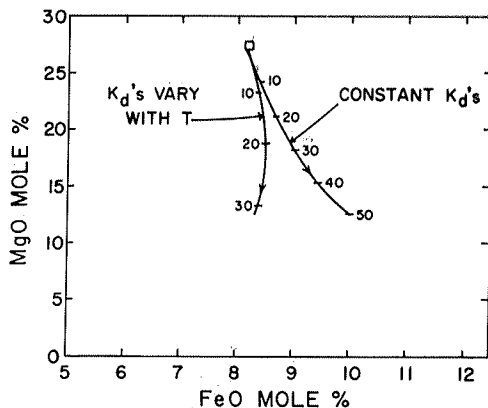


Fig. 11. Illustration of the errors involved in using constant  $K_d$ 's for calculations of crystallization. The left-hand curve is calculated for fractional crystallization using the methods presented in this paper. The right-hand curve is calculated using the Rayleigh fractionation equation for the constant  $K_d$ 's for MgO (2.1) and FeO (0.7).

and mixing can be calculated only when liquid lines of descent can be calculated numerically [Langmuir (1980)].

Finally, it is important to stress that although the calculations presented here use single-component distribution coefficients, they do not simply involve substitution of major element  $K_d$ 's into the mass balance equation [e.g., Eq. (9)]. Figure 11 compares the correct liquid line of descent for the fractional crystallization of olivine to an erroneous liquid line of descent calculated with the  $K_d$ 's kept constant, so that the temperature dependence of the  $K_d$ 's and the stoichiometric constraints are not taken into account. When constant  $K_d$ 's are used, the calculated extent of crystallization is far too large, the sense of curvature of the liquid line of descent is opposite to what it should be, and the components in olivine do not sum to one.

## Conclusions

Phase equilibria can be calculated in both simple and complex systems using single-component distribution coefficients, mass balance, and the stoichiometric constraints imposed by the solid phases. This approach can be illustrated in simpler systems exhibiting eutectic, peritectic, and solid-solution behavior. More importantly, the approach allows calculation of liquid lines of descent for multicomponent, silicate liquids. Crystallization of olivine and plagioclase from liquids of basaltic composition has been accurately calculated. Such calculations allow the determination of fractional and equilibrium crystallization liquid lines of descent, the effects of the MgO/FeO and An/Ab ratios on the olivine-plagioclase cotectic, and the effects of complex crystallization processes.



## Acknowledgments

J. Grover, T. N. Irvine, S. Shirey, and S. Weaver reviewed earlier drafts. The research was supported by N.S.F. Grant OCE78-20058 (Submarine Geology and Geophysics) and Grant EAR 76-13354 (Geochemistry).

## References

- Andersen, O., 1915, The system anorthite–forsterite–silica, *Am. J. Sci.*, **39**, 407–454.
- Banno, S., and Y. Matsui, 1973, On the formulation of partition coefficients for trace elements distributed between minerals and magma, *Chem. Geol.* **11**, 1–15.
- Barth, T. F. W., 1962, *Theoretical Petrology*, 2nd Ed., Wiley, New York.
- Bender, J. F., F. N. Hodges, and A. E. Bence, 1978, Petrogenesis of basalts from the project FAMOUS area: experimental study from 0 to 15 kilobars, *Earth Planet. Sci. Lett.*, **41**, 277–302.
- Bowen, N. L., 1913, Melting phenomenon of plagioclase feldspars, *Am. J. Sci.*, **35**, 577–599.
- Bowen, N. L., and O. Andersen, 1914, The binary system MgO–SiO<sub>2</sub>, *Am. J. Sci.*, **37**, 487–500.
- Brady, J. B., and J. H. Stout, 1980, Normalizations of thermodynamic properties and some implications for graphical and analytical problems in petrology, *Am. J. Sci.*, **280**, 173–189.
- Burnham, C. W., 1979, The importance of volatile constituents, in *The Evolution of Igneous Rocks*, edited by H. S. Yoder, Jr., pp. 439–482, Princeton University Press, Princeton, N.J.
- French, W. J., 1971, The correlation between “anhydrous” crystallization temperatures and rock compositions, *Contrib. Mineral. Petrol.*, **31**, 154–158.
- Hanson, G. N., and C. H. Langmuir, 1978, Modelling of major elements in mantle-melt systems using trace element approaches, *Geochim. Cosmochim. Acta*, **42**, 725–741.
- Herzberg, C. T., 1979, The solubility of olivine in basaltic liquids: an ionic model, *Geochim. Cosmochim. Acta*, **43**, 1241–1252.
- Hostetler, C. J., and M. J. Drake, 1978, Predicting major element mineral/melt equilibria, *Trans. Am. Geophys. Union*, **59**, 1219.
- Irving, A. J., 1978, A review of experimental studies of crystal–liquid trace element partitioning, *Geochim. Cosmochim. Acta*, **42**, 743–770.
- Langmuir, C. H., 1980, A major and trace element approach to basalts, Ph.D. Thesis, SUNY Stony Brook.
- Langmuir, C. H., J. F. Bender, A. E. Bence, G. N. Hanson, and S. R. Taylor, 1977, Petrogenesis of basalts from the FAMOUS area: mid-Atlantic ridge, *Earth Planet. Sci. Lett.*, **36**, 133–156.
- Langmuir, C. H., and G. N. Hanson, 1980, An evaluation of major element heteroge-

- neity in the mantle sources of basalts, *Philos. Trans. Roy. Soc. London A* **297**, 383-407.
- Leeman, W. P., 1978, Distribution of Mg between olivine and silicate melt, and its implications regarding melt structure, *Geochim. Cosmochim. Acta*, **42**, 789-800.
- Longhi, J., D. Walker, and J. F. Hays, 1978, The distribution of Fe and Mg between olivine and lunar basaltic liquids, *Geochim. Cosmochim. Acta*, **42**, 1545-1558.
- Morse, S. A., 1976, The lever rule with fractional crystallization and fusion, *Am. J. Sci.*, **276**, 330-346.
- O'Hara, M. J., 1976, in *Progress in Experimental Petrology—Third Report*, NERC Publ. Ser. D 6.
- O'Hara, M., 1977, Geochemical evolution during fractional crystallization of a periodically refilled magma chamber, *Nature*, **268**, 36-38.
- Osborne, E. F., 1942, The system  $\text{CaSiO}_3$ -diopside-anorthite, *Am. J. Sci.*, **240**, 751-788.
- Roeder, P. L., 1974, Activity of iron and olivine solubility in basaltic liquids, *Earth Planet. Sci. Lett.*, **23**, 397-410.
- Roeder, P. L., 1975, Thermodynamics of element distribution in experimental mafic silicate-liquid systems, *Fortschr. Mineral.* **52**, 61-73.
- Roeder, P. L., and R. F. Emslie, 1970, Olivine-liquid equilibrium, *Contrib. Mineral. Petrol.*, **29**, 275-289.
- Schilling, J.-G., 1966, Rare earth fractionation in Hawaiian volcanic rocks, Ph.D. Thesis, Mass. Inst. of Technology.
- Walker, D., T. Shibata, and S. DeLong, 1979, Abyssal tholeiites from the Oceanographer Fracture Zone: II. Phase equilibria and mixing, *Contrib. Mineral. Petrol.*, **70**, 111-125.
- Watson, E. B., 1977, Partitioning of Mn between forsterite and silicate liquid, *Geochim. Cosmochim. Acta*, **41**, 1363-1374.
- Weill, D. F., R. Hon, and A. Navrotsky, 1979, The igneous system diopside-anorthite-albite: variations on a classic theme by Bowen, *Physics of Magmatic Processes*, in Bowen Memorial Volume, edited by R. B. Hargraves, Princeton University Press, Princeton, N.J.