

## **An algebraic method for determining equilibrium crystallization and fusion paths in multicomponent systems\***

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### **ABSTRACT**

For an  $n$ -component petrologic system, Korzhinskii adopted a method for balancing chemical equations involving  $n + 1$  phases by the use of determinants. This method is applied to crystal-liquid phase equilibria in known portions of multicomponent systems to develop (1) a simple criterion for distinguishing between eutectic and peritectic points and (2) procedures for calculating crystal and liquid paths for equilibrium crystallization and fusion. For a given bulk composition, points on crystal and liquid paths are calculated by trial-and-error searches of balanced equations. Successful trials are those in which the bulk composition is expressed in terms of positive proportions of the phases in equilibrium. The types of quantitative information normally obtained from a phase diagram (temperature of appearance and disappearance of phases, phase compositions, phase proportions) are calculated, and no theoretical limit exists on the number of components that can be rigorously handled. However, from a practical standpoint, studies of equilibria in which the variance is greater than two will be difficult, a constraint that limits the usefulness of the method when the number of components is large and the number of phases is small. The method will be most applicable to studies of crystal-liquid phase relationships at near-solidus temperatures in which the number of phases is large. Such studies, which are quite feasible on systems with as many as six components, are potentially capable of providing much more general and rigorous constraints on models of magma generation than exist at the present.

### **INTRODUCTION**

Experimental studies of model systems relevant to the melting and crystallization behavior of rocks have been hampered, ever since their inception, by the inability to represent diagrammatically all the compositional relationships in systems of more than four components. Projections of various types have been used, but these projections invariably result in the loss of some information. Experimental petrologists have turned increasingly in the last 20 years to melting studies of actual rock compositions. Although these studies avoid the problem of extrapolating from three or four components in laboratory studies to about ten components in natural rocks, they do not provide the level of rigorous understanding obtainable from a phase-equilibrium diagram. Given adequate representational methods, a more systematic and generalized understanding of fusion and crystallization processes could be obtained by carrying studies of model systems to systems of more than four components.

Korzhinskii (1959) and others (for example, Greenwood, 1967; Thompson, 1982a, 1982b; Spear et al., 1982) have shown how linear algebraic methods can be used to describe and manipulate compositional relationships in

multicomponent systems, but these methods have been applied exclusively to subsolidus phase equilibria. Similar mathematical methods are also useful in treating liquidus phase relationships. An algebraic method, applicable in principle to systems of any number of components, is presented here for quantitatively calculating equilibrium fusion and crystallization paths. All of the quantitative advantages and power of a compositional phase diagram are retained except for the visual clarity inherent in a diagrammatic representation. The method involves an application of the procedure described by Korzhinskii (1959, p. 103–106) for balancing chemical reactions with the aid of determinants and depends on the pre-existence of a comprehensive body of experimental data on the compositions of coexisting liquid and crystalline phases. Given this data set, the crystal and liquid paths can be calculated for any arbitrary bulk composition within limits of the known multicomponent space. The method is not suitable for deducing crystal and liquid paths that extend beyond the range of data available.

To illustrate and explain the method, examples will be drawn from well-known ternary liquidus phase diagrams and several hypothetical phase diagrams constructed to illustrate specific points. Emphasis will be placed on procedures for deducing isobaric crystal-liquid equilibria at various temperatures given a particular bulk composition.

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However, the method is equally applicable to isothermal polybaric liquidus relationships and to liquidus relationships in which the chemical potential of one or more components is constant. Equilibrium crystallization and fusion will be considered together because these two processes are reversible. That is, the same phase assemblage is produced at a given temperature regardless of whether that temperature is approached from above or below. Fractional crystallization and fusion (Presnall, 1969, 1979) will be dealt with in a subsequent paper.

**BALANCING OF CHEMICAL EQUATIONS**

Korzhinskii (1959, p. 103–106) showed that in a system of  $n$  components, a chemical equation involving  $n + 1$  phases can be balanced by the use of determinants. For a three-component system, he wrote the composition of each of four phases ( $A, B, C, D$ ) in terms of proportions ( $k_1, l_1, m_1$ , etc.) of the three components ( $X, Y, Z$ ), as follows:

$$\begin{aligned} A &= k_1X + l_1Y + m_1Z \\ B &= k_2X + l_2Y + m_2Z \\ C &= k_3X + l_3Y + m_3Z \\ D &= k_4X + l_4Y + m_4Z \end{aligned}$$

He then wrote the following determinant and showed that it equals zero:

$$|M| \equiv \begin{vmatrix} A & k_1 & l_1 & m_1 \\ B & k_2 & l_2 & m_2 \\ C & k_3 & l_3 & m_3 \\ D & k_4 & l_4 & m_4 \end{vmatrix} = 0.$$

Expansion of  $|M|$  yields

$$\begin{aligned} &\begin{vmatrix} k_2 & l_2 & m_2 \\ k_3 & l_3 & m_3 \\ k_4 & l_4 & m_4 \end{vmatrix} A - \begin{vmatrix} k_1 & l_1 & m_1 \\ k_3 & l_3 & m_3 \\ k_4 & l_4 & m_4 \end{vmatrix} B \\ &+ \begin{vmatrix} k_1 & l_1 & m_1 \\ k_2 & l_2 & m_2 \\ k_4 & l_4 & m_4 \end{vmatrix} C - \begin{vmatrix} k_1 & l_1 & m_1 \\ k_2 & l_2 & m_2 \\ k_3 & l_3 & m_3 \end{vmatrix} D = 0. \end{aligned}$$

The coefficients for the balanced equation are the minors of each of the phase labels and correspond to the proportions of each of the phases involved. Mathematically, there is no requirement that  $A, B, C$ , and  $D$  represent actual phases. They could just as well represent arbitrary compositions, and this flexibility will be utilized in the discussion that follows. Thus, symbols used in equations that follow will refer simply to labeled composition points on the appropriate diagram without any additional significance, even though, in many cases, these points also coincide with the compositions of components or phases. In all the subsequent discussion, equations will be written so that all coefficients are positive.

Several other methods for balancing equations by using the methods of matrix algebra are available, but unlike Korzhinskii's method, they do not yield a solution if a singularity occurs (Spear et al., 1982). Because singularity

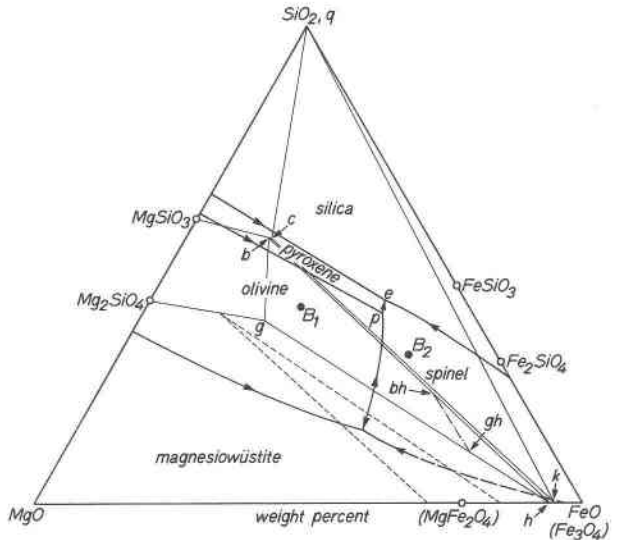


Fig. 1. The system MgO–iron oxide–SiO<sub>2</sub> in equilibrium with CO<sub>2</sub>, after Presnall (1979, Fig. 3-1) as redrawn after Muan and Osborn (1956), Phillips et al. (1961), and Speidel and Osborn (1967). All iron oxide is calculated as FeO, and compositions in parentheses are projected from oxygen. Heavy lines with arrows indicating directions of decreasing temperature are liquidus boundary lines. Light lines show crystalline-phase compatibility at solidus temperatures. Dashed lines are inferred. The dash-dot line is part of a crystal path (see text). See Presnall (1966, 1969) for further explanation.

ties frequently occur when working with compositional relationships on phase diagrams, I shall use Korzhinskii's method exclusively.

**EUTECTIC AND PERITECTIC POINTS**

In the absence of compositional degeneracy (for example, see Zen, 1966), a point on a univariant  $P$ - $T$  curve involving a liquid phase is either an isobaric eutectic or peritectic point on a temperature-composition liquidus diagram. In the former case, the liquid composition can be characterized by positive proportions of the crystalline phases in equilibrium with it. In the latter case, it cannot (Masing, 1944, p. 11–12). By solving a determinant incorporating the compositions of all the  $n + 1$  phases in equilibrium, an isobaric liquidus invariant point can be quickly determined to be either a eutectic or peritectic point. If the solution results in the liquid composition appearing alone on one side of the equation, the invariant point is a eutectic. If the liquid composition is joined on the same side of the equation by one or more of the crystalline phases, the invariant point is a peritectic.

Figure 1 illustrates both of these situations for a ternary system. Point  $e$  is a liquid at an invariant point in equilibrium with a silica phase  $q$ , pyroxene  $c$ , and spinel  $k$ . From the geometry, it can be seen visually that the result of using a determinant to balance the equation involving all the coexisting phases would be  $e = q + c + k$ . The determinant solution would, of course, also yield coeffi-

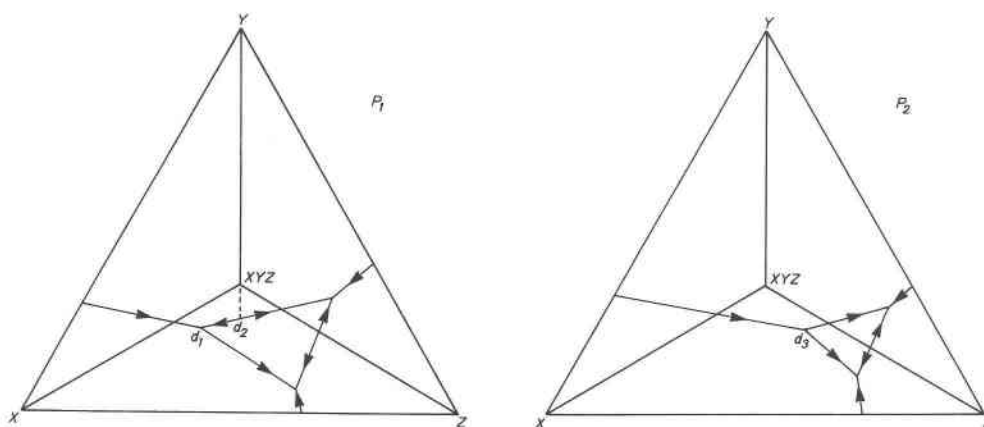


Fig. 2. Isobaric liquidus equilibrium diagrams for the imaginary system  $X$ - $Y$ - $Z$  at two different pressures,  $P_1$  and  $P_2$ . Lines with arrows indicating directions of decreasing temperature are liquidus boundary lines. The three bounding binary systems  $X$ - $Y$ ,  $Y$ - $Z$ , and  $X$ - $Z$  are drawn as eutectic diagrams, and none of the crystalline phases shows solid solution. The primary phase field for  $XYZ$  is the triangular region in the central part of each diagram.

cients for each of the phases corresponding to their proportions. The liquid composition is alone on one side of the equation and is thus a eutectic liquid that can be described by positive proportions of all the coexisting crystalline phases.

Point  $p$  is a liquid in equilibrium with pyroxene  $b$ , olivine  $g$ , and spinel  $h$ . In this case, the equation would be  $p + g = b + h$ . The liquid  $p$  is joined on the same side of the equation by a crystalline phase and is therefore a peritectic liquid not capable of being described by positive proportions of all the coexisting crystalline phases.

For a reaction involving a liquid along a univariant curve in  $P$ - $T$  space, the compositions of the crystalline and liquid phases frequently are strong functions of pressure and temperature, so that the chemographic relationships of the various phases change. Thus, a univariant  $P$ - $T$  curve could be represented by a peritectic reaction along one part of its length and by a eutectic reaction along another (for example, see Bell and Roseboom, 1969). The point of transition would be a singular point marked by some kind of compositional degeneracy. If complete data on the compositions of the phases were available all along the curve, the location of the singular point could be determined precisely by noting, in successive determinant solutions, the point at which a crystalline phase moves to the opposite side of the balanced equation. Compositional degeneracy at the singular point would appear in the determinant solution as a zero coefficient for the phase that moves to the opposite side of the equation.

An equation that has the liquid phase and one crystalline phase together on one side of the equation (peritectic) may also change by the transfer of a second crystalline phase to that side of the equation. Again, a singular point is generated whose location can be determined from successive determinant solutions as already described. The reaction is of the peritectic type on both sides of the singular point.

The geometry of this situation is illustrated in Figure 2. At pressure  $P_1$ , the equation for the peritectic point  $d_1$  (type B peritectic of Ricci, 1951, p. 239) is

$$X + XYZ = d_1 + Y. \quad (1)$$

At pressure  $P_2$ , the equation for the peritectic point  $d_3$  (type A peritectic of Ricci) on the other side of the singular point is

$$XYZ = d_3 + Y + X. \quad (2)$$

At pressure  $P_2$ , the peritectic liquid  $d_3$  and phase  $Y$  have been joined on the right side of the equation by a second crystalline phase  $X$ . The singular point occurs at a pressure between  $P_1$  and  $P_2$  just as the liquid composition moves across the dashed extension of the  $Y$ - $XYZ$  join. Note that at  $P_1$  a singular equation occurs ( $XYZ = d_2 + Y$ ). This isobarically invariant equation corresponds to a point on a univariant line in  $P$ - $T$  space that starts at the singular point and extends toward  $P_1$ . The singular (binary) univariant curve involves one less phase and one less component than the ternary univariant line defined by Equations 1 and 2, and the equation defining the singular curve as it exists at the singular point can be determined simply by deleting the phase  $X$  that transfers from the left to the right side of Equations 1 and 2.

Phase relationships at the pressure of the singular point are shown in Figure 3a. At this pressure, the invariant-point liquid is not classified as either a ternary peritectic or eutectic because it lies on the extension of the join  $Y$ - $XYZ$ . Point  $L$  does, however, correspond to a binary peritectic point defined by the equation  $XYZ = L + Y$  and is the starting point in  $P$ - $T$  space for the singular univariant curve.

#### DEDUCING CRYSTALLIZATION AND FUSION PATHS

When an equilibrium crystallization or fusion path is deduced from a known temperature-composition phase

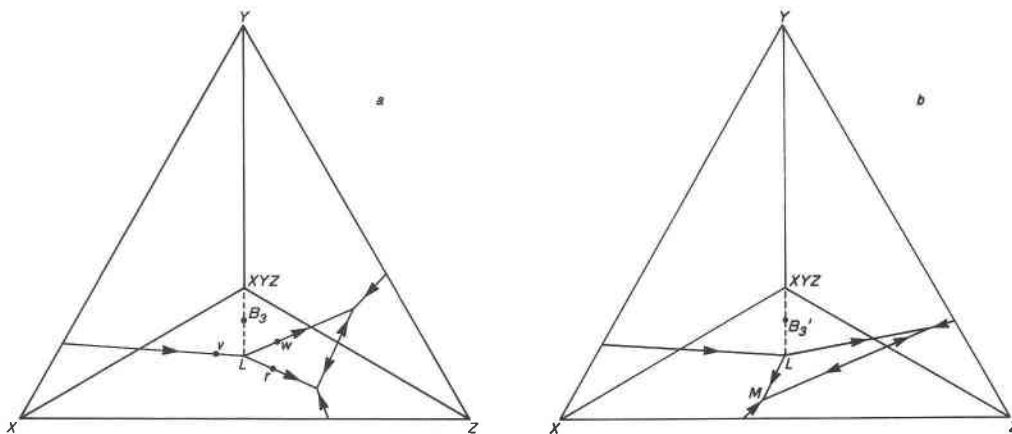


Fig. 3. Two alternative isobaric liquidus equilibrium diagrams for the imaginary system  $X$ - $Y$ - $Z$ . Lines and symbols are as in Fig. 2.

diagram, the validity of any assumed phase assemblage on the path can be tested simply by visually comparing the chosen bulk composition with the composition space defined by the phases present. If the bulk composition is contained within this space, a point on the crystallization or fusion path has been found. The same result can be obtained algebraically for a system of any number of components by finding a balanced chemical equation in which the bulk composition is alone on one side of the equation and the phases in equilibrium are on the other. Such an equation is an algebraic statement of the fact that the bulk composition is capable of being expressed by positive proportions of all the phases in equilibrium. The remaining discussion is essentially an elaboration of this basic principle as applied to isobarically invariant, univariant, and divariant equilibria. Because equilibrium crystallization and fusion paths are identical but merely traversed in opposite directions, the discussion applies equally to each one.

#### ISOBARIC INVARIANT EQUILIBRIA

In the isobaric melting or crystallization history of a particular bulk composition, the liquid path (Presnall, 1969) may include one or more liquidus invariant points. Each test of a chosen bulk composition against an invariant point that may lie on the liquid path involves three tasks: (1) determining if the invariant point lies on the liquid path, (2) determining, if the first task is passed, the assemblage of crystalline phases in equilibrium at the invariant point, and (3) determining, again if the first task is passed, the phase assemblages on the liquid path immediately above and below the temperature of the invariant point. Note that when the invariant-point liquid is part of the liquid path, the complete crystalline assemblage in equilibrium with this invariant-point liquid is not always part of the crystal path (see discussion of Fig. 3 below).

A test of an invariant-point liquid against a chosen bulk composition  $B$  is accomplished by deleting one of the  $n + 1$  phases in equilibrium at the invariant point and writing

a balanced equation involving  $B$  and the  $n$  remaining phases. Repetition of this procedure for each of the  $n + 1$  phases yields a set of  $n + 1$  trial equations, each involving  $n + 1$  compositions. This task is most easily accomplished by Korzhinskii's method, which also yields coefficients for each of the compositions. Solutions are desired in which (1)  $B$  is alone on one side of the equation and (2) the liquid phase either with or without additional phases is on the other. Equations that meet both these conditions will be designated *successful solutions* and correspond to situations in which  $B$  can be expressed in terms of positive amounts of one or more phases including the liquid phase.

For each set of  $n + 1$  trial equations corresponding to a test of a particular invariant point, one of the trials will be the liquid-absent equation. It may seem superfluous to list this equation in view of the stated purpose of searching for equations involving the liquid phase. It will be seen, however, that important information can be lost when this equation is omitted.

If a test yields no successful solutions, the invariant point is not on the liquid path. That is, the bulk composition  $B$  cannot be expressed by positive proportions of an assemblage of phases including the invariant-point liquid. One situation of this type is illustrated in Figure 1. Given the bulk composition  $B_1$ , we wish to determine if its liquid path includes the eutectic  $e$ . Liquid  $e$  is in equilibrium with  $q$ , pyroxene  $c$ , and spinel  $k$ . When  $B_1$  is substituted for each of the phases in equilibrium at the invariant point, the resulting set of equations is

$$\begin{aligned} (e) \quad & B_1 + q = c + k \\ (q) \quad & B_1 + e = c + k \\ (c) \quad & B_1 + q + k = e \\ (k) \quad & B_1 + q = c + e. \end{aligned}$$

In this and all subsequent sets of equations, the absent composition that serves as a label for each equation is shown in parentheses, and the positive coefficients, which would appear in equations solved by determinants, are omitted. None of the equations show  $B_1$  alone on one side

of the equation and the liquid composition  $e$  on the other. Therefore, the eutectic liquid  $e$  is not part of the liquid path, a conclusion easily verified by visual inspection of the diagram.

Now consider a trial in which the invariant point is part of the liquid path. Bulk composition  $B_2$  and the peritectic  $p$  (Fig. 1) illustrate one such case. Liquid  $p$  is in equilibrium with pyroxene  $b$ , olivine  $g$ , and spinel  $h$ . The set of trial equations is

$$\begin{aligned} (p) \quad & B_2 + g = b + h \\ (b) \quad & B_2 = p + g + h \\ (g) \quad & B_2 = p + b + h \\ (h) \quad & B_2 + b = g + p. \end{aligned}$$

Two equations, (b) and (g), are successful and show  $B_2$  alone on the left and the liquid  $p$  plus other phases on the right. Therefore, peritectic  $p$  is a point on the liquid path.

The second task of determining the phase assemblage in equilibrium with the invariant-point liquid is accomplished by listing the combined set of phases on the right-hand sides of the two equations that show  $B_2$  alone on one side of the equation. In addition to the invariant-point liquid  $p$ , these phases are  $b$ ,  $g$ , and  $h$ . Thus, the complete crystalline assemblage  $b + g + h$  in equilibrium with  $p$  occurs and is part of the crystal path, as defined by Presnall (1969). In this particular example, the two equations that show  $B_2$  alone on one side of the equation are both successful solutions, but in some cases (see the following example), only one will be successful.

The third task of determining the phase assemblage immediately above and below the invariant-point temperature is accomplished by again inspecting the right-hand sides of equations (b) and (g). Equation (b) shows one assemblage to be  $p + g + h$  and equation (g) shows the other to be  $p + b + h$ . Two points on the crystal path are given by the two crystalline assemblages  $g + h$  and  $b + h$ , the proportion of each phase being weighted according to its coefficient. These two points are shown on Figure 1 as  $bh$  and  $gh$ . Line  $bh$ - $gh$  is the segment of the crystal path corresponding to point  $p$  on the liquid path. Equation (b) represents the equilibrium immediately above the invariant point and (g) immediately below it. At the invariant point, the proportions of the phases change according to the equation  $p + g = b + h$ , with appropriate coefficients.

Finally, consider a case in which the invariant-point liquid is again part of the liquid path but in which only one successful solution occurs. Such a case is illustrated by a test of eutectic  $e$  against the bulk composition  $B_2$  (Fig. 1). The set of trial equations is

$$\begin{aligned} (e) \quad & B_2 = q + c + k \\ (q) \quad & B_2 = e + c + k \\ (c) \quad & B_2 + q = e + k \\ (k) \quad & B_2 + q + c = e. \end{aligned}$$

Equation (q) is a successful solution because  $B_2$  is alone on one side and the liquid  $e$  is present on the other. Therefore, the eutectic  $e$  is part of the liquid path. The next step is to examine both equations, (e) and (q), that show  $B_2$

alone on one side. The combined set of phases on the right-hand side of these two equations is  $e$ ,  $c$ ,  $k$ , and  $q$ . This is the complete set of phases that coexist at the invariant point, so it is concluded that the crystalline assemblage in equilibrium with the invariant-point liquid is part of the crystal path for  $B_2$ . Again, the phase assemblages for  $B_2$  immediately below and above the temperature of the invariant point are given by the right-hand sides of equations (e) and (q), and the proportions of these phases in each assemblage are given by their coefficients. In this example, the eutectic point  $e$  is the lowest-temperature liquid on the liquid path and the right-hand side of equation (e) gives the subsolidus assemblage  $q + c + k$  that exists immediately below the temperature of the eutectic.

The procedure that has been described up to this point is adequate for dealing with most situations. However, a complication that may arise is the occurrence of a zero coefficient for one or more of the compositions in a given equation. Such a result indicates that compositional degeneracy exists (for example, see Zen, 1966, p. 32). The composition or compositions with zero coefficients will be missing from the equation, which will cause two or more of the trial equations to be identical. If all the coefficients for a trial equation are zero, the composition chosen to be absent is "absolutely indifferent" (Zen, 1966, p. 31), and no unique equation can be written.

The situation in which a successful solution has one or more zero coefficients will be called *special degeneracy*. In this case, the bulk composition has a special compositional relationship to the invariant-point liquid. For example, if the bulk composition  $B$  coincides with the composition of the invariant-point liquid  $L$ , the equation  $B = L$  will occur. As another example, if  $B$  lies along a line between  $L$  and a coexisting crystalline phase  $C$ , the equation  $B = L + C$  will occur. When special degeneracy occurs, the procedure for testing an invariant point against a bulk composition must be modified. All other types of degeneracy can, for present purposes, be ignored. That is, if the invariant-point liquid and two other crystalline phases in equilibrium with it all lie along a single line, degeneracy exists. However, because the bulk composition is not involved in this degeneracy, no complications arise in the testing procedures explained above. Similarly, if the bulk composition lies, for example, along the line defined by two crystalline phases, degeneracy also occurs. In this case, the invariant-point liquid is not involved in the degeneracy, and again no complications arise. Special degeneracy requires the involvement of both the bulk composition and the invariant-point liquid and is the only type of degeneracy that requires a modified testing procedure.

Even when special degeneracy occurs, the procedures for (1) determining if an invariant-point liquid lies on the liquid path and (2) determining the assemblage of phases in equilibrium with the invariant-point liquid remain unchanged. Only the procedure for determining the phase assemblages immediately above and below the invariant-point temperature must be modified. For cases involving

special degeneracy, these phase assemblages depend not only on the chemography of the phases in equilibrium at the invariant-point temperature but also on the positions of the liquidus boundary lines as they leave the invariant point.

These relationships are best understood by considering an example. The two phase diagrams in Figures 3a and 3b show identical compositions for the invariant-point liquid  $L$ , the bulk compositions  $B_3$  and  $B'_3$ , and the three crystalline phases  $X$ ,  $Y$ , and  $XYZ$  in equilibrium with the invariant-point liquid. The diagrams differ, however, in the positions of some of the liquidus univariant lines coming from the invariant-point liquid. Note that special degeneracy occurs in both diagrams because  $B_3$  and  $B'_3$  lie along a line between the crystalline phases  $Y$  and  $XYZ$  and the invariant-point liquid  $L$ .

Before proceeding to a test of  $B_3$  and  $B'_3$  against  $L$ , it is useful to note, for each diagram, the crystal and liquid paths in the temperature range near  $L$ . First consider Figure 3a. During crystallization, the crystal path starts at  $Y$  as the liquid moves along the dashed line from  $B_3$  to  $L$ ; the phase assemblage is  $Y + \text{liquid}$ . Then, as the liquid remains at  $L$ , the average composition of the crystals moves along the line  $Y$ - $XYZ$  to  $XYZ$ . During this part of the cooling history,  $Y$  dissolves as  $XYZ$  crystallizes and the phase assemblage is  $Y + XYZ + L$ . Just as the average composition of the crystals reaches  $XYZ$ ,  $Y$  vanishes and the phase assemblage momentarily is  $XYZ + L$ . The liquid then moves out along the boundary line  $L$ - $r$  as the average composition of the crystals moves a small distance toward  $X$  from  $XYZ$ ; at this stage the assemblage is  $X + XYZ + \text{liquid}$ .

In Figure 3b, the first part of the crystallization history is the same down to the point at which the liquid is ready to leave  $L$ . At this point, the liquid does not move out along the boundary line  $L$ - $M$  but instead moves directly away from  $XYZ$  across the  $XYZ$  primary phase field. The assemblage at this stage is  $XYZ + \text{liquid}$ . Thus, the two sequences of phase assemblages, going down-temperature, are as follows:

Figure 3a	Figure 3b
$Y + \text{liquid}$	$Y + \text{liquid}$
$Y + XYZ + L$	$Y + XYZ + L$
$XYZ + L$	$XYZ + L$
$X + XYZ + \text{liquid}$	

The difference in the two sequences is caused by the different positions of the boundary lines  $L$ - $r$  (Fig. 3a) and  $L$ - $M$  (Fig. 3b).

In Figure 3a, a test of  $B_3$  against  $L$  yields the following trial equations:

$$\begin{aligned} (L) \quad & B_3 + Y = XYZ \\ (X) \quad & \text{no unique equation} \\ (Y) \quad & B_3 = L + XYZ \\ (XYZ) \quad & B_3 = L + Y. \end{aligned}$$

When  $X$  is absent, no unique equation exists because  $Y$ ,

$XYZ$ ,  $B_3$ , and  $L$  lie along the same line. This degeneracy would be indicated in a determinant solution by zero coefficients for each of the compositions. In equations (Y) and (XYZ), the crystalline phase  $X$  has a zero coefficient and is therefore missing, which causes each of these equations to be identical to two of the three possible equations that could be written for (X). Because both (Y) and (XYZ) are successful solutions with a zero coefficient for  $X$ , special degeneracy exists. As in the general procedure already described, the existence of these successful solutions indicates that  $L$  is part of the liquid path. Also, the phase assemblage at the invariant-point temperature is  $L + Y + XYZ$ , which is obtained in the normal way from the combined list of phases on the right-hand sides of the two equations, (Y) and (XYZ), that show  $B_3$  alone on one side of the equation. The final task of determining the phase assemblages immediately below and above the invariant-point temperature would, by the normal procedure, be given by the right-hand sides of equations (Y) and (XYZ), that is,  $XYZ + L$  and  $Y + L$ . From the previous discussion of the crystal and liquid paths, it can be seen that the high-temperature assemblage,  $Y + L$ , is correct, but the presumed low-temperature assemblage,  $XYZ + L$ , occurs while the liquid is still at  $L$ , not at temperatures immediately below that of  $L$ . Note that the standard procedure does not give incorrect information because the assemblage  $XYZ + L$  does occur. The information given, however, is incomplete because the assemblage at temperatures immediately below that of  $L$  is not given.

Now consider Figure 3b. The set of trial equations in this case is identical to that for Figure 3a because the chemography of the phases in equilibrium at the invariant point is the same. The equations are

$$\begin{aligned} (L) \quad & B'_3 + Y = XYZ \\ (X) \quad & \text{no unique equation} \\ (Y) \quad & B'_3 = L + XYZ \\ (XYZ) \quad & B'_3 = L + Y. \end{aligned}$$

The standard procedure correctly yields the same assemblage at the invariant-point temperature,  $Y + XYZ + L$ , and the same presumed assemblages immediately above and below the invariant-point temperature,  $Y + L$  and  $XYZ + L$ . In contrast to the result from Figure 3a, comparison with the previous discussion of the crystallization history shows that the presumed assemblages above and below the invariant-point temperature are correct and complete. The differing results for these two cases with identical chemography at the invariant-point temperature illustrate the point that when special degeneracy occurs, the phase assemblages deduced from the trial equations are correct but sometimes incomplete, and do not necessarily indicate the phase assemblages immediately above and below the invariant-point temperature.

When special degeneracy occurs, another method must be used to determine the two phase assemblages immediately above and below the invariant-point temperature. The procedure is to examine each of the liquidus univariant lines coming from the invariant point, then all the

divariant areas between these lines, etc., until the two assemblages are found. In the present example (Fig. 3a), points  $v$ ,  $w$ , and  $r$  are chosen on each of the univariant boundary lines coming from  $L$  and are used to determine if a reaction can be written with  $B_3$  alone on one side and the phases in equilibrium at the chosen point on the other. Liquid  $v$  is in equilibrium with  $X$  and  $Y$ , so the equation would be  $B_3 + X = v + Y$ . The test fails. For  $w$ , the equation would be  $B_3 + Y = XYZ$ . Again, the test fails. For  $r$ , the equation would be  $B_3 = r + X + XYZ$ . This test is successful, and the phase assemblage on the down-temperature side of the invariant point is given by the right side of the equation,  $r + X + XYZ$ . It is important in making these tests to choose points on the univariant lines close to the invariant point because in some cases the liquid path will leave the univariant line only a small distance away from the invariant point. In Figure 3a, points  $v$ ,  $w$ , and  $r$  have been chosen some distance away from  $L$  to facilitate visualization.

At this stage, all of the univariant lines have been examined but only the down-temperature phase assemblage has been found. Therefore, to find the up-temperature phase assemblage, it is necessary next to examine all the divariant areas that touch the invariant point. Consider first the divariant liquidus surface bounded by the univariant lines  $v-L$  and  $L-r$ . A liquid that moves across this surface directly into the invariant point  $L$  must cross a line (not shown) between  $v$  and  $r$  if  $v$  and  $r$  both lie sufficiently close to  $L$ . Liquids on this surface are in equilibrium with  $X$ , so the test is performed by solving the equation involving  $B_3$ ,  $v$ ,  $r$ , and  $X$ . If the liquid path lies on this surface and extends directly into  $L$ , the equation will show  $B_3$  alone on one side and all the remaining compositions on the other. Inspection of the diagram shows that the equation is  $v = B_3 + X + r$ . Therefore, the liquid path does not lie on this divariant surface. Consider next the divariant surface bounded by the univariant lines  $L-w$  and  $L-r$ . Liquids on this surface are in equilibrium with crystals of  $XYZ$ , so the equation is  $B_3 + w = XYZ + r$ . Again, the liquid path does not pass across this divariant surface. The third and final possibility is the liquidus surface bounded by  $v-L$  and  $L-w$ . Liquids on this surface are in equilibrium with crystals of  $Y$ , so the equation is  $B_3 = Y + v + w$ . Thus, the phase assemblage above the invariant-point temperature is  $L + Y$ , and the task is complete.

A summary of the sequence of tests for invariant points and the phase assemblages at temperatures immediately above and below these points is as follows:

1. Determine whether or not the liquid composition at the invariant point is part of the liquid path. If at least one equation is found with the bulk composition alone on one side and the liquid, with or without other phases, on the other side (a successful solution), the invariant-point liquid is part of the liquid path. If no successful solutions are found, the invariant-point liquid is not part of the liquid path.

2. If test one is passed, determine the phase assemblage in equilibrium with the invariant-point liquid. This as-

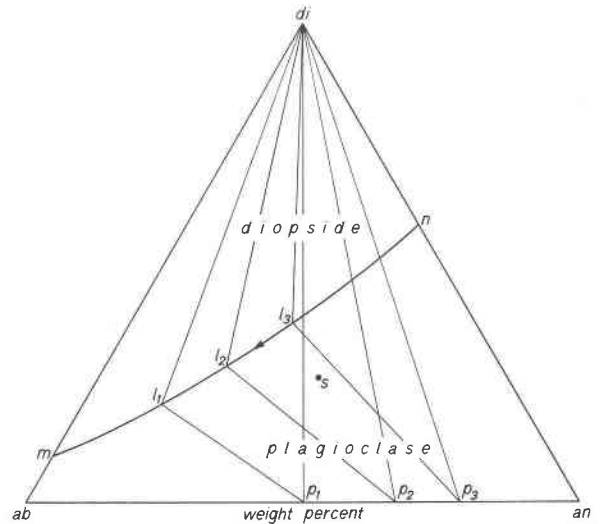


Fig. 4. The system diopside-albite-anorthite after Bowen (1915), Schairer and Yoder (1960), and Osborn and Tait (1952), with illustration of univariant phase relationships. Boundary line  $m-n$  separates the diopside and plagioclase primary-phase fields.

semblage is the combined list of all the phases present in the two equations that show the bulk composition alone on one side of the equation. In the absence of special degeneracy, this procedure will yield the complete assemblage of phases in equilibrium with the invariant-point liquid.

3. Check the successful solutions to see if any of the coefficients are zero. If not, the phase assemblages present in the two equations that show the bulk composition alone on one side of the equation are the same as the phase assemblages immediately above and below the invariant-point temperature. If the successful solution or solutions have one or more zero coefficients, special degeneracy occurs, and the phase assemblages immediately above and below the invariant-point temperature must be found by trial and error testing of each univariant line, divariant area, etc., that starts from the invariant point.

#### ISOBARIC UNIVARIANT EQUILIBRIA

For isobarically invariant equilibria, which involve  $n + 1$  phases, Korzhinskii's method is ideally suited to the task of balancing equations. For isobarically univariant equilibria, which involve only  $n$  phases, Korzhinskii's method can be used by including the bulk composition of the system as one of the chemical entities. Application of this procedure to define univariant phase assemblages immediately above and below the temperature of an isobaric invariant point has been explained in the preceding section.

To illustrate some further aspects of the treatment of univariant equilibria, we shall use a ternary example, the system diopside-albite-anorthite (Fig. 4). Because of small amounts of solid solution of Al in diopside and Mg in plagioclase, this system is not strictly ternary, but this



detail is of no concern here. If we hypothesize a situation in which the number of components is too great for this system to be represented graphically, experiments could still be carried out in which the compositions of diopside (always taken to be pure  $\text{CaMgSi}_2\text{O}_6$ ) and plagioclase in equilibrium with all liquids along the boundary line  $m-n$  could be determined. For example, an experiment on the bulk composition  $s$  could be carried out that would yield liquid  $l_2$  in equilibrium with pure diopside  $di$  and plagioclase  $p_2$ . With this data set and without any knowledge of the geometrical appearance of Figure 4, all the univariant phase relationships for any arbitrary bulk composition in the system could be calculated.

Suppose, for example, it is desired to determine the phase relationships (compositions and proportions of phases, temperature) at the solidus for the bulk composition  $s$ . A determinant is set up involving the compositions  $s$ ,  $l_2$ ,  $di$ , and  $p_2$ . It can be seen visually in Figure 4 that the solution would be  $s = l_2 + di + p_2$ , with appropriate coefficients. Therefore, the bulk composition  $s$  consists partly of liquid, and the solidus lies at a lower temperature. Another trial solution involving  $s$ ,  $l_1$ ,  $di$ , and  $p_1$  would yield the equation  $s + l_1 = di + p_1$ . The bulk composition  $s$ , having been joined by  $l_1$  on the same side of the equation, can no longer be expressed by positive amounts of an assemblage of phases including a liquid, and we have therefore passed across the solidus temperature. Intermediate trial solutions would bracket the point at which the liquid phase changes from the right to the left side of the equation; this point would be the solidus. Proportions and compositions of coexisting phases at the solidus temperature of  $s$  would then be determined.

As the temperature of composition  $s$  is increased above its solidus, liquid compositions will move along the line  $m-n$  toward  $n$ . The last liquid produced along line  $m-n$  during equilibrium fusion can be found by trial determinant solutions just as the solidus temperature was found. As long as the liquid remains on line  $m-n$ , determinant solutions would be of the form  $s = l_2 + di + p_2$ . Trial solutions for liquids at higher temperatures, such as at  $l_3$ , would yield solutions of the form  $s + di = l_3 + p_3$ . Solutions for liquid compositions along  $m-n$  intermediate between  $l_2$  and  $l_3$  would bracket the point at which  $di$  changes to the left side of the equation; this change marks the last liquid composition produced along the line  $m-n$ . For each point on the liquid path along  $m-n$ , a point on the crystal path can be located by solving an equation of the form  $s = l_2 + di + p_2$ . The coefficients for  $di$  and  $p_2$  in such an equation give the relative proportions of  $di$  and  $p_2$  in the crystalline assemblage and thereby a point on the crystal path.

If the bulk composition  $s$  had been located in the primary phase field of diopside, solutions at temperatures above the point at which a liquid could exist along the line  $m-n$  would be of the form  $s + p_3 = l_3 + di$ . A symmetry is evident. When the bulk composition lies in the plagioclase primary-phase field, diopside changes to the left side of the equation. When the bulk composition lies in the

diopside primary-phase field, plagioclase changes. Also, it can be seen that the divariant phase assemblage that occurs just above the temperature at which the liquid composition leaves the line  $m-n$  is revealed simply by deleting from the balanced equation the crystalline phase that changes to the other side of the equation.

These ternary relationships can be generalized as follows. An isobaric univariant equilibrium involving a liquid on a boundary line will occur when balanced equations show the bulk composition alone on one side of the equation and a liquid and two crystalline phases on the other. This is simply another way of stating that the bulk composition must be capable of being expressed in terms of positive proportions of the phases in equilibrium. The univariant relationship may be terminated at the high- or low-temperature end by an invariant point. Alternatively, the termination could occur by loss of a phase to produce a divariant situation, and the termination would be marked by a solid or liquid phase moving to the opposite side of the equation to join the bulk composition. The nature of the divariant equilibrium is revealed by deleting the phase that changes sides. Thus, if the liquid phase changes sides, it is deleted from the equation, and the divariant equilibrium is expressed by the bulk composition on one side of the equation and two crystalline phases on the other. In this case, the solidus has been encountered. On the other hand, if a crystal phase changes sides, deletion of this phase results in an equation with the bulk composition on one side and the liquid plus one solid phase on the other. This marks the movement of the liquid composition off the univariant line into a divariant primary phase field.

When these ternary relationships are further generalized to a system of  $n$  components, the same treatment applies. The bulk composition will still occur alone on one side of the equation if an isobaric univariant equilibrium occurs, and the high- and low-temperature terminations of this equilibrium will be marked either by an invariant point or by loss of a phase, producing a divariant situation. Loss of a phase would be marked by the transfer of this phase from one side of the equation to the other.

Figure 4 illustrates the univariant situation in which both solid phases crystallize on cooling. If one of the solid phases dissolves while the other crystallizes, the method of treatment remains the same. Inspection of the coefficients in determinant solutions over a range of temperature reveals whether or not one of the solid phases dissolves. If dissolution continues to complete exhaustion of the solid phase so that the liquid path leaves the boundary line and moves out across a divariant primary phase field, the point of complete exhaustion is marked, as before, by the transfer of the exhausted solid phase to the other side of the equation. The new divariant equilibrium is obtained by deleting the transferred phase from the equation.

#### ISOBARIC DIVARIANT EQUILIBRIA

As the variance increases beyond one ( $n$  phases in an isobaric  $n$ -component system), it is necessary to include



“dummy” compositions in order to obtain solutions. When the variance is two, one dummy composition is included in addition to the bulk composition of the mixture. For example, in a ternary system, one solid phase in equilibrium with one liquid phase is divariant. If the bulk composition and one dummy composition are included with the two phases in equilibrium, a solution can be obtained. A problem associated with the introduction of dummy compositions is that they must be eliminated later in order to define the phase assemblages that exist.

Figure 5 illustrates a divariant situation in which a dummy composition is first introduced to allow solutions to be calculated and then is eliminated. It is desired to determine the point  $a_2$  on the divariant equilibrium liquid path  $x-y$  along which plagioclase of varying composition crystallizes during cooling of the bulk composition  $x$ . To determine this point, it is necessary to have relatively complete data on plagioclase compositions in equilibrium with liquids throughout the plagioclase primary phase field. With such a data set, we can attempt several trial solutions. A random dummy composition  $t$  is chosen, and three liquid compositions  $a_1$ ,  $a_2$ , and  $a_3$  are tried as possible points on the liquid path. Corresponding plagioclase compositions  $u_1$ ,  $u_2$ , and  $u_3$  in equilibrium with each of the three liquids are known. The objective is to look for a solution in which the coefficient of  $t$  is zero so that  $t$  can be deleted from the reaction. For the liquid  $a_1$ , the equation would be  $a_1 + u_1 = t + x$ . For  $a_3$ , the equation would be  $a_3 + u_3 + t = x$ . Because  $t$  has moved to the other side of the equation, there must be an intermediate solution at which the coefficient for  $t$  passes through zero and leaves the desired result  $a_2 + u_2 = x$ . If the data set is complete, the point  $a_2$  and others like it on the path  $x-y$  can be bracketed as closely as desired by successive trial solutions.

The enormous amount of work involved in assembling a complete data set would usually be prohibitive, but approximate solutions could still be obtained. In general, it is desirable to carry out initial solutions based on good experimental data until two are found that bracket the desired result. Approximate intermediate solutions can then be found by interpolating between the data points, and these results can in turn be used as guides for more refined experimental data in the composition region of interest.

#### PETROLOGIC APPLICATIONS

For an  $n$ -component system with a variance  $F$  greater than one, the methods developed here require the introduction of  $F - 1$  dummy compositions. There is a reasonable chance of dealing with this situation for  $n - 1$  phases ( $F = 2$ ) and one dummy composition. Two or more dummy compositions can theoretically be handled, but the practical difficulties increase sharply for each additional dummy composition that must be added. For example, location of a single point on a trivariant portion of a liquid path would require simultaneous elimination of two dummy compositions. This could be accomplished

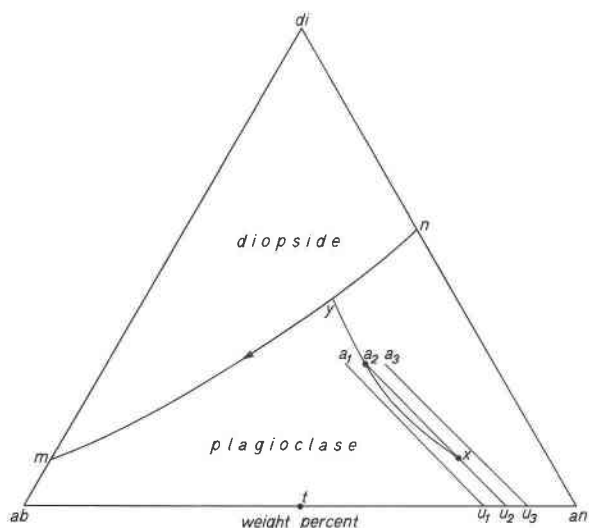


Fig. 5. The system diopside-albite-anorthite with illustration of divariant phase relationships.

by finding determinant solutions for a two-dimensional grid of possible liquid compositions. Location of several points on this portion of the liquid path would require a three-dimensional grid of possible liquid compositions with data on the coexisting crystalline phase compositions for each liquid; the task of data collection and handling would rapidly become enormous.

In natural magmatic systems, the number of major components is large, about nine or ten, and the number of phases varies from two or three near the liquidus to about six or seven near the solidus. Thus, the most obvious immediate application of this method is to near-solidus temperatures where the variance and the number of dummy compositions needed are as small as possible.

Studies of near-solidus melting relationships in model systems of five and six components are currently within reach and offer an exciting possibility for tightening phase-equilibrium constraints on magma generation. Consider the situation for basaltic rocks. About 99% of the composition of the Earth's mantle and about 95% of the composition of basalt can be characterized by the six-component system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-FeO}$ . During the early stages of partial melting of a simplified peridotite in this system, the number of coexisting phases would be five and sometimes six. Thus, the potential for clarifying the polybaric melting relationships of peridotite to a very close approximation and with a high degree of rigor is excellent. For arbitrarily chosen simplified peridotite compositions in this six-component system, it would be possible to calculate at any pressure the phase compositions and proportions versus percent melting and the temperature of appearance and disappearance of phases. A key feature is the ability to calculate these results for simplified peridotites with varying phase compositions and phase proportions. Preliminary calculations of this sort have already been carried out for simplified peridotite in

the five-component system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O}$  (Presnall and Hoover, 1982; Hoover and Presnall, 1982).

A similar situation exists with respect to granitic rocks. About 92–97% of the composition of granitic rocks and probably the deep parts of thickened continental crust beneath granitic batholiths can be represented in the six-component system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-K}_2\text{O}$ . A rigorous understanding of melting relationships in the relevant parts of this system in the pressure range 10–25 kbar would allow a richly detailed understanding of phase relationships bearing on the generation of granitic batholiths far exceeding that gained from the simplified four-component approach of Presnall and Bateman (1973). Some difficulties associated with studies of granitic systems are slow reaction rates and the need to add still other components such as  $\text{H}_2\text{O}$  and  $\text{FeO}$ . Nevertheless, the path toward a more rigorous and systematic set of phase-equilibrium constraints on the generation of granitic rocks seems obvious.

Even for the most ideal situations in which the variance is two or less, the methods developed here require comprehensive data on the compositions of all phases in equilibrium over the temperature-pressure range of interest. Thus, the task of assembling experimental and analytical data on multicomponent systems is not minimized; merely a method of manipulating these data is provided. Because of the many large determinants that must be solved, the only practical approach is to use a computer. A combination of phase-equilibrium studies of multicomponent model systems, determination of coexisting phase compositions by microprobe, and manipulation of the data by computer offers the prospect of obtaining a very general and rigorous set of phase-equilibrium constraints on which to base significantly improved models of magma generation.

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