

The use of mineral solid solutions to measure chemical potential gradients in rocks

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Abstract

An algebraic method of paragenetic analysis is presented that may be applied to mineral assemblages containing any number of mineral solid-solutions and components. The method may be used to deduce the qualitative properties of chemical potential gradients in rocks and to obtain numerical estimates of the magnitude of the gradients. The method consists of solving a system of simultaneous equations that express analytically the relations between P , T , μ_i and $X_{i,A}$ for a given mineral assemblage. The system of equations includes (1) a Gibbs-Duhem equation for each mineral, (2) mass action equations between the chemical potentials of the components of the minerals, and (3) equations of the form $(d\mu_i - d\mu_j) = -(\tilde{S}_{i,A} - \tilde{S}_{j,A})dT + (\tilde{V}_{i,A} - \tilde{V}_{j,A})dP + \tilde{G}_{i,A}dX_{i,A} + \dots + \tilde{G}_{i(j-1)A}dX_{(j-1)A}$. Examples are given of applications of the method to igneous and metamorphic rocks.

Introduction

The direction and magnitude of chemical potential gradients of chemical components in rocks are of fundamental importance to petrogenetic studies because such gradients may exert as strong a control on mineral parageneses as pressure or temperature. Chemical potential gradients are especially important in metasomatic rocks for they are the driving force behind the diffusive movement of chemical components through rocks. Mineral solid solutions are useful in measuring chemical potential gradients because they change composition in response to changing environmental conditions and provide a continuously variable monitor of the magnitude of the gradients. Basic knowledge of metasomatic processes can be obtained even when thermodynamic data are not adequate for numerical calculation of the magnitude of the gradients. For example, it may be possible by mapping the *direction* of the gradients to distinguish regional processes from local effects.

The study of chemical potential gradients also provides the clues necessary to solve the classic petrological mystery of the nature of the magmatic or fluid phase that may have once been present in rocks but has been expelled. Verification of the presence or absence of gradients distinguishes between components whose chemical potentials were buffered locally during petrogenesis and those controlled by the magma or fluid. The magnitude of the gradients and

their areal distribution measure the degree and scale of magma or fluid inhomogeneity.

The purpose of this paper is to present an algebraic method for studying chemical potential gradients in rocks. The method is applicable to assemblages of coeval minerals that attained local chemical equilibrium during petrogenesis. The method facilitates deducing the qualitative nature of the gradients and can also be used to obtain quantitative estimates of their magnitude. Because of its algebraic nature, the method may be applied to complex natural mineral assemblages containing any number of components and phases. The plan of the paper is to begin with simple examples that can be analyzed both graphically and algebraically and then to proceed to examples that can be analyzed only algebraically. The examples discussed all pertain to the petrological problem described in the second paragraph of the introduction; however, the method is, in principle, equally applicable to metasomatic rocks.

Examples

Consider a hypothetical cumulate igneous rock, consisting of orthopyroxene and olivine, found in a stratiform ultramafic-gabbroic intrusion. The rock consists of layers that are defined by different proportions of olivine and orthopyroxene. The Fe/(Fe+Mg) ratio of the minerals is constant in each layer but differs from layer to layer. The olivine consistently

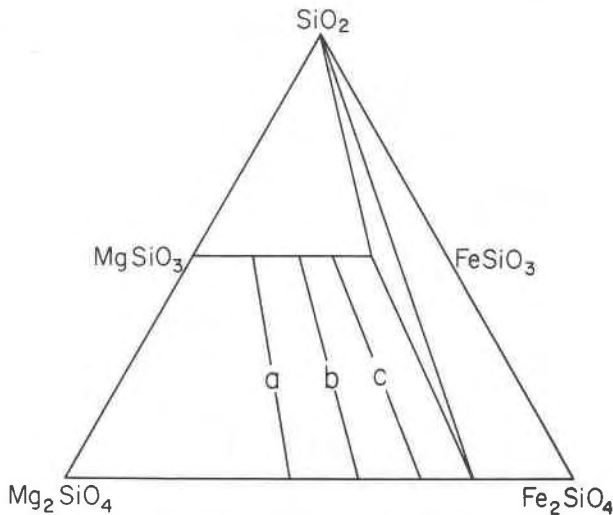


FIG. 1. Compositions of coexisting orthopyroxene and olivine from a hypothetical stratiform ultramafic intrusion. Letters *a*, *b*, and *c* denote assemblages found in separate cumulate layers (after Smith, 1971).

has a higher Fe/(Fe+Mg) ratio than coexisting orthopyroxene as required by equilibrium (Fig. 1). For the purposes of this discussion it will be assumed that all the crystals in the layers crystallized from magma at the same *P* and *T*. In such a case, Figure 1 may be regarded as an isothermal, isobaric ternary phase diagram depicting phase relations under the *P* and *T* conditions of crystallization.

What may be deduced from these relations concerning the nature of the magma from which the minerals precipitated? Using graphical analysis, such as the method of rocking tangent planes or the "method of equipotential lines" (Korzhinskii, 1959, p. 80–88), it may be inferred from Figure 1 that assemblage *c* crystallized at a higher value of μ_{SiO_2} than assemblage *a* and that assemblage *b* was intermediate between the two (Fig. 2). The magma from which *c* crystallized had a higher value of μ_{SiO_2} than the magma from which *a* crystallized. Thus, the magma must have been more silica-rich during equilibrium crystallization of *c* and less so during crystallization of *a*. It is worth emphasizing that this conclusion was reached without recourse to any data other than the measured mineral compositions and the intrinsic properties of ternary phase diagrams.

The graphical methods of Korzhinskii (1959) and others for analyzing binary, ternary, and quaternary mineral systems afford a powerful basis for drawing general conclusions about petrogenetic processes. Graphical methods, however, cannot treat systems requiring more than four components for representa-

tion. The aim of the algebraic analysis that follows is to free the petrologist from a dependence on graphical methods so that more complex mineral systems can be understood.

Consider again the example of an orthopyroxene–olivine cumulate rock in a stratiform intrusion (Fig. 1). This example is useful, for the results of the algebraic analysis can be confirmed graphically. A mathematical expression relating the variation of μ_{SiO_2} to mineral composition in the two-phase assemblage orthopyroxene–olivine is required. Such an expression is obtained by compiling a list of thermodynamic relations that together constitute a linear system of simultaneous equations. The system of equations may be solved by the methods of matrix algebra. The list begins with two Gibbs-Duhem equations (Prigogine and Defay, 1954, p. 71, eq. 6.38), one for each mineral. (Symbols are defined in Table 1.)

$$\bar{S}_{\text{opx}}dT - \bar{V}_{\text{opx}}dP + X_{2,\text{opx}}(d\mu_2 - d\mu_3) + d\mu_3 = 0 \quad (1)$$

$$\bar{S}_{\text{ol}}dT - \bar{V}_{\text{ol}}dP + X_{4,\text{ol}}(d\mu_4 - d\mu_5) + d\mu_5 = 0 \quad (2)$$

In these equations the substitutions $X_{3,\text{opx}} = 1 - X_{2,\text{opx}}$ and $X_{5,\text{ol}} = 1 - X_{4,\text{ol}}$ have been made and terms rearranged. The components of olivine and orthopyroxene are not independent and are related by the equation

$$2(d\mu_2 - d\mu_3) - (d\mu_4 - d\mu_5) = 0 \quad (3)$$

which must be added to the list. The variable $d\mu_1$ is included in the list by adding the equation

$$d\mu_1 - 2d\mu_3 + d\mu_5 = 0 \quad (4)$$

Finally, in order to add the variables of mineral composition, $dX_{2,\text{opx}}$ and $dX_{4,\text{ol}}$ the following equations

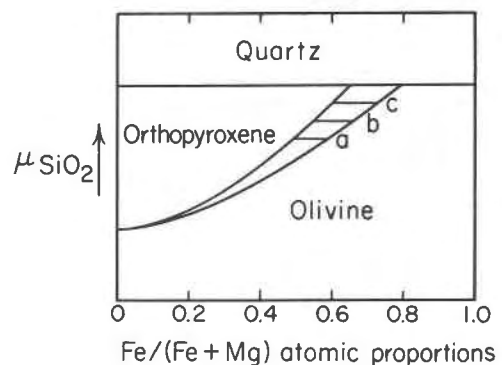


FIG. 2. Variation of μ_{SiO_2} with orthopyroxene and olivine composition in the two-phase assemblage olivine + orthopyroxene. Letters *a*, *b*, and *c* denote assemblages found in separate cumulate layers.

TABLE 1. Explanation of symbols

P : Pressure (bars).

T : Temperature ($^{\circ}\text{K}$).

μ_i : Chemical potential of component i (kcal/mole).

μ°_i : Chemical potential of pure component i (kcal/mole).

\bar{S}_{iA} : Partial molar entropy of component i in phase A (kcal/ $^{\circ}\text{K}$ mole).

\bar{V}_{iA} : Partial molar volume of component i in phase A (kcal/bar mole).

\bar{S}_A : Molar entropy of phase A (kcal/ $^{\circ}\text{K}$ mole).

\bar{V}_A : Molar volume of phase A (kcal/bar mole).

$\bar{G}_{i i A} \equiv (\partial^2 \bar{G}_A / \partial X_{iA}^2)_{P, T, \text{ all } X_{jA} \neq X_{iA}}$: Principal curvature of molar Gibbs free energy of phase A with respect to component i (kcal/mole).

$\bar{G}_{i j A} \equiv [\partial(\partial \bar{G}_A / \partial X_{iA})_{P, T, \text{ all } X_{jA} \neq X_{iA}} / \partial X_{jA}]_{P, T, \text{ all } X_{(j-1)A} \neq X_{jA}}$ (kcal/mole).

\bar{G}_A : Molar Gibbs free energy of phase A (kcal/mole).

X_{iA} : Mole fraction of component i in phase A.

ν_i : Stoichiometric coefficient.

Phase subscripts: opx, orthopyroxene; ol, olivine; Q, quartz; Mt, magnetite; Wm, white mica; Ch, chlorite; Ct, chloritoid; St, staurolite; I, ilmenite.

Component subscripts: 1, SiO_2 ; 2, FeSiO_3 ; 3, MgSiO_3 ; 4, Fe_2SiO_4 ; 5, Mg_2SiO_4 ; 6, $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$; 7, Fe_3O_4 ; 8, $\text{Fe}_9\text{Al}_6\text{Si}_5\text{O}_{20}(\text{OH})_{16}$; 9, $\text{Mg}_9\text{Al}_6\text{Si}_5\text{O}_{20}(\text{OH})_{16}$; 10, $\text{Fe}_4\text{Al}_{18}\text{Si}_8\text{O}_{48}\text{H}_2$; 11, $\text{Mg}_4\text{Al}_{18}\text{Si}_8\text{O}_{48}\text{H}_2$; 12, $\text{Fe}_2\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_4$; 13, $\text{Mg}_2\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_4$; 14, FeTiO_3 ; 15, Fe_2O_3 ; 16, H_2O ; 17, O_2 ; 18, H_2 .

are necessary (J. B. Thompson, Jr., class lectures, Harvard University, 1965):

$$-(\bar{S}_{2,\text{opx}} - \bar{S}_{3,\text{opx}})dT + (\bar{V}_{2,\text{opx}} - \bar{V}_{3,\text{opx}})dP - (d\mu_2 - d\mu_3) + (\partial^2 \bar{G}_{\text{opx}} / \partial X_{2,\text{opx}}^2)_{P,T} dX_{2,\text{opx}} = 0 \quad (5)$$

and

$$-(\bar{S}_{4,\text{ol}} - \bar{S}_{5,\text{ol}})dT + (\bar{V}_{4,\text{ol}} - \bar{V}_{5,\text{ol}})dP - (d\mu_4 - d\mu_5) + (\partial^2 \bar{G}_{\text{ol}} / \partial X_{4,\text{ol}}^2)_{P,T} dX_{4,\text{ol}} = 0 \quad (6)$$

Equations (5) and (6) are obtained by writing the

formal relation

$$d(\mu_2 - \mu_3) = [\partial(\mu_2 - \mu_3) / \partial T]_{P, X_{2,\text{opx}}} dT + [\partial(\mu_2 - \mu_3) / \partial P]_{T, X_{2,\text{opx}}} dP + [\partial(\mu_2 - \mu_3) / \partial X_{2,\text{opx}}]_{P,T} dX_{2,\text{opx}} \quad (7)$$

and substituting (cf. Rumble, 1974a, p. 202-203)

$$-(\bar{S}_{2,\text{opx}} - \bar{S}_{3,\text{opx}}) = [\partial(\mu_2 - \mu_3) / \partial T]_{P, X_{2,\text{opx}}} \\ (\bar{V}_{2,\text{opx}} - \bar{V}_{3,\text{opx}}) = [\partial(\mu_2 - \mu_3) / \partial P]_{T, X_{2,\text{opx}}}$$

$$\begin{pmatrix}
 \bar{S}_{\text{opx}} & -\bar{V}_{\text{opx}} & X_{2,\text{opx}} & +1 & 0 & 0 & 0 & 0 & 0 \\
 \bar{S}_{\text{o1}} & -\bar{V}_{\text{o1}} & 0 & 0 & X_{4,\text{o1}} & +1 & 0 & 0 & 0 \\
 0 & 0 & +2 & 0 & -1 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & -2 & 0 & +1 & +1 & 0 & 0 \\
 -\Delta\bar{S}_{i,\text{opx}} & +\Delta\bar{V}_{i,\text{opx}} & -1 & 0 & 0 & 0 & 0 & \bar{G}_{22,\text{opx}} & 0 \\
 -\Delta\bar{S}_{i,\text{o1}} & +\Delta\bar{V}_{i,\text{o1}} & 0 & 0 & -1 & 0 & 0 & 0 & \bar{G}_{44,\text{o1}}
 \end{pmatrix}
 \begin{pmatrix}
 dT \\
 dP \\
 (d\mu_2 - d\mu_3) \\
 d\mu_3 \\
 (d\mu_4 - d\mu_5) \\
 d\mu_5 \\
 d\mu_1 \\
 dX_{2,\text{opx}} \\
 dX_{4,\text{o1}}
 \end{pmatrix}
 =
 \begin{pmatrix}
 0 \\
 0 \\
 0 \\
 0 \\
 0 \\
 0 \\
 0 \\
 0 \\
 0
 \end{pmatrix}
 \quad (8)$$

and

$$(\partial^2 \bar{G}_{\text{opx}} / \partial X_{2,\text{opx}})_{P,T} = [\partial(\mu_2 - \mu_3) / \partial X_{2,\text{opx}}]_{P,T}$$

(Haase, 1948)

The structure of the system of equations is most easily seen in matrix notation (equation 8) where

$$\Delta\bar{S}_{i,\text{opx}} = (\bar{S}_{2,\text{opx}} - \bar{S}_{3,\text{opx}}), \Delta\bar{V}_{i,\text{opx}} = (\bar{V}_{2,\text{opx}} - \bar{V}_{3,\text{opx}})$$

and

$$\bar{G}_{22,\text{opx}} = (\partial^2 \bar{G}_{\text{opx}} / \partial X_{2,\text{opx}}^2)_{P,T}.$$

The system of equations contains nine unknowns and six equations giving three degrees of freedom, a value that is in agreement with the variance computed from Gibbs phase rule for an assemblage of two phases in a ternary chemical system. Solutions to the system of equations are obtained by first setting P and T to fixed values ($dT = dP = 0$) in accord with the conditions of Figures 1 and 2. The resulting system contains seven unknowns and six equations. Then, solutions such as $(\partial\mu_1 / \partial X_{2,\text{opx}})_{P,T}$ are found by dividing both sides of the matrix equation by one of the unknowns ($dX_{2,\text{opx}}$) and solving the resulting set of inhomogeneous equations by Cramer's rule (Aitken, 1956, p. 55-56).

The inhomogeneous system of equations is given in equation (9). Thus the relation

$$(\partial\mu_1 / \partial X_{2,\text{opx}})_{P,T} = 2\bar{G}_{22,\text{opx}}(X_{4,\text{o1}} - X_{2,\text{opx}}) \quad (10)$$

describes the variation in μ_{SiO_2} as a function of orthopyroxene composition in an orthopyroxene-olivine assemblage at constant P and T . The sign

of the right-hand side of equation (10) may be deduced because the quantity $\bar{G}_{22,\text{opx}}$ is necessarily positive for binary solutions stable with respect to diffusion (Prigogine and Defay, 1954, p. 242, eq. 16.20). Furthermore, measured chemical compositions of the minerals show that $X_{4,\text{o1}} > X_{2,\text{opx}}$; therefore, an increase in the Fe/(Fe + Mg) ratio of an orthopyroxene in equilibrium with olivine at constant P and T measures an increase in the equilibrium value of μ_{SiO_2} for that assemblage. The result of the algebraic analysis is in complete agreement with that of the graphical analysis (*cf.* Fig. 2).

Algebraic analysis also affords the opportunity to estimate the magnitude of the chemical potential gradient in μ_{SiO_2} . If it is assumed that the orthopyroxene is a disordered ideal solid solution at the P and T of magmatic crystallization, then

$$\begin{aligned}
 \bar{G}_{\text{opx}} &= X_{2,\text{opx}}\mu_{2,\text{opx}}^\circ + X_{3,\text{opx}}\mu_{3,\text{opx}}^\circ \\
 &+ RT(X_{2,\text{opx}}\ln X_{2,\text{opx}} + X_{3,\text{opx}}\ln X_{3,\text{opx}}) \quad (11)
 \end{aligned}$$

and

$$(\partial^2 \bar{G}_{\text{opx}} / \partial X_{2,\text{opx}}^2)_{P,T} = RT / X_{2,\text{opx}} X_{3,\text{opx}} \quad (12)$$

Equation (10) may then be evaluated by substituting (12) and either by integrating the resulting expression

$$\begin{pmatrix}
 X_{2,\text{opx}} & +1 & 0 & 0 & 0 & 0 \\
 0 & 0 & X_{4,\text{o1}} & +1 & 0 & 0 \\
 +2 & 0 & -1 & 0 & 0 & 0 \\
 0 & -2 & 0 & +1 & +1 & 0 \\
 -1 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & -1 & 0 & 0 & \bar{G}_{44,\text{o1}}
 \end{pmatrix}
 \begin{pmatrix}
 (d\mu_2 - d\mu_3) / dX_{2,\text{opx}} \\
 d\mu_3 / dX_{2,\text{opx}} \\
 (d\mu_4 - d\mu_5) / dX_{2,\text{opx}} \\
 d\mu_5 / dX_{2,\text{opx}} \\
 d\mu_1 / dX_{2,\text{opx}} \\
 dX_{4,\text{o1}} / dX_{2,\text{opx}}
 \end{pmatrix}_{P,T}
 =
 \begin{pmatrix}
 0 \\
 0 \\
 0 \\
 0 \\
 -\bar{G}_{22,\text{opx}} \\
 0
 \end{pmatrix}
 \quad (9)$$

TABLE 2. Composition of minerals in hypothetical assemblages A, B, C

| Mineral | Fe/(Fe+Mg) | | | $X_{\text{FeTiO}_3, \text{I}}$ | | |
|------------|------------|------|------|--------------------------------|------|------|
| | A | B | C | A | B | C |
| Staurolite | 0.92 | 0.89 | 0.88 | | | |
| Chloritoid | 0.90 | 0.88 | 0.86 | | | |
| Chlorite | 0.69 | 0.59 | 0.55 | | | |
| Ilmenite | | | | 0.98 | 0.92 | 0.90 |

or $dX_{12, \text{Ct}}$ could have been chosen equally well. With $dT = dP = 0$, there are 16 unknowns and 15 equations. Solutions can be obtained as in the previous example by dividing through by one of the unknowns, such as $dX_{8, \text{Ch}}$, and applying Cramer's rule to the resulting inhomogeneous system of equations. The following solutions are pertinent to interpretation of fluid phase properties:

$$(\partial \mu_{16} / \partial X_{8, \text{Ch}})_{P, T} = \bar{G}_{88, \text{Ch}}(24X_{10, \text{St}} + 45X_{8, \text{Ch}} - 69X_{12, \text{Ct}}) / 207 \quad (14)$$

$$(\partial \mu_{17} / \partial X_{8, \text{Ch}})_{P, T} = 2\bar{G}_{88, \text{Ch}}(72X_{8, \text{Ch}} + 20X_{10, \text{St}} - 69X_{12, \text{Ct}} - 23) / 69 \quad (15)$$

$$(\partial \mu_{18} / \partial X_{8, \text{Ch}})_{P, T} = \bar{G}_{88, \text{Ch}}(46X_{12, \text{Ct}} - 57X_{8, \text{Ch}} - 12X_{10, \text{St}} + 23) / 69 \quad (16)$$

$$(\partial \mu_{17} / \partial X_{14, \text{I}})_{P, T} = -6\bar{G}_{1414, \text{I}}X_{14, \text{I}} \quad (17)$$

Equation (14) gives the variation of $\mu_{\text{H}_2\text{O}}$ with chlorite composition in the assemblages of seven minerals. The term $\bar{G}_{88, \text{Ch}}$ is necessarily positive for stable binary solutions (Prigogine and Defay, 1954, p. 242, Eq. 16.20), and the coefficient of $\bar{G}_{88, \text{Ch}}$ is negative according to chemical analyses of the minerals (Table

3). Therefore, algebraic analysis together with chemical analyses shows that an increase in Fe/(Fe + Mg) ratio of chlorite in the mineral assemblage records a decrease in $\mu_{\text{H}_2\text{O}}$. By similar reasoning it may be seen that an increase in Fe/(Fe + Mg) ratio of chlorite measures a decrease in μ_{O_2} (Eq. 15), a result in agreement with the work of Chinner (1960) and Mueller (1960). Equation (16) demonstrates that μ_{H_2} increases with increasing Fe/(Fe + Mg) ratio of chlorite. Equation (17) shows that an increase in FeTiO₃ content in ferrian ilmenite with magnetite present measures a decrease in μ_{O_2} (cf. Buddington and Lindsley, 1964, p. 316, Fig. 5). The reader may verify for himself that addition to the system of equations of a Gibbs-Duhem equation for a fluid consisting of the species H₂O, H₂, O₂, CO₂, CO, and CH₄, together with appropriate equations of homogeneous equilibrium does not change the variance of the system and leaves equations (14)–(17) unchanged.

Algebraic analysis has succeeded, where graphical analysis could not, in supplying vital evidence on how the fluid phase constituents H₂O, O₂, and H₂ behaved during metamorphism of the hypothetical quartzite. The algebraic method verifies the presence of gradients in the chemical potentials of the fluid constituents between adjacent sedimentary beds and gives the gradient direction. These important results are obtained without recourse to data other than the measured mineral compositions and the inherent properties of a stable binary solution. The numerical magnitude of the gradients may be estimated by guessing the T of metamorphism, assuming the chlorite minerals are an ideal Fe–Mg binary solution, and substituting in equations (14)–(16) (Rumble, 1974b, p. 379, Table 36)

$$\bar{G}_{88, \text{Ch}} = 9RT / X_{8, \text{Ch}}X_{9, \text{Ch}}$$

TABLE 3. Coefficients of $\bar{G}_{88, \text{Ch}}$ in equations (14)–(16)

| Equation | Coefficient of $\bar{G}_{88, \text{Ch}}$ | | | Average Uncertainty* |
|----------------------------------------------------------|------------------------------------------|-------|-------|----------------------|
| | A | B | C | |
| $(\partial \mu_{16} / \partial X_{8, \text{Ch}})_{P, T}$ | -0.04 | -0.06 | -0.07 | 0.008 |
| $(\partial \mu_{17} / \partial X_{8, \text{Ch}})_{P, T}$ | -0.49 | -0.68 | -0.73 | 0.06 |
| $(\partial \mu_{18} / \partial X_{8, \text{Ch}})_{P, T}$ | +0.20 | +0.28 | +0.30 | 0.02 |

*Average uncertainty based on assigned uncertainty of 0.02 in Fe/(Fe+Mg)

and $X_{\text{FeTiO}_3, \text{I}}$.

Summary

A given equilibrium assemblage of minerals can be described analytically in terms of the intensive parameters P , T , μ_i , and $X_{i,A}$ by compiling a list of simultaneous equations that include the following three types:

1. A Gibbs-Duhem equation for each mineral

$$\bar{S}_A dT - \bar{V}_A dP + X_{i,A}(d\mu_i - d\mu_j) + \dots \\ + X_{j-1,A}(d\mu_{j-1} - d\mu_j) + d\mu_j = 0$$

Chemical components of the minerals are most appropriately chosen as the end-member compositions of the solid solution series. This practice is in accord with Gibbs' original definition of "actual" components (Gibbs, reprinted 1961, p. 63-64; cf. Thompson, 1959; and Brady, 1975).

2. Equations of mass action expressing the conditions of equilibrium among the chemical potentials of the components of the minerals

$$\sum \nu_i d\mu_i = 0$$

The choice of specific equations is arbitrary as long as they are all linearly independent and of sufficient number to eliminate the dependent μ_i .

3. Equations expressing the relation between the exchange potentials ($\mu_i - \mu_j$) of a mineral solid solution and P , T , and mineral composition.

$$-(d\mu_i - d\mu_j) - (\bar{S}_{i,A} - \bar{S}_{j,A})dT + (\bar{V}_{i,A} - \bar{V}_{j,A})dP \\ + \bar{G}_{i,A} dX_{i,A} + \dots + \bar{G}_{i(j-1),A} dX_{(j-1),A} = 0$$

One of these equations is required for each independent exchange potential of a given mineral solid solution. A binary solution requires one such equation, a ternary requires two, and so on. Examples of the application of this method to ternary solutions are given in Rumble (1973) and Rumble (1974b). The choice of which variables $dX_{i,A}$ to add to the system of equations is arbitrary, and should be determined by convenience.

The method of algebraic analysis described in this paper may be applied to mineral assemblages with any number of degrees of freedom (Rumble, 1974a). However, assemblages with variance greater than one require the imposition of additional constraints, as dictated by the requirements of the petrologic process under study, in order to obtain solutions to the system of equations. In the examples presented above trivariant assemblages were investigated under isothermal, isobaric conditions; therefore the constraints $dT = dP = 0$ were imposed. Assemblages of still higher variance may be analyzed by imposing

additional constraints of the type $dX_{i,A} = 0$. For example, a quadrivariant assemblage in which a minor component such as MnO occurs in small but constant amount in a mineral A , may be investigated by adding the constraint $dX_{MnO,A} = 0$.

The qualitative nature of chemical potential gradients can be deduced from the results of the algebraic analysis by considering measured mineral composition and the intrinsic properties of stable solid-solutions. At the qualitative level the algebraic method represents an extension of graphical analysis to systems requiring more than four components for representation. Quantitative estimates of the magnitudes of the gradients can be obtained simply by guessing the temperature of equilibration during petrogenesis and assuming that the components of one of the mineral solid-solutions mix ideally. Still more accurate measurements of the gradients may be obtained upon acquisition of complete thermodynamic data on the minerals and verification of the P and T of petrogenesis.

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