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Crystallographic projection of chemical potential relationships as an aid in the interpretation of metasomatic zoning

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Abstract

An extension of Korzhinskii's (1959) derivation of chemical potential diagrams for inert components permits the rapid construction of models in terms of three components, with the possibility of contouring the models in terms of a fourth. Such problems are concerned with the relative slopes of planes and lines in space, and concepts from crystallography may be employed. The treatment arises directly from equations of the form $\Sigma v_i d\mu_i = 0$, for equilibrium between solid and solution at constant P, T, and μ_m. For a simple three-component system, the coefficients in the equation (ν_i obtained from inspection of the mineral formulae) are proportional to the reciprocals of the intercepts made by the equivalent plane on the three axes of a chemical potential model, and these coefficients are thus equivalent to Miller indices of crystallography. Planes of constant chemical potential for a fourth component may be similarly indexed. From a stereogram of the planes and lines in chemical potential space, an orthographic projection is obtained as in crystal drawings.

The method is illustrated by derivation of a qualitative model used in the preliminary interpretation of zoned skarn from Albion Basin, Alta, Utah, and by construction of a quantitative model based on the discussion of the Salton Sea geothermal system by Helgeson (1967).

Introduction

The development of diffusional metasomatic zonation depends on the migration of chemical species, which in turn is dependent upon gradients in the chemical potentials of the species involved. Understanding of the systematics involved was advanced significantly by Korzhinskii (1959). For a system with three "inert" components, he derived a simple inverse relationship between a tie line on an orthogonal compositional diagram and the equivalent field boundary on a chemical-potential diagram. The chemical-potential diagrams thus formed are in terms of two independent variables, contoured in terms of a third dependent variable. The method has since been used to advantage by, for example, Helgeson (1967), Burt (1974), and Joesten (1974).

Given the common multicomponent nature of natural metasomatism, it would be advantageous to extend this method to more variables, as long as the complexity introduced does not outweigh this advantage. This paper aims to show how the method may be readily extended to encompass four variables, with graphical representation involving nothing more complex than the methods of elementary crystallography. Some relevant theory is reviewed, then a specific example used to demonstrate the method, and finally a quantitative example used to suggest the scope of the method.

Equilibria in chemical potential space

Consider local equilibria between solid phases of fixed composition and aqueous solution in an isothermal isobaric system, in which the chemical potentials of all components (i) other than $i = 1,2,3,4$ are externally fixed. Let one of these other components be H_2O.

For any equilibrium one can write an equation of the form $\sum \nu_i \mu_i = 0$, and with the above restrictions, we obtain for maintenance of equilibrium

$$\nu_i d\mu_1^F + \nu_2 d\mu_2^F + \nu_3 d\mu_3^F + \mu_4 d\mu_4^F = 0,$$

where the coefficients (ν_i) simply depend on the compositions of the solid phases, and μ_i^F is the chemical potential of component (i) in the aqueous fluid (F).

This equation shows that variation of all four chemical potentials cannot be independent.

If i_4 does not participate in an equilibrium or if i_4 is conserved in an equilibrium (as when i_4 is inert) or if μ_4 is held constant, we obtain

$$\nu_1 d\mu_1^F + \nu_2 d\mu_2^F + \nu_3 d\mu_3^F = 0.$$

This defines the slope of a plane in μ_1–μ_2–μ_3 space. For equilibrium between a single solid phase and solution, the stability field of the solid will generally be a volume in μ_1–μ_2–μ_3 space if i_4 is a constituent of the phase, and the slope of isopotential planes (constant μ_4) is given by equations of the above form. If the composition of the solid is pure i_4 (as for periclase and MgO in the following example), the stability field will be restricted to such an isopotential surface at constant temperature and pressure. If i_4 is not a constituent of the solid phase, the stability field will lie in a plane whose slope is given by an equation of the above form. The stability fields of single solid phases are thus restricted in μ_1–μ_2–μ_3 space as shown in Table 1.

The variables may be considered in terms of chemical potentials, logarithms of activities or fugacities of oxides or of ions in aqueous solutions, without alteration of the slopes concerned (*e.g.* Helgeson, 1968, p. 858).

In particular, for an equilibrium in which i_4 does not participate or is conserved, we can write an expression for the equilibrium constant (K_a) in terms of the activities (a_i^F) in the fluid phase, assuming $a(H_2O) \sim 1$:

$$\log K_a = \nu_1 \log a_1^F + \nu_2 \log a_2^F + \nu_3 \log a_3^F .$$

If K_a is known, such an equation defines the slope and position of the plane in which the equilibrium lies in $\log a_1$–$\log a_2$–$\log a_3$ space. And even if K_a is unknown, the slope of the plane is given by

$$\nu_1 d \log a_1^F + \nu_2 d \log a_2^F + \nu_3 d \log a_3^F = 0$$

Table 1. Restrictions on stability fields and isopotential planes for equilibrium between a solid phase and solution

Composition of solid phase in terms of components present				Stability field	Isopotential plane for constant μ_4
1	2	3	4		
X	X	X	X	volume	plane
X	X	-	X	volume	plane $\parallel \mu_3$
X	-	-	X	volume	plane $\parallel \mu_2, \mu_3$
-	-	-	X	plane	plane
X	X	X	-	plane	-
X	X	-	-	plane $\parallel \mu_3$	-
X	-	-	-	plane $\parallel \mu_2, \mu_3$	-

Further, components may be considered as oxides or as more realistic species in solution, the translation from one form to the other being accomplished by a relationship such as the following (after Helgeson, 1968, p. 857), where M represents a cation and z the charge thereon,

$$MO_{z/2} + zH^+ = M^{z+} + z/2\ H_2O.$$

Crystallographic projection of chemical potential relationships

Albion Basin skarn

Let us now consider a specific example, in the system CaO–Al_2O_3–SiO_2–MgO–CO_2–H_2O under constant external conditions, pressure, temperature, $\mu(CO_2)$ and $\mu(H_2O)$, such that there are only four intensive variables, *e.g.* $\mu(CaO)$, $\mu(Al_2O_3)$, $\mu(SiO_2)$ and $\mu(MgO)$. Assume the presence of an aqueous solution through which four corresponding species may diffuse.

Consider equilibrium between grossular and solution, where $\bar{G}$ is Gibb's free energy per mole:

$$Ca_3Al_2Si_3O_{12} = 3CaO + 2\ AlO_{1.5} + 3\ SiO_2$$
$$\bar{G}(Ca_3Al_2Si_3O_{12}) = 3\mu^F(CaO) + 2\mu^F(AlO_{1.5}) + 3\mu^F(SiO_2)$$

Because the left-hand side is a function of only P and T for fixed composition, we have, for maintenance of equilibrium

$$3d\mu^F(CaO) + 2d\mu^F(AlO_{1.5}) + 3d\mu^F(SiO_2) = 0.$$

This equilibrium in terms of oxides can be readily translated into terms of more realistic species in solution, as noted in the previous section, yielding

$$Ca_3Al_2Si_3O_{12} + 24\ H^+ = 3\ Ca^{2+} + 2\ Al^{3+} + 3\ Si^{4+} + 12\ H_2O$$

and hence, for maintenance of equilibrium, we obtain

$$3d \log a_{Ca^{2+}}/(a_{H^+})^2 + 2d \log a_{Al^{3+}}/(a_{H^+})^3 + 3d \log a_{Si^{4+}}/(a_{H^+})^4 = 0$$

which may be compared with the previous equation in terms of oxides: the coefficients of corresponding terms are the same.

Thus, for brevity and without implication as to the precise nature of the species in solution, we can write equations of the form

$$\nu_{Ca} d\mu_{Ca} + \nu_{Al} d\mu_{Ai} + \nu_{Si} d\mu_{Si} + \nu_{Mg} d\mu_{Mg} = 0 ,$$

where the $d\mu_i$ terms can be expanded into terms of oxides or ratios of cations as desired.

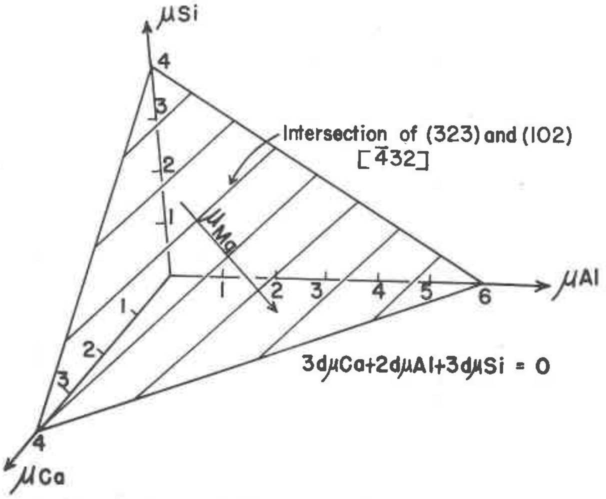

Fig. 1. Derivation of the Miller Index for the plane in μ_{Ca}–μ_{Al}–υ_{Si} space representing equilibrium between grossular and solution and the isopotential lines for constant μ_{Mg} in the case where diopside is an additional phase in the equilibrium.

For the purpose of graphical representation, let μ_{Ca}, μ_{Al}, and μ_{Si} be the independent variables, μ_{Mg} the dependent one. Then, recalling the restrictions outlined in the previous section, μ_{Ca}, μ_{Al}, and μ_{Si} may be used as the axes of a three-dimensional figure on which relevant equilibria can be shown. For the six-component system considered, the given conditions limit the maximum number of solid phases in an equilibrium assemblage to four. In μ_{Ca}–μ_{Al}–μ_{Si} space, at most one solid phase can exist in a volume, two on a surface, three on a line, and four at a point.

Let us endeavour to show such equilibria in a convenient way: the problem involves the inter-relationships of planes of definite slopes but (commonly) indefinite positions in three-dimensional space, which smacks of problems in elementary crystallography.

Consider equilibrium between grossular and solution once more.

$$3d\mu_{Ca} + 2d\mu_{Al} + 3d\mu_{Si} = 0.$$

This is an equation for the slope of the corresponding stability surface in μ_{Ca}–μ_{Al}–μ_{Si} space, as illustrated in Figure 1 (*c.f.* Fisher, 1974). At the position arbitrarily chosen for the plane, the ratio of the intercepts on the three axes (μ_{Ca}: μ_{Al}: μ_{Si}) is 4:6:4, and the ratio of the rationalized reciprocals is 3:2:3, which is that of the corresponding coefficients in the above equation.

Thus one can assign to this plane the Miller index (323) (*e.g.*, Bloss, 1971, p. 52; Phillips, 1971, p. 42).

Diopside and solution can be stable within a volume in μ_{Ca}–μ_{Al}–μ_{Si} space, with planes of constant μ_{Mg} parallel to the μ_{Al}–axis (see Table 1). The relevant equations are:

$$d\mu_{Ca} + d\mu_{Mg} + 2d\mu_{Si} = 0\ ,$$
$$d\mu_{Mg} = 0\ ,$$
$$\therefore\ (1)\ d\mu_{Ca} + (0)d\mu_{Mg} + (2)d\mu_{Si} = 0\ ,$$

and thus the Miller index of the planes of constant μ_{Mg} is (102).

Grossular, diopside, and solution can only be in mutual equilibrium under conditions given by the place (323) contoured in terms of μ_{Mg} parallel to the "zone axis" between (323) and (102) *i.e.* [$\bar{4}$32], as illustrated in Figure 1.

From a stereogram of such planes and lines in chemical potential space, an orthographic projection can be made as in crystal drawings, (*e.g.*, Phillips, 1971, p. 232–235).

To illustrate this simple procedure, consider Figure 2, in which are shown *hypothetical* equilibria between solution and grossular (323), calcite (100), corundum (010), and quartz (001). On the left is a stereogram showing these planes and a conveniently chosen plane of projection (*PP*), with pole *N*. To determine the direction in orthographic projection of, say, the zone axis between (001) and (010), find the intersection of this zone and the plane of projection (*OD*) and rotate *N* to the center of the stereogram such that the plane of projection is now horizontal and *OD* is rotated to *OD′*. The required direction is normal to *OD′*, as shown. Similar construction for the other zone axes yields the drawing on the right in which slopes are fixed, but lengths are not.

Let us apply this to possible interpretation of skarn from Albion Basin, Alta, Utah, where periclase marble was intruded by granitic finger dikes, giving rise to well-developed bimetasomatic zones. As seen in Figure 3, macroscopic zones include the dike rock (*D*), a brown garnet-rich zone (*G*), green diopside-rich zone (*P*), dun forsterite-rich zone (*O*), and then marble (*M*).

More detailed zonation appears under the microscope, and preliminary petrographic and probe data yield a succession of assemblages involving, to a first approximation, three-phase assemblages separated by seven buffering four-phase assemblages, six of which contain diopside.

That these assemblages may be compatible with one another can be shown in a four-component compositional tetrahedron, but is more readily obvious in the stereographic projection of Figure 4 (Grant,

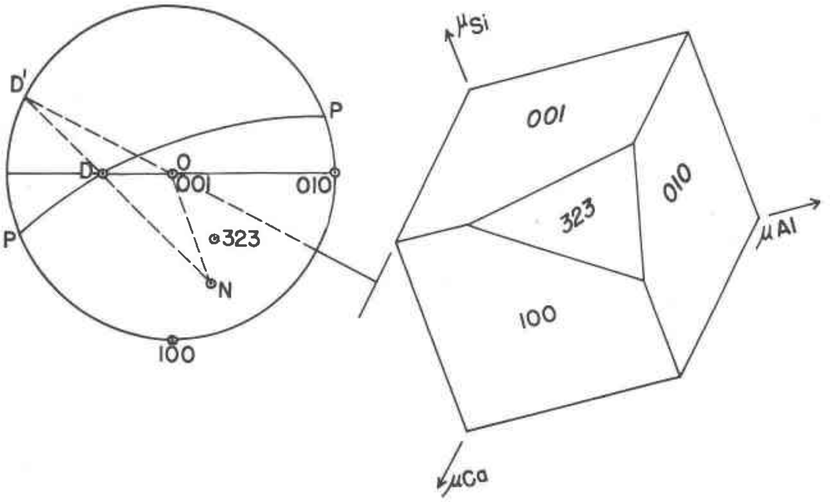

Fig. 2. Illustration of the method of orthographic projection.

1976). To show the six diopside-bearing assemblages one projects from diopside onto a convenient plane, in this case the reference sphere for stereographic projection. With diopside at the center and corundum at the north pole, the six assemblages appear as spherical triangles, tie-lines between coexisting phases being arcs of great circles. We have, with diopside

I Quartz–anorthite–hornblende
II Quartz–anorthite–garnet
III Quartz–garnet–calcite
IV Garnet–calcite–corundum
V Calcite–corundum–spinel
VI Calcite–spinel–forsterite
and VII Calcite–spinel–forsterite–periclase

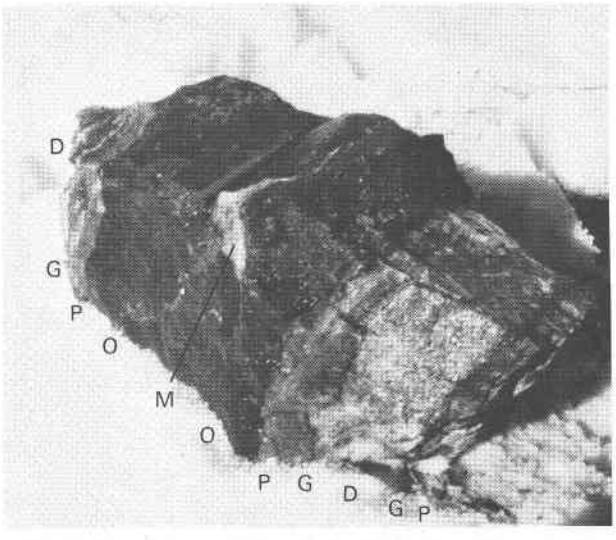

Fig. 3. Zoned skarn, Albion Basin, Utah. *D* = dike rock, *G* = garnet-rich zone, *P* = pyroxene-rich zone, *O* = olivine-rich zone, *M* = marble. (A xanthophyllite-bearing zone between *O* and *P* is not considered here, for clarity of presentation.)

By the method outlined above, these data were translated into the orthographic projection shown in Figure 5. In this figure, the seven four-phase assemblages appear at the points indicated by Roman numerals, as many as three phases may coexist on a line, two on a plane, and one in a volume. The light lines are contours for constant μ_{Mg}, increasing away from

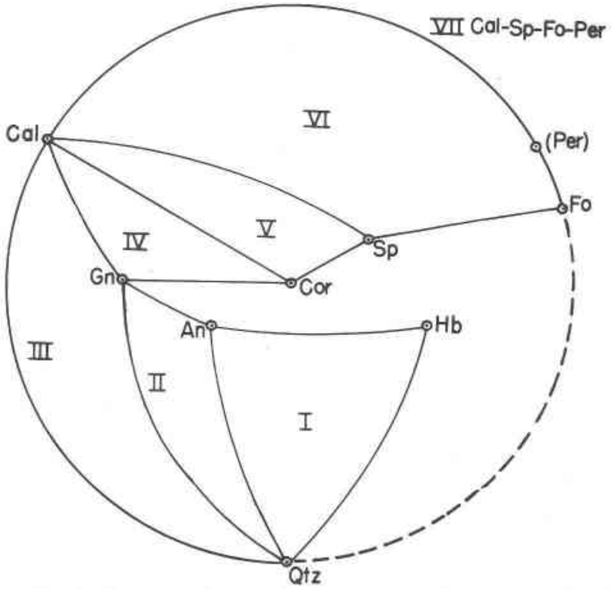

Fig. 4. Stereographic projection of four-phase assemblages including diopside, in the system Al_2O_3–CaO–MgO–Si_2O_6 (after Grant, 1976). Abbreviations are Qtz = quartz, Hb = hornblende, An = anorthite, Gn = garnet, Cal = calcite, Cor = corundum, Sp = spinel, Fo = forsterite, Per = periclase, Di = diopside.

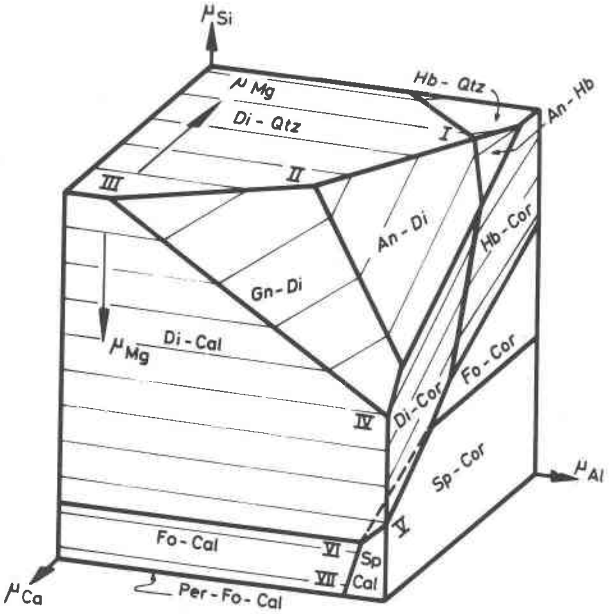

Fig. 5. Orthographic projection of chemical potential relationships pertinent to the Albion Basin skarn. Abbreviations as in the caption for Fig. 4.

near point III. The sequence of four-phase assemblages defines a diffusion path, which suggests that the zoned skarn could be interpreted by a simple diffusion model, involving

(a) outward decrease in μ_{Si} from a value buffered by quartz,

(b) inward decrease in μ_{Ca} from a value buffered by calcite,

(c) inward decrease in μ_{Mg} from a value buffered by periclase, to a shallow minimum within the garnet zone, followed by an increase into the center of a dike. Possibly, this involves uphill diffusion (Cooper, 1974, p. 23).

(d) a minimum in μ_{Al} coinciding with that in μ_{Mg}, and a maximum within the exoskarn, where corundum appears. Again local uphill diffusion is a possibility.

It should be emphasized that this is only a first approximation, used for illustrative purposes. A considerable amount of petrographic and probe work is underway and must precede further interpretation of the skarn.

Table 2. Miller indices of equilibria from Helgeson (1967, Table 4)

Equilibrium	Stochiometric coefficient			Miller index		
	νK^+	νNa^+	νMg^{2+}	h	k	l
Ch - Ka	0	0	5	0	0	1
Ch - Mt	0	-2	35	0	$\bar{2}$	(35)
Ch - Ab	0	-2	5	0	$\bar{2}$	5
Ch - Or	-2	0	5	$\bar{2}$	0	5
Ch - Mu	-2	0	15	$\bar{2}$	0	(15)
Mt - Ka	0	2	0	0	1	0
Ab - Mu	-1	3	0	$\bar{1}$	3	0
Ab - Mt	0	6	0	0	1	0
Or - Mu	2	0	0	1	0	0
Or - Ab	1	-1	0	1	$\bar{1}$	0
Mu - Ka	2	0	0	1	0	0
Mu - Mt	7	-3	0	7	$\bar{3}$	0

Abbreviations: Ch = chlorite, Ka = kaolinite, Mt = montmorillonite, Ab = albite, Or = K-feldspar, Mu = muscovite.

Salton Sea geothermal system

This method is, of course, not restricted to qualitative interpretation of complex natural zonation. It can be readily used to illustrate quantitative relationships.

Consider, for example, the discussion by Helgeson (1967) on solution chemistry and metamorphism, specifically the equilibria illustrated in his Figures 10, 11, and 12 and listed in his Table 4. It will suffice to consider only the equilibria that may be described by

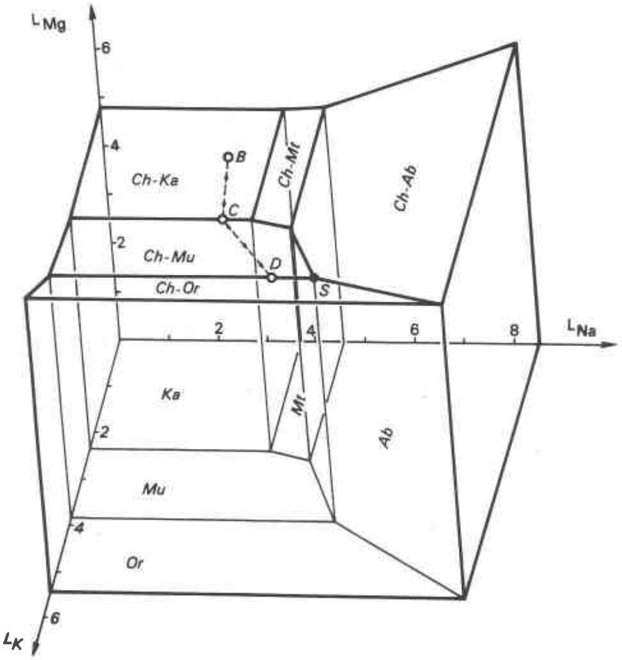

Fig. 6. Orthographic projection of activity relationships pertinent to the Salton Sea geothermal system, as discussed by Helgeson (1967),

$$L_K = \log a_{K+}/a_{H+},\ L_{Na} = \log a_{Na+}/a_{H+},\ L_{Mg} = a_{Mg}{}^{2+}/(a_{H+})^2.$$

Other abbreviations are given in Table 2.

the system $MgO-K_2O-Na_2O-Al_2O_3-SiO_2-H_2O$ under the conditions and with the approximations that he used, particularly $T = 300°C$, $a_{H_2O} = 1$, $a_{SiO_2} = 1$ and neglecting solid solution. All twelve equilibria were written conserving Al_2O_3 and thus were portrayed in terms of log a_{K^+}/a_{H^+}, log a_{Na^+}/a_{H^+}, and log $a_{Mg^{2+}}/(a_{H^+})^2$ in three two-dimensional diagrams. It is a simple matter to combine the relationships into one three-dimensional model, which could be contoured in terms of log $a_{Al^{3+}}/(a_{H^+})^3$. All twelve equilibria involve only two aluminous solid phases, each equilibrium being stable on a plane in the model and each aluminous phase in a volume. The twelve equilibria are summarized in Table 2.

The resultant model is shown here as Figure 6, on which are also shown the path of changing solution compositions *B–C–D* and the composition of the Salton Sea brine (*S*), discussed by Helgeson. This model integrates the information given in his figures 10a, 11a and 12b into one simple illustration.

Conclusion

It is apparent that the language of local equilibrium between solid phases and solution, in terms of chemical potentials of diffusing species, can be readily translated into the language of crystallography, to develop a picture worth several words in either tongue.

Acknowledgments

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