The exploration of reaction space

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Abstract—An efficient method of determining whether or not two multicomponent mineral assemblages can have equilibrated at the same metamorphic grade is to explore the reaction space defined by a matrix representing the compositions of the phases of both assemblages. If reactions having the minerals of one assemblage as products and the other as reactants (termed incompatibility reactions) can be found, the assemblage cannot have equilibrated under the same conditions.

Examination of the relationship between composition space and reaction space of the system SiO_2-MgO-FeO shows that assemblages which intersect or overlap in composition space are characterized by a reaction space containing incompatibility reactions. The regions of reaction space characterized by incompatibility reactions are bounded by univariant equilibria which are themselves incompatibility reactions. If mineral compositions change so as to reduce the area of overlap in composition space, the area of reaction space containing incompatibilities also diminishes, and finally disappears when the compositional overlaps disappear. At that point, the bounding univariant reactions change from incompatibility reactions to compatibility reactions. Consequently, the nature of reactions throughout reaction space can be determined simply by investigating the character of the univariant reactions defined by a composite assemblage.

INTRODUCTION

GREENWOOD (1967) SHOWED that we can determine whether or not a pair of mineral assemblages could have equilibrated at the same metamorphic grade by analyzing the form of reactions between phases of the two assemblages. Two cases must be distinguished.

1. If a reaction having the minerals of one assemblage as reactants and those of the other as products can be written, the tie lines defining the assemblages intersect in composition space (*e.g.* Fig. 1A). The bulk compositions at the intersections can then be represented by either assemblage. But one assemblage must be more stable than the other under arbitrary values of P, T and activities of externally fixed components (KORZHINSKII, 1959, p. 62), so both cannot have equilibrated under the same arbitrary conditions. In this paper, such assemblages are referred to as *incompatible,* and reactions which have minerals of one assemblage as reactants and the other as products are designated *incompatibility reactions.*

2. If no reactions reflecting an incompatibility between two assemblages can be found, the assemblages do not intersect in composition space (*e.g.* Fig. 1B); they simply have different compositions, and could have equilibrated under the same conditions. Such assemblages are here termed *compatible,* and reactions involving minerals of two assemblages on at least one side are termed *compatibility reactions.*

Singular value decomposition (see PRESS *et al.,*

1986, p. 52–64 for a lucid discussion of this matrix technique) provides a simple and efficient method both for modeling mineral assemblages in multicomponent space and for determining whether or not two assemblages are compatible. FISHER (1989) showed that taking the singular value decomposition (SVD) of a composite matrix containing the phases of two assemblages can be used to: (1) construct a composite model fitting both assemblages within any desired level of analytical uncertainty; (2) determine a set of basis vectors for the composition space needed to represent the model; and (3) determine a set of basis vectors for the reaction space needed to characterize reactions between the minerals of the model assemblages. The reaction space of this paper differs somewhat from that used by THOMPSON (1982) because the reactions considered here express relations between phases of metamorphic assemblages, while those discussed by Thompson express relations among components of metamorphic phases.

In order to determine whether or not the model assemblages intersect in composition space, it is necessary to explore the reaction space of the composite to see whether it contains a reaction indicating an incompatibility. FISHER (1989) stated but did not demonstrate that this exploration can be carried out simply by writing all possible univariant reactions involving the phases of the model composite assemblage. Given the importance of this point, it seems worthwhile to provide further justification for this statement.

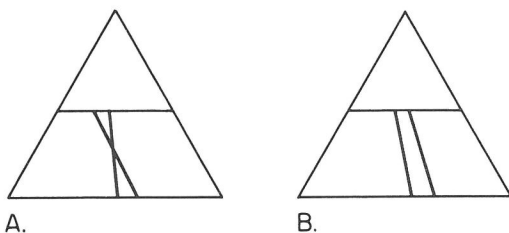This paper analyzes three hypothetical assemblages in the system SiO_2-MgO-FeO to illustrate

FIG. 1. Mineral assemblages in a hypothetical three-component system. A shows two two-phase assemblages, which intersect, and so cannot have equilibrated under the same external conditions; B shows two two-phase assemblages which do not intersect, and so can have equilibrated under the same conditions.

how the set of possible univariant reactions provides a map to all parts of reaction space. The generalization to more complex systems is straightforward.

Hans Eugster devoted much of his life to exploring P-T-activity space, often using the principles worked out by SCHREINEMAKERS (1915–1925), as an aid to navigation. This paper shows that the same rules which govern P-T-activity space can be used to explore reaction space.

A SIMPLE EXAMPLE

Consider four hypothetical assemblages (M1, M2, M3, and M4) from the system SiO_2-MgO-FeO, with mineral compositions listed in Table 1. A plot of these assemblages in composition space (Fig. 2), shows that: (1) M1 and M3 do not intersect, and can have formed under the same external conditions; (2) M1 intersects a part of M2, and so cannot have formed under the same conditions; (3) M4 completely encloses M2, and cannot have formed under the same conditions. Our task is to find a general method for distinguishing these three cases in multicomponent systems using SVD.

Reactions between M1 and M2

To determine a set of basis vectors for the reaction space defined by M1 and M2, we first write a matrix representing the composite M1 + M2:

$$\mathbf{M12} = \begin{array}{ccccc} 1.00 & 1.00 & 1.00 & 1.00 & 1.00 \\ 0.00 & 0.60 & 0.75 & 0.40 & 0.70 \\ 0.00 & 0.40 & 1.25 & 0.60 & 1.30, \end{array}$$

in which rows represent the components SiO_2, MgO and FeO, the first three columns represent the minerals of M1 (qz_1, op_1 and ol_1 in that order), and the last two the minerals of M2 (op_2 and ol_2). The abbreviations used in this paper are qz = quartz, ol

= olivine, op = orthopyroxene and ox = oxide; subscripts indicate the number of the mineral assemblage. Taking the SVD of **M12** gives three matrices which are useful for interpreting M1 and M2 (FISHER, 1989):

$$\mathbf{W} = \begin{array}{ccccc} 3.072 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.912 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.276 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 0.000, \end{array}$$

$$\mathbf{U} = \begin{array}{ccccc} -0.697 & 0.706 & -0.126 & 0.000 & 0.000 \\ -0.394 & -0.231 & 0.890 & 0.000 & 0.000 \\ -0.599 & -0.670 & -0.439 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 1.000 \\ 0.000 & 0.000 & 0.000 & 1.000 & 0.000, \end{array}$$

$$\mathbf{V} = \begin{array}{ccccc} -0.227 & 0.774 & -0.456 & 0.000 & -0.376 \\ -0.382 & 0.329 & 0.839 & 0.172 & -0.111 \\ -0.567 & -0.333 & -0.028 & -0.686 & -0.310 \\ -0.395 & 0.232 & -0.122 & -0.172 & 0.863 \\ -0.570 & -0.358 & -0.268 & 0.686 & -0.066. \end{array}$$

The diagonal elements of **W** are the singular values of **M12**; the fact that three are non-zero shows that the matrix is of rank three (written $R(\mathbf{M12}) = 3$), thereby confirming that M1 and M2 can be represented by a three component system, and indicating that the composite assemblage of five phases involves a reaction space of $5 - R(\mathbf{M12}) = 2$ dimensions. The first three columns of U (those corresponding to the non-zero elements of **W** constitute an orthonormal basis for composition space; the last two columns of V (corresponding to the zero elements of **W**) give the coefficients of two

Table 1. Compositions of minerals in hypothetical SiO_2-MgO-FeO assemblages

		qz	op	ol	ox
M1	SiO_2	1.000	1.000	1.000	
	MgO	0.000	0.600	0.750	
	FeO	0.000	0.400	1.250	
M2	SiO_2		1.000	1.000	
	MgO		0.400	0.700	
	FeO		0.600	1.300	
M3	SiO_2		1.000	1.000	
	MgO		0.300	0.500	
	FeO		0.700	1.500	
M4	SiO_2	1.000		1.000	0.000
	MgO	0.000		1.000	0.325
	FeO	0.000		1.000	0.675

ol = olivine, op = orthopyroxene, ox = oxide, qz = quartz; compositions expressed in oxide formula units (e.g. $op_1 = Mg_{0.6}Fe_{0.4}SiO_3$).
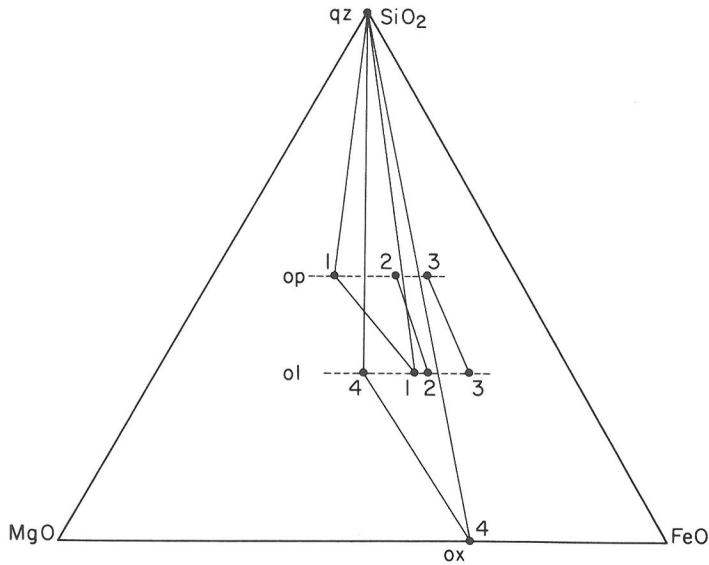
FIG. 2. The assemblages of Table 1 plotted in SiO_2-MgO-FeO space. Abbreviations are ol = olivine, op = orthopyroxene, ox = oxide, and qz = quartz; numerals show assemblage to which minerals belong (*e.g.* op_1 belongs to M1).

reactions which provide an orthonormal basis for reaction space:

$$V4: \quad 0.686\ ol_1 + 0.172\ op_2$$
$$= 0.172\ op_1 + 0.686\ ol_2,$$

$$V5: \quad 0.376\ qz_1 + 0.111\ op_1 + 0.310\ ol_1$$
$$+ 0.066\ ol_2 = 0.863\ op_2,$$

where negative coefficients in the basis vectors are taken to represent reactants, and positive coefficients products.

V4 has phases of both M1 and M2 as both reactants and products, and V5 has phases from both assemblages as reactants, so neither represents an incompatibility between the two assemblages. But we need to determine whether reactions reflecting an incompatibility exist anywhere in the space spanned by V4 and V5.

The reaction coefficients of each mineral are obviously linear functions of the basis vectors V4 and V5, and so can be represented by contours in V4–V5 space (Fig. 3). The five zero contours in Fig. 3 have special significance. They represent lines in V4–V5 space where each of the five phases of the matrix **M12** have zero coefficients, and do not participate in the reaction. They therefore involve only four phases in the system SiO_2-MgO-FeO and correspond to the five univariant reactions defined by

the five sets of four phases in **M12**. These zero contours can be labeled by enclosing the phases not participating in each reaction in brackets, as is commonly done with univariant reactions, and the reaction coefficients can be calculated from **M12** using the method of KORZHINSKII (1959, p. 103ff) or computer programs such as MULTI of FISHER (1989):

$[qz_1]\ \ 4.00\ ol_1 + 1.00\ op_2 = 1.00\ op_1 + 4.00\ ol_2;$

$[op_1]\ \ 1.00\ qz_1 + 2.00\ ol_1 = 2.00\ op_2 + 1.00\ ol_2;$

$[ol_1]\ \ 2.50\ op_2 = 1.00\ qz_1 + 0.50\ op_1 + 1.00\ ol_2;$

$[op_2]\ \ 2.00\ op_1 + 9.00\ ol_2 = 1.00\ qz_1 + 10.00\ ol_1;$

$[ol_2]\ \ 1.00\ qz_1 + 0.25\ op_1 + 1.00\ ol_1 = 2.25\ op_2.$

Each zero contour or reaction line in Fig. 3 has a positive and a negative direction, characterized by reaction coefficients of opposite sign. We are free to designate either direction as positive. However, it will be convenient to define the positive direction of one reaction arbitrarily, then let the positive directions of the other reactions be established by placing labels designating products and reactants on opposite sides of each reaction element, and applying the rules used to distinguish stable and metastable portions of univariant reactions in P-T-activity diagrams (SCHREINEMAKERS, 1915–1925;
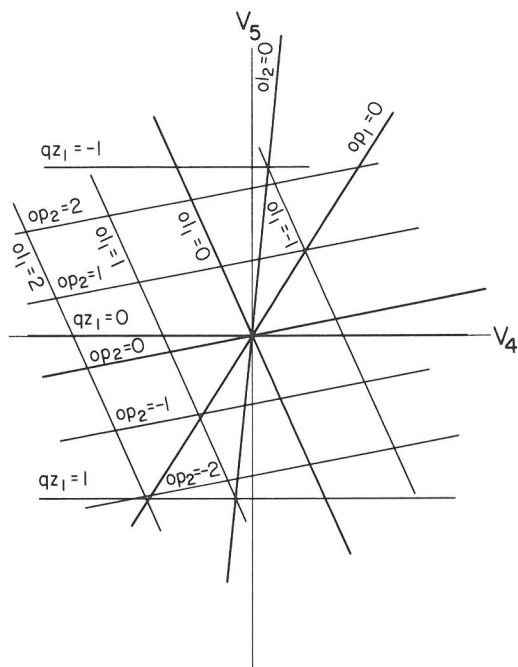
FIG. 3. V4–V5 space, contoured to show values of reaction coefficients. Zero contours (heavy lines) shown for all phases; non-zero contours (light lines) are omitted for op_1 and ol_2 for clarity.

cording to the convention adopted above—must be a product in all reactions below [qz_1]. Consequently, reactions at points in reaction space just below [qz_1] must have the form $ol_1 + op_2 = qz_1 + op_1 + ol_2$. Similar reasoning shows that reactions immediately to the right of [ol_1] have the same form, so reactions of this form characterize the entire space between [ol_1] and [qz_1].

Of the five reactions in Fig. 4, two ([op_1] and [ol_2]) have the minerals of M1 and M2 on opposite sides. They are therefore incompatibility reactions, and confirm algebraically that M1 and M2 do intersect in composition space. Reactions in the sector between these two reactions are also incompatibilities, as can be seen by inspection of the coefficients of [ol_2] and [op_1]. Ol_2 is a product of reaction [op_1], and so must be a product in all parts of reaction space to the right of [ol_2]; consequently reactions immediately right of [ol_2] must have the form of the incompatibility reaction $qz_1 + op_1 + ol_1 = op_2 + ol_2$. Likewise, op_1 is a reactant of [ol_2], and so must be a reactant in reactions to the left of [op_1]. Consequently, reactions immediately to the left of [op_1] represent the same incompatibility reaction.

Similar reasoning shows incompatibility reactions occur *only* between [op_1] and [ol_2]. The sectors bounded by [op_1] or [ol_2] and one compatibility

ZEN, 1966).[1] Because [qz_1] and V4 are identical, it is sensible to choose the positive direction of [qz_1] to coincide with the positive direction of V4. With this convention, Schreinemakers' rules are obeyed if and only if reactants are written on the counterclockwise side of each reaction, and products on the clockwise side (Fig. 4).

The reactions plotted in Fig. 4 divide the plane representing V4–V5 space into 10 sectors, each bounded by the positive or negative ends of two reactions. The character of the reactions within each sector can be inferred by inspection of the bounding reactions. For example, consider reactions in the space between [qz_1] and [ol_1]. The line [qz_1] represents the zero contour for the qz_1 coefficient. Reactions plotting just below [qz_1] have a form similar to [qz_1], but involve a small amount of qz_1. Because qz_1 lies on the clockwise side of reactions [ol_1] and [op_2], it is a product in those reactions, and—ac-

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[1] There is no requirement that the positive ends of reactions in reaction space be defined by the Schreinemakers rule, because they are not constrained by any condition comparable to that of minimizing Gibbs free energy (cf. ZEN, 1966, p. 7–9). However, there is no reason not to adopt the convention used here, and doing so leads to an internally consistent way of writing reactions which is useful in analyzing the geometry of reaction space.
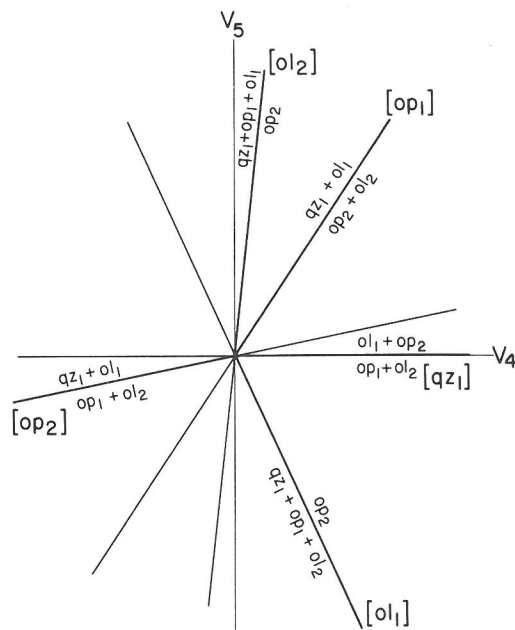

FIG. 4. Configuration of zero contours of reaction coefficients for **M1M2** composite assemblage in V4–V5 space, drawn using conventions adopted in text. Positive ends of zero contours shown by heavy lines, negative ends by light lines.

reaction contain only compatibility reactions, as can be seen by considering the space just to the right of [op_1]. Reactions in this area have coefficients similar to [op_1], but with small op_1 coefficients. Because op_1 is a product in [qz_1], it must be a product everywhere to the right of [op_1], and reactions just to the right of that reaction must have the form $qz_1 + ol_1 = op_1 + op_2 + ol_2$, a compatibility reaction. Comparable arguments show that compatibility reactions characterize reaction space immediately to the left of [ol_2].

The form of the reactions in each sector remains constant so long as no zero coefficient contours (either positive or negative) are crossed. But because one coefficient must change sign as each zero contour is crossed, the character of reactions must change whenever one is crossed. For example, the large arc between [ol_1] and [op_2] is made up of three sectors, two outer ones in which the reactions are compatibilities, and a central sector in which the reactions are incompatibilities. This central sector is simply the negative portion of the sector between [ol_2] and [op_1], analyzed above.

These arguments demonstrate that the reaction space defined by assemblages M1 and M2 contains incompatibility reactions in the sectors between both positive and negative portions of [op_1] and [ol_2], and only in those sectors; all other portions of reaction space are occupied by compatibility reactions.

Reactions between M1 and M3

To search for incompatibilities between M1 and M3, we form a composite matrix giving the composition of the minerals of both M1 and M3 and take its SVD, which gives a reaction space with two basis vectors,

V_4': $0.472\ qz_1 + 0.449\ ol_1 + 0.023\ ol_3$

$$= 0.217\ op_1 + 0.727\ op_3;$$

V_5': $0.543\ ol_1 + 0.453\ op_3$

$$= 0.453\ op_1 + 0.543\ ol_3.$$

Using the conventions adopted above, we divide this reaction space into sectors bounded by four-phase reactions (Fig. 5). All the reactions of Fig. 5 involve phases of both assemblages as reactants or products, and so represent compatibilities. Because compatibility reactions cannot change to incompatibilities when another phase is added, all sectors of reaction space in Fig. 5 must contain compatibility reactions. This observation confirms algebraically the message conveyed by Fig. 2; M1 and M3 do not intersect in composition space.
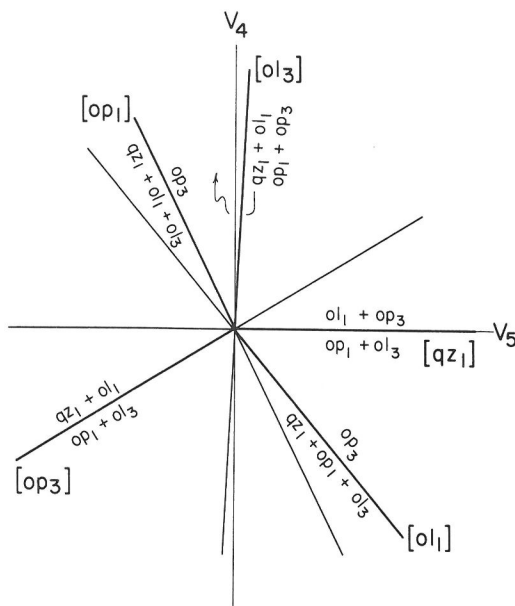

FIG. 5. Configuration of zero contours of reactions coefficients for **M1M3** composite assemblage in V4–V5 space. Positive ends of zero contours shown by heavy lines, negative ends by light lines. Note that the positions of V4 and V5 are reversed from that of Fig. 4, so as to maintain [qz_1] in the same orientation.

The reasons for the different character of reactions in **M1M2** and **M1M3** can be seen by comparing the chemography of M1, M2 and M3 (Fig. 2) with the form of reaction space (Figs. 4 and 5). As op_2 approaches the qz_1-ol_1 tie line in composition space, reactions [op_1] and [ol_2] of Fig. 4 approach one another in reaction space, narrowing the sectors characterized by incompatibilities. When the composition of op_2 becomes collinear with qz_1 and ol_1, reactions [op_1] and [ol_2] become degenerate and merge, eliminating the sector occupied by incompatibilities altogether. Once op_2 moves outside the qz_1-op_1-ol_1 triangle, reaction [op_1] moves to the left of [ol_2], giving the reaction space geometry of Fig. 5, which contains compatibility reactions only. The key point here is that the univariant reactions change from incompatibilities to compatibilities at precisely the point where the sector of reaction space characterized by incompatibility reactions disappears.

Reactions between M4 and M2

To search for incompatibilities between M4 and M2, we form a composite matrix giving the composition of the minerals of both M4 and M2 and take its SVD, which gives a reaction space with two basis vectors,

V4″:   0.609 op_2 + 0.104 ol_2

= 0.567 qz_4 + 0.145 ol_4 + 0.526 ox_4;

V5″:   0.593 ox_4 + 0.593 op_2

= 0.049 ol_4 + 0.543 ol_2.

Using the conventions adopted above, we divide this reaction space into sectors bounded by four-phase reactions (Fig. 6). Two of these reactions ([op_2] and [ol_2]) are incompatibility reactions, reflecting the fact that M4 encloses M2 in composition space (Fig. 2). Inspection of reaction coefficients shows that two sectors of reaction space are characterized by incompatibility reactions: that between the positive end of [op_2] and the negative end of [ol_2], and that between the positive end of [ol_2] and the negative end of [op_2].

The differences between the reaction space geometries of Figs. 4 and 6 can be understood by imagining the changes that would occur were the compositions of op_1 and ol_1 to approach the compositions of ol_4 and ox_4, respectively, so that ol_2 crosses into the qz_1-op_1-ol_1 triangle across the qz_1-ol_1 tie line (Fig. 2). Were this to happen, reaction [op_2] of Fig. 4 would rotate counterclockwise and merge with the negative end of [op_1] when ol_2 becomes collinear with qz_1-ol_1 (to avoid a further degeneracy, we assume that ol_1 becomes deficient in SiO_2). The reaction rotates further when ol_2 enters the M1 phase triangle, and the reactions assume the configuration of Fig. 6. At the degeneracy the form of both reactions changes from A + B = C + D to A + B + C = D, and [op_1] becomes a compatibility, while [op_2] becomes an incompatibility. Consequently the sector of reaction space containing incompatibilities becomes bounded by the reactions [op_2] and [ol_2] rather than by [op_1] and [ol_2].

This example shows how the differences in chemography of M1 + M2 and M4 + M2 are reflected in the form of the incompatibility reactions. In M4 + M2, both M2 minerals are enclosed in the M4 triangle, so both incompatibilities are terminal reactions. In M1 + M2, only op_2 is enclosed in the M1 triangle, and only op_2 participates in a terminal reaction; the form of the incompatibility involving ol_2 is a direct reflection of the tie line intersections of Fig. 2.

DISCUSSION AND CONCLUSIONS

These examples demonstrate four points governing relations between the univariant reactions defined by a composite mineral assemblage and the vector space representing reactions within that composite.
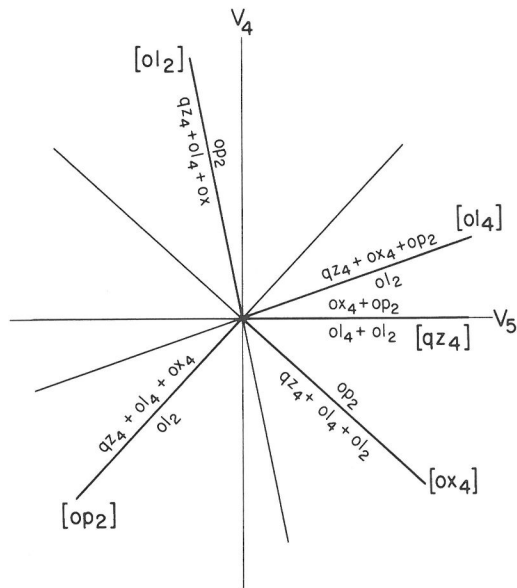

FIG. 6. Configuration of zero contours of reaction coefficients for **M4M2** composite assemblage in V4–V5 space. Positive ends of zero contours shown by heavy lines, negative ends by light lines. Note that the positions of V4 and V5 are reversed from that of Fig. 4, so as to maintain [qz_1] in the same orientation.

1. The univariant reactions represent lines in reaction space along which one or more reaction coefficients change sign, and reactions change character; they divide reaction space into sectors characterized by reactions of uniform character.

2. If the assemblages of the composite do not overlap in composition space, none of the univariant reactions represent incompatibilities, and no sectors of reaction space contain incompatibility reactions.

3. If the assemblages do overlap in reaction space, the univariant reactions include incompatibility reactions, and those reactions bound sectors of reaction space characterized by incompatibilities.

4. As changes in mineral composition narrow the overlap of assemblages in composition space, the sectors of reaction space characterized by incompatibilities also narrow. At the point where mineral compositions become collinear and univariant reactions become degenerate, the part of reaction space characterized by incompatibilities collapses into that one degenerate reaction. Any further compositional changes eliminate the collinearity and the degeneracy (thereby eliminating the last vestiges of reaction space characterized by incompatibilities) and simultaneously change the univariant reactions to compatibilities.

In addition, the nature of any overlap in com-

position space is reflected by the form of incompatibility reactions: minerals of one assemblage enclosed in the polyhedron defined by the minerals of the other assemblage participate in terminal reactions, while those outside the polyhedron are involved in reactions whose form reflects intersections of tie lines or tie surfaces.

These conclusions emerged from consideration of a three-component composite assemblage defining a two-dimensional reaction space, but they are easily extended to include multicomponent assemblages and multidimensional reaction space.

In a reaction space of three dimensions, the zero contour lines of Figs. 4, 5 and 6 become zero contour surfaces in that reaction space. Those surfaces intersect in lines along which two minerals have zero reaction coefficients; those lines correspond to univariant reactions, and within each zero contour surface, they have properties exactly like those of Figs. 4, 5 and 6, dividing each contour surface into sectors characterized by compatibility reactions or incompatibility reactions. These sectors then govern the character of reactions in the volumes between the surfaces just as the univariant lines of Figs. 4, 5 and 6 govern the character of reactions in the intervening sectors. And just as in the examples discussed above, changes in the chemography of composition space produce changes in reaction character as compositional collinearities lead to reaction degeneracies, reflected by the collapse of three-dimensional elements of reaction space into surfaces and lines.

Relations in reaction spaces of more than three dimensions are still more complex. But despite these complexities and the difficulty of visualizing either compositional relations in multicomponent assemblage diagrams or univariant reactions in multidimensional reaction space, the mathematical relations between mineral composition and reaction stoichiometry which give rise to the points summarized above still hold true. Univariant reactions defined by a composite assemblage are lines in reaction space along which the reaction coefficients of one or more minerals equal zero. They bound multi-dimensional sectors of reaction space, and the character of reactions in those sectors ultimately reflects the character of the bounding univariant reactions just as in the simple examples analyzed above. Consequently, even the most complex reaction space can be explored by systematically investigating the form of the univariant reactions defined by a composite mineral assemblage.

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