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TOPOLOGICAL CONSTRUCTION OF NETS IN TERNARY (n + 3)-PHASE MULTISYSTEMS, WITH APPLICATION TO Al_2O_3–SiO_2–H_2O and MgO–SiO_2–H_2O

WEIJI CHENG[1] AND HUGH J. GREENWOOD
Department of Geological Sciences, University of British Columbia, Vancouver, British Columbia V6T 2B4

ABSTRACT

A method is presented for the construction of ternary $(n+3)$-phase nets of invariant points and univariant lines. It is based on the exact correspondence between the sequence of univariant lines around an invariant point and the chemography of the system. A rule is presented for the unambiguous labeling of bundles so as to correspond to the chemography. Application of the rule to the sixteen non-degenerate chemographies of a ternary 6-phase multisystem results in the deduction of 35 distinct nets. Compositional degeneracies are shown to be special cases of nondegenerate solutions and can be derived directly from them. The procedure is applied to the systems Al_2O_3–SiO_2–H_2O and MgO–SiO_2–H_2O. The initial net thus derived is tested against slopes calculated for each reaction. Any invariant points of the initial net that are not consistent with the calculated sequence of slopes are successively transposed until a consistent net for the system is obtained. Computed *P–T* diagrams have the same topologies as those deduced for the consistent nets.

Keywords: multisystem, Schreinemakers, invariant point, chemographic analysis, topology.

SOMMAIRE

Nous présentons ici une méthode pour construire des réseaux ternaires de points invariants à $(n+3)$ phases et de lignes univariantes qui les lient. Elle est fondée sur la correspondance exacte entre la séquence de telles lignes autour d'un point invariant et la chimiographie du système. Nous présentons une règle pour identifier de façon non ambiguë les faisceaux de lignes pour correspondre à la chimiographie. L'application de cette règle à seize exemples de chimiographie non dégénérée dans un système ternaire à six phases mène à 35 réseaux distincts. Les dégénérescences compositionnelles seraient des cas spéciaux de solutions non dégénérées, et nous pouvons les dériver de celles-ci. Les systèmes Al_2O_3–SiO_2–H_2O et MgO–SiO_2–H_2O servent d'illustrations. Le réseau initial ainsi dérivé est vérifié à la lumière des pentes calculées pour chaque réaction. Tout point invariant du réseau initial qui n'est pas compatible à la séquence calculée est transposé successivement jusqu'à l'obtention d'un réseau cohérent pour le système. Les diagrammes *P–T* calculés possèdent la même topologie que celle des diagrammes que nous déduisons à partir de ces réseaux cohérents.

(Traduit par la Rédaction)

Mots-clés: multisystème, Schreinemakers, point invariant, analyse chimiographique, topologie.

INTRODUCTION

Univariant reaction curves in systems of petrological interest in *P-T* space may be approximated by straight lines in the neighborhood of invariant points. In consequence, straight-line nets are topological analogs of real petrological phase diagrams. The possibility that some invariant points may occur twice does not invalidate methods using the straight-line assumption, but it introduces the possibility that the *P–T* net may contain "mirror planes" across which whole topologies of invariant points are "reflected".

Straight-line nets have been utilized previously in studies by Kujawa *et al.* (1965), Day (1972, 1976), Usdansky *et al.* (1978), Mohr (1978), Mohr & Stout (1980), Usdansky & Stout (1981), Cheng (1983, 1986), and recently by Cheng & Guo (1989), O'Hanley (1987) and Usdansky (1981, 1987). Chemographic analysis of closed nets has been well treated by Zen (1966, 1967), Zen & Roseboom (1972), Roseboom & Zen (1982), Guo (1980a,b,c, 1981, 1984), and Guo & Cai (1982).

Day (1972) presented a method of chemographic analysis through which can be established the complete set of possible nets with maximum closure for a ternary $n+3$ multisystem. Mohr & Stout (1980) and Stout (1985) extended this method, generating all topologically possible potential nets in a system of $n+3$ phases given only the phase chemography.

Cheng (1983) presented the results of an alternate chemographic approach to the same problem. In that paper, it is shown that every "invariant map" (Mohr & Stout 1980) consistent with Schreinemakers bundles can be labeled uniquely to illustrate the correspondence between chemographic diagrams and the bundles. The method of labeling leads to the same information deduced by Mohr & Stout (1980) and Stout (1985) in a rapid and direct way.

The purpose of this paper is to extend and apply the labeling method developed by Cheng (1983) to ternary $n+3$ phase systems in order to construct the nets with maximum closure as initial potential solutions. These can then be used to generate all potential solutions.

[1]Current address: Department of Geosciences, University of Arizona, Tucson, Arizona 85721, U.S.A.

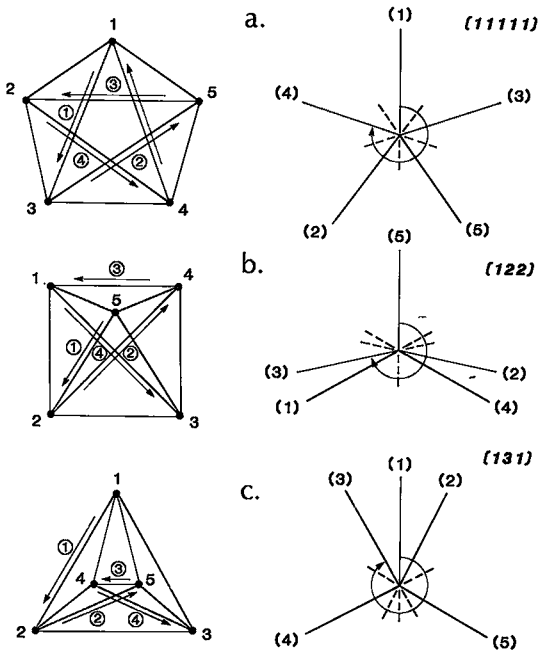


FIG. 1. Correspondence relationships between the positions of the phases on the chemographic diagram and the sequence of univariant lines of the Schreinemakers bundle. The anticlockwise sequence of arrows corresponds to the clockwise sequence of univariant lines.

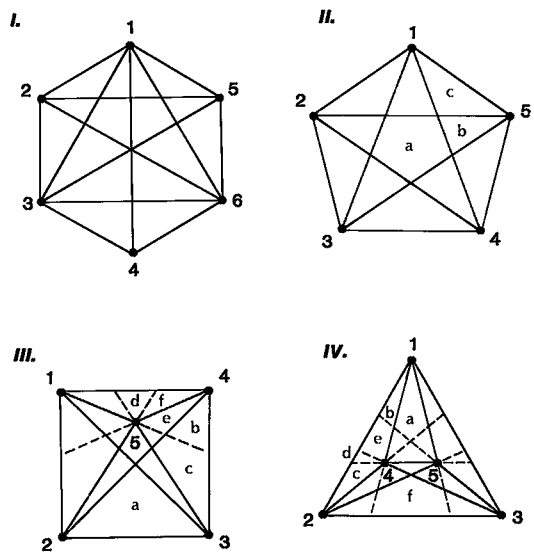


FIG. 2. The sixteen nondegenerate chemographies of six phases in a ternary system. The alphabetic characters represent the possible positions of the sixth phase.

CHEMOGRAPHIES AND SCHREINEMAKERS ANALYSIS

Ternary (n+2)-phase systems

There are three nondegenerate chemographies of five phases in the ternary system A–B–C (Figs. 1a, 1b, 1c), and there are three univariant configurations, one corresponding to each chemography (Figs. 1a, 1b, 1c). These configurations may be constructed by hand following the procedures summarized by Zen (1966). It should be noted that the symbols of all univariant lines on each configuration correspond uniquely to the symbols on its chemographic diagram. Conventions relating to the geometry of chemographic and *P–T* diagrams are given in the following paragraph.

The following symbol conventions have been used: 1) (a) refers to a univariant line with phase 'a' absent from the reaction. 2) [a] refers to an invariant point with phase 'a' absent; "a" (without quotes) refers to phase "a" itself. 3) The statement "a is colinear with b and c" refers to colinearity in the chemographic diagram. 4) The statement "[a] is colinear with [b] and [c] " refers to colinearity of three invariant points in a *P–T* net. 5) The bracket [1,3,1] refers to the Schreinemakers pencil corresponding to the arrangement of lines at an invariant point. 6) The symbol (( )) identifies an entire net. For example, ((6)) is a *P–T* net in which phase 6 is stable everywhere and invariant point [6] is metastable.

The rule for labeling chemographic diagrams and their corresponding invariant maps can be understood with reference to Figure 1. The first step is to insert a line of mirror symmetry into the chemographic diagram. In Figure 1a, there are five such lines of symmetry, whereas Figures 1b and 1c each have only one, passing through phase 5 in Figure 1b, and through phase 1 in Figure 1c. Second, begin labeling the chemographic diagram with the phase on the mirror plane and list the phases sequentially while proceeding in an anticlockwise sense through the chemographic diagram. The sequence of listed phases will correspond to the sequence of univariant curves around the invariant point in a *clockwise* sense. The first phase in the list will be the index of the univariant line that forms a plane of symmetry in the *P–T* diagram, or univariant-invariant map. In the chemography of Figure 1a, where no phase is internal to the array, the Schreinemakers pencil notation is [1,1,1,1,1], signifying that every sector of the invariant point diagram has exactly one metastable extension. In the chemography of Figure 1b, where one phase (5) is internal to the others, there must be sectors that have two metastable extensions, and symmetry requires that the notation must be [1,2,2]. Similarly, in Figure 1c, with two phases internal to the chemography, there must be a sector with three metastable extensions, leading to the notation [1,3,1].

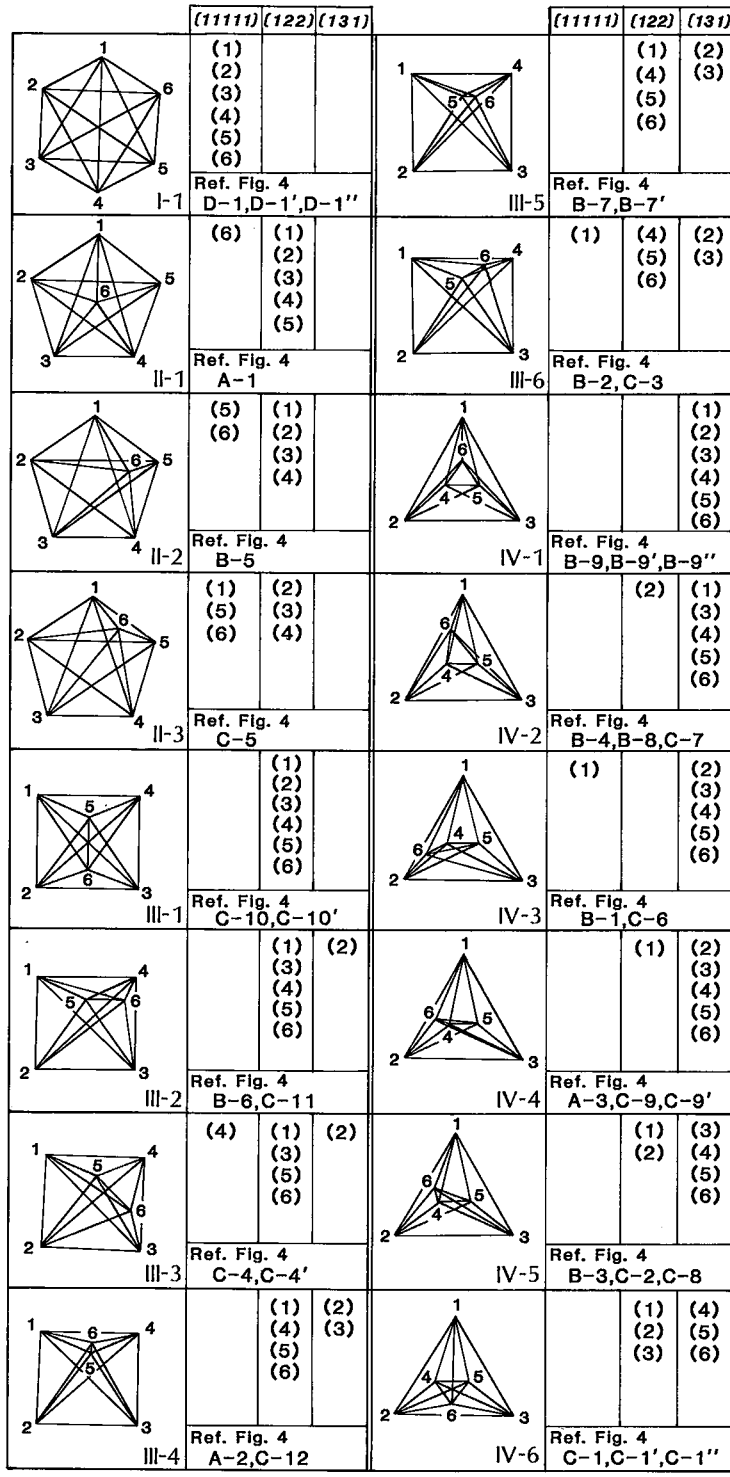
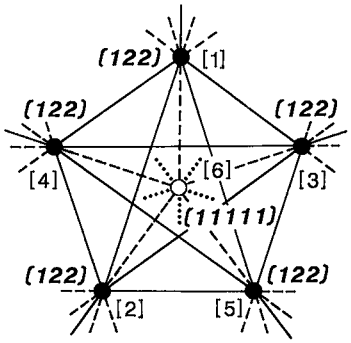
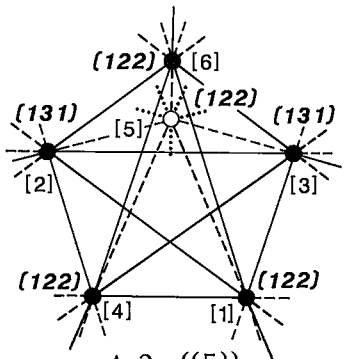


FIG. 3. The sixteen nondegenerate chemographies of six phases in a ternary system, expanded from Figure 2. Also shown are the Schreinemakers pencils of each invariant point on the corresponding nets of Figure 4.



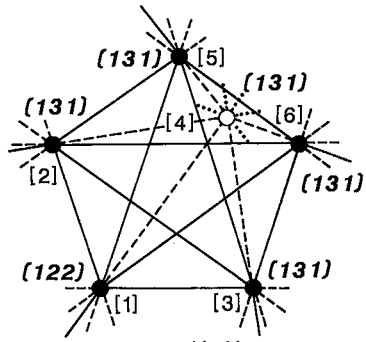
A-1 ((6))

Ref. Fig. 3, II-1



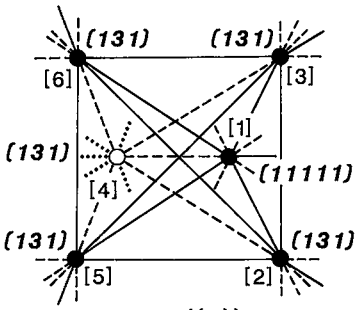
A-2 ((5))

Ref. Fig. 3, III-4



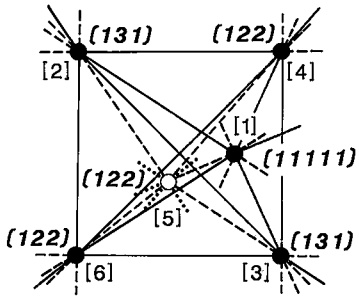
A-3 ((4))

Ref. Fig. 3, IV-2



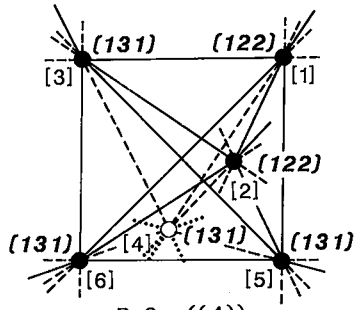
B-1 ((4))

Ref. Fig. 3, IV-3



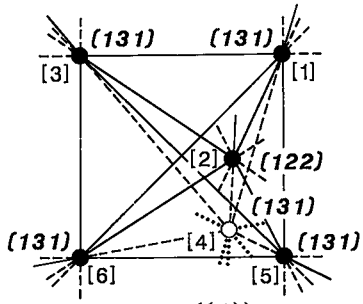
B-2 ((5))

Ref. Fig. 3, III-6



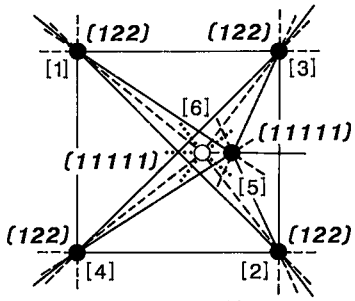
B-3 ((4))

Ref. Fig. 3, IV-5



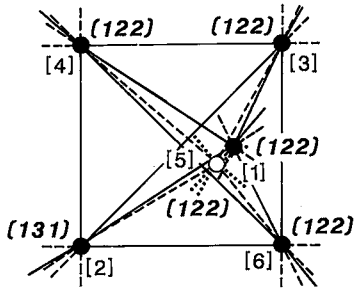
B-4 ((4))

Ref. Fig. 3, IV-2



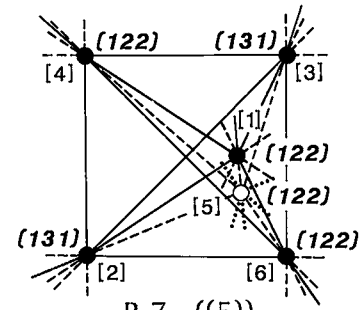
B-5 ((1))

Ref. Fig. 3, II-2



B-6 ((5))

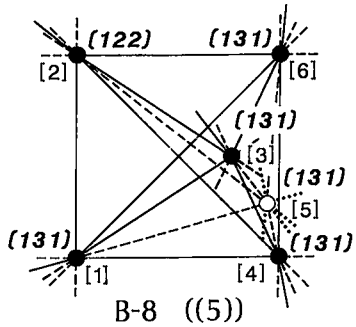
Ref. Fig. 3, III-2



B-7 ((5))

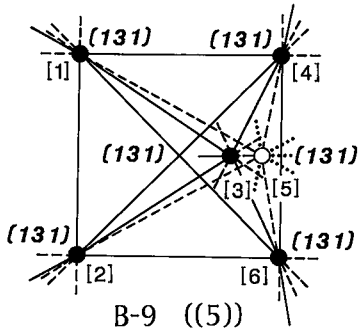
{B-7′ ((6))}

Ref. Fig. 3, III-5



B-8 ((5))

Ref. Fig. 3, IV-2



B-9 ((5))

{B-9′ ((6))
B-9″ ((4))}

Ref. Fig. 3, IV-1

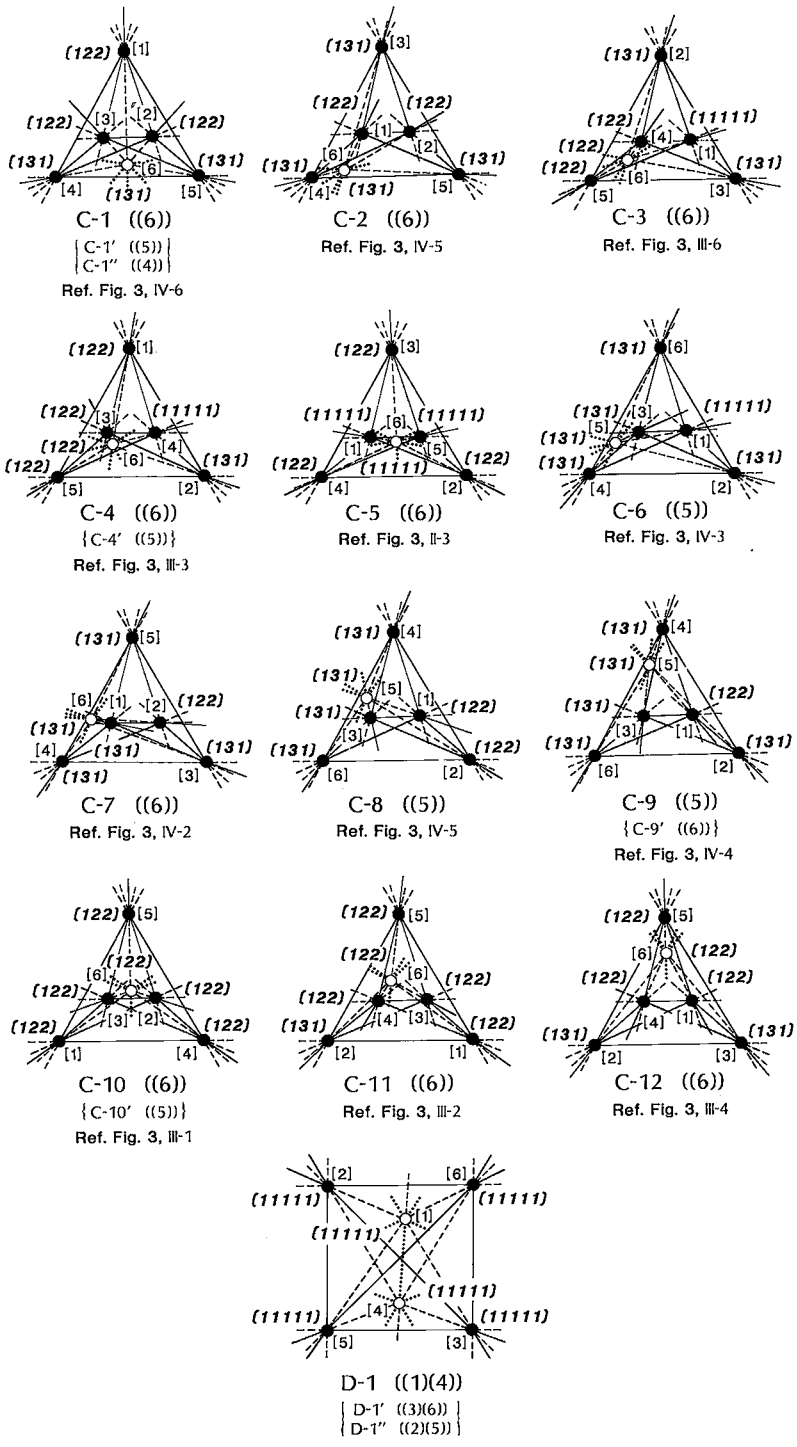


FIG. 4. The thirty-two possible 5-point nets and three 4-point nets corresponding to all nondegenerate chemographies in a ternary $n+3$ multisystem. The Schreinemakers symbols are used for all invariant points, their pencils, and nets. The diagram of the corresponding chemography is shown as a reference to Figure 3; *e.g.*, net ((6)) is shown in Figure 4, C-12, and referred to the chemography in Figure 3, III-4.

For the chemography in which five phases form a pentagon (Fig. 1a), one may compare the sequence of univariant lines of the Schreinemakers bundle with the positions of the phases in the chemography. Thus, if the sequence of symbols of the univariant lines is (1)–(3)–(5)–(2)–(4) clockwise (Fig. 1a), the corresponding sequence of symbols on the chemography must be as shown by clockwise arrows 1–3–5–2–4 (Fig. 1a), and the Schreinemakers pencil notation (Zen 1966) is [1,1,1,1,1].

For the chemography in which four phases form a bounding quadrilateral (Fig. 1b), the construction is most clearly seen by starting with the univariant line that lies in a Schreinemakers pencil having only one metastable univariant line. The clockwise sequence of symbols of the univariant lines is (5)–(2)–(4)–(1)–(3) (Fig. 1b), the corresponding sequence of phases on the chemography follows the arrows in sequence 5–2–4–1–3, and the Schreinemakers pencil notation is [1,2,2].

Likewise, for the chemography in which three phases form a bounding triangle (Fig. 1c), the clockwise sequence of symbols of univariant lines is (1)–(2)–(5)–(4)–(3), the corresponding sequence of phases on the chemographic diagram is as shown by the arrows in Figure 1c, 1–2–5–4–3, and the Schreinemakers pencil notation is [1,3,1].

Application of the rule permits easy construction of the Schreinemakers bundles characteristic of each chemography. For example, the chemography of Figure 1b requires that the Schreinemakers bundle and its symbols be as shown in Figure 1b or its mirror image.

Ternary (n + 3)-phase multisystems

Figures 2 and 3 summarize all of the sixteen nondegenerate chemographies of six phases in a ternary system, as derived by Day (1972) and by Zen & Roseboom(1972). The sixteen nondegenerate chemographies may be divided into four sets: six phases forming a hexagon, which constitutes only one case (Fig. 2-I); five phases forming a pentagon with one phase inside, the possible positions of which are given by the letters *a*, *b*, *c*, forming three possible cases (Fig. 2-II); four phases forming a quadrilateral with two phases inside, which has six possible cases (Fig. 2-III, where letters *a* through *f* show the possible placements of the sixth phase); and three phases forming a triangle with three other phases inside, which has six possible cases (Fig. 2-IV).

If the six phases are numbered as shown, one may obtain the Schreinemakers pencil of each invariant point for the various configurations of the phase diagram. For example, for the chemography I (Fig. 2), the Schreinemakers pencil of the invariant point [1] must be [1,1,1,1,1], because the remaining phases without considering the absent phase 1 form a pentagon (Fig. 1a). Likewise, the respective Schreinemakers pencils of [2], [3], [4], [5] and [6] are also [1,1,1,1,1]. As another example, consider the chemography illustrated in Figure 2-III (position *c*, Fig. 2-III, and case III-3 in Fig. 3). The Schreinemakers pencil of the invariant point [1] must be [1,2,2], because the chemography of phases 2,3,4 and 5 in the absence of phase 1 forms a quadrilateral with phase 6 inside, which corresponds to the chemography of Figure 1b. Similarly, the Schreinemakers pencil of invariant point [2] is [1,3,1], corresponding to Figure 1c, with phases 5 and 6 inside. Thus, four of the five possible positions of phase 6 (a, b, c, d, e, of Fig. 2-III) lead to a pencil notation of [1,2,2], whereas position 'f' (Fig. 2-III) leads to a notation of [1,1,1,1,1]. Refer to Figure 3, case III-6.

In like manner, every chemography in Figure 3 can be used with Figure 2, to derive the Schreinemakers pencils that apply. These are given in Figure 3 beside each of the sixteen chemographies. For example, case III-4 of Figure 3 yields the following set: [1],[1,2,2]; [2],[1,3,1]; [3],[1,3,1]; [4],[1,2,2]; [5],[1,2,2]; [6],[1,2,2]. That is, two of [1,3,1] and four of [1,2,2].

In the next section, we show that there are thirty-two possible 5-point nets, each of which may be associated with its underlying chemography. Thus if one derives the set of Schreinemakers pencils for a given chemography (or finds it in Fig. 3), one knows that there is a unique net that corresponds. Figure 4 shows all possible nets, so that it is only necessary to find the one net among the possible nets that has the same set of Schreinemakers pencils.

Construction of Nets with Maximum Closure

If all univariant curves are required to be straight lines, *P–T* nets with six stable invariant points are not geometrically possible. Thus at least one point must be metastable. The "maximum closure net" (Day 1972) may thus be defined as a five-point net in which one invariant point is metastable. If some univariant lines are curved so as to intersect another curve twice, it may be possible to have a *P–T* net with six stable invariant points, a special case of which can be taken as a net with a repeated invariant point. There follows a derivation of all possible nondegenerate configurations of five-point nets for ternary systems of six phases in which one invariant point is metastable.

There are three possible geometric configurations of five stable invariant points: five stable points form a pentagon; four stable points form a quadrilateral with one inside; three stable points form a triangle with two inside. By connecting all invariant points, one can easily show that the single metastable invariant point cannot lie outside of the polygons described above because at least one of the invari-

ant points will then violate the Rule of Schreinemakers. Thus we consider only the cases where the single metastable point is inside the polygon of invariant points described above.

For the case where five stable invariant points form a pentagon with one metastable point inside, there are three possible nets (Fig. 4, A-1, A-2, A-3), corresponding to the three topologically distinct ways of placing the metastable invariant point in a general position inside the polygon. Consider the configuration A-1 as an example. In this configuration only one invariant point has the Schreinemakers pencil [1,1,1,1,1], and five points have the Schreinemakers pencil [1,2,2]. This may be compared with the chemography II-1 (Fig. 3), which corresponds to a topological net where the point (6) is [1,1,1,1,1] and the five points (1), (2), (3), (4) and (5) are [1,2,2]. Thus the configuration A-1 must correspond to the chemography II-1. Because the Schreinemakers pencil of the metastable point is [1,1,1,1,1], the symbol of the metastable point must be [6]. Thus it is possible to label directly all six points on the configuration and ensure that the Schreinemakers symbols around the invariant point are correct. It should be noted that the phase abbreviation [6] (phase 6 absent), serving as the symbol of the metastable invariant point, must be inside the pentagon on the chemography II-1.

Likewise, the Schreinemakers pencils of each invariant point on nets A-2 and A-3 correspond to the chemographies III-4 and IV-4, respectively. In net A-2, points [6] and [5] both have pencils [1,2,2],

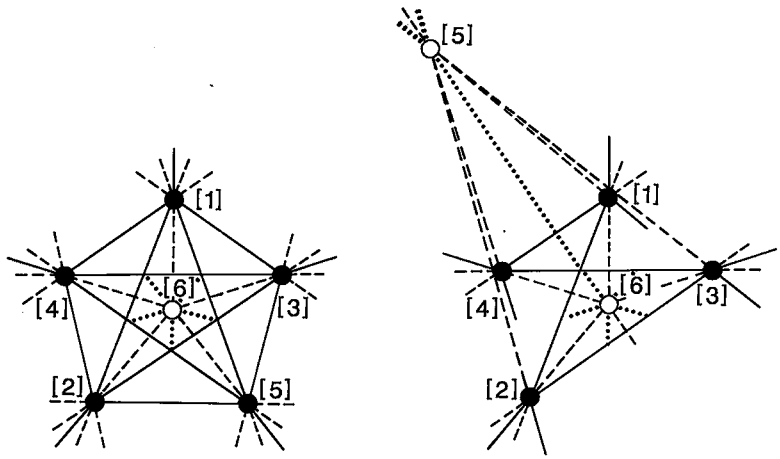


FIG. 5. Illustration of the transposition of an external invariant point [5].

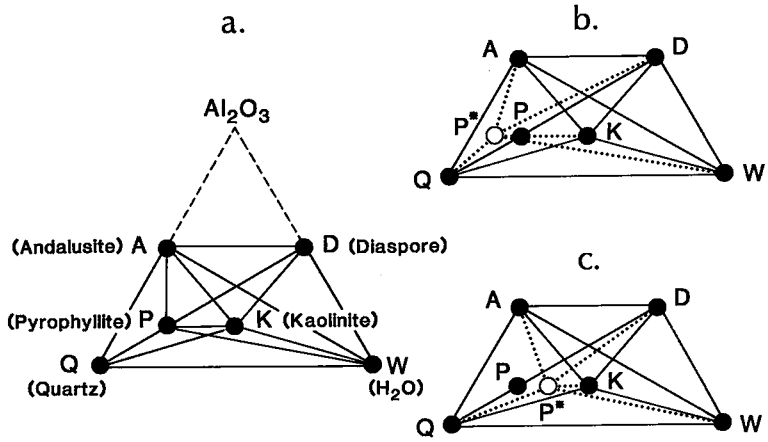


FIG. 6. (a) Chemography of six phases in the system Al_2O_3 – SiO_2 – H_2O. (b) Deformation of the degenerate chemography to a nondegenerate form (P moves to the left). (c) Deformation of the degenerate chemography to a nondegenerate form (P moves to the right).

but the metastable point is required to be inside the polygon, identifying [5] as the metastable invariant point. If the chemography is labeled as in Figure 3, III-4, then the invariant-point map must be labeled as in Figure 4, A-2. Similarly, chemography IV-4 corresponds to the net A-3 if both the net and the chemography are labeled as shown. In Figure 3, the sets of Schreinemakers pencils are unique for each chemography except chemographies III-4 and III-5. These both give [2] and [3] = [1,3,1] and [1], [4], [5] and [6] = [1,2,2]. These two chemographies have different nets in spite of having the same Schreinemakers pencils.

For the case where four stable invariant points form a quadrilateral, with one stable point and one metastable point inside, there are nine possible configurations (Fig. 4, B-1 through B-9). Following the same steps as above, each net is matched with the proper chemography (Fig. 3) according to the set of Schreinemakers pencils. In chemography III-5, there is parity between phases 5 and 6 in the sense that [6] may be made metastable by permutation of the labels. Thus for the corresponding net B-7, through the permutation of symbols in symmetrical positions, that is $1=4$, $2=3$, $5=6$, we can obtain another net {B-7′ ((6))}, where the metastable point is [6]. For the same reasons, through the permutation of chemographic points in chemographies III-1 and III-3, we may obtain two other nets C-10′ and C-4′ where the metastable point is [5]. Thus there are a total of twelve nets derived from this case.

For the case in which three stable invariant points form a triangle, with two stable points and one metastable point inside, there are twelve possible configurations (Fig. 4, C-1 through C-12, and Fig. 3). Because of the parity of chemographies IV-1, IV-4, and IV-6, the symbols on the net B-9, C-9 and C-1 may be symmetrically permuted. In total this leads to seventeen nets.

Therefore, there are altogether thirty-two possible five-point nets in ternary $(n+3)$-phase multisystems. These correspond to all nondegenerate chemographies in ternary $(n+3)$-phase multisystems except the chemography I-1, in which the six phases outline a hexagon. In chemography I-1, there is no five-point net, but rather one four-point net D-1 to

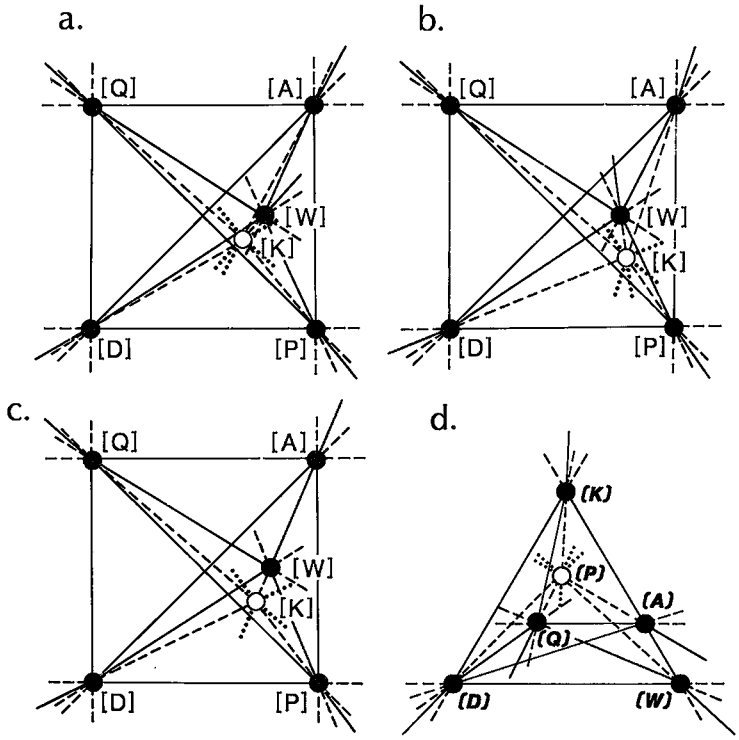


FIG. 7. (a) B-6 type of net corresponding to the deformation chemography in Figure 6b. (b) B-7 type of net corresponding to the deformation chemography in Figure 6c. (c) First potential solution to the degenerate chemography of Figure 6a after moving [W] into colinearity with [K] and [A]. (d) Initial possible net corresponding to the degenerate chemography of Figure 2a after moving [K] into colinearity with [A] and [W].

correspond to its chemography. On the net D-1, there are two metastable points. Considering the parity of the phases in chemography I-1, we can perform symmetrical permutations on net D-1, that is [1]=[3], [4]=[6], to form net D-1′ or [1]=[2], [4]=[5] to form net D-1″. So there are three nets; ((1)(4)), ((3)(6)), and ((2)(5)). These are the Schreinemakers symbols for the nets. For example, D-1 is a net ((1)(4)) where phases 1 and 4 are stable everywhere and invariant points [1] and [4] are metastable.

Transposition of Points and Permutation of Nets

Mohr & Stout (1980), in studying $(n+3)$-phase multisystems, introduced an operation they called transposition and demonstrated how it could be used to derive all nets for a multisystem from one complete net. Transposition, which can be performed only on an external invariant point, is simply illustrated in Figure 5. The external invariant point [5]

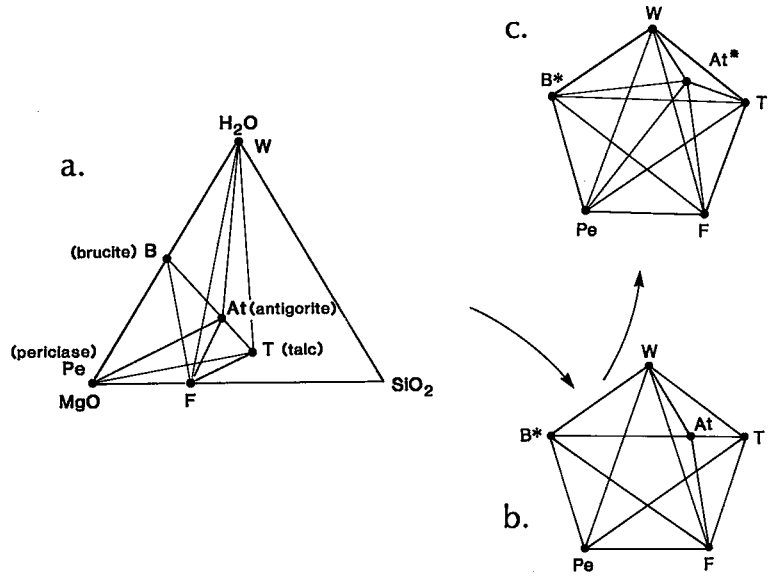


FIG. 8. Chemography of six phases in the system MgO–SiO_2–H_2O. "Deformation" of the degenerate chemography (a) to a supposed nondegenerate form (c) *via* (b). B and At are moved to B* and At*, respectively.

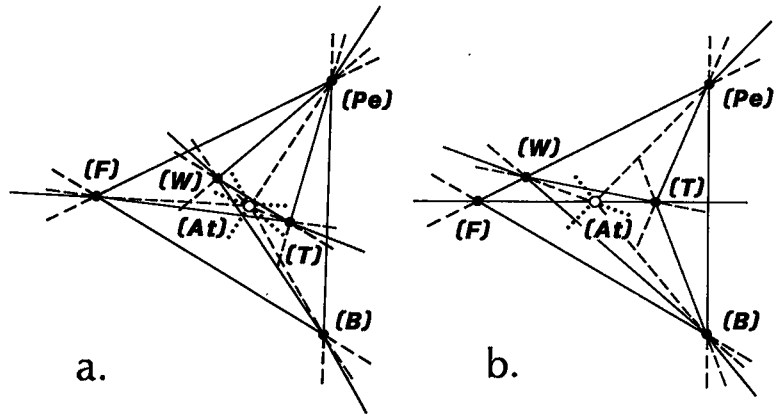


FIG. 9. (a) The initial possible net corresponding to the "deformed" chemography in Figure 4c. (b) The initial possible net corresponding to the degenerate chemography of Figure 4a after moving [W] into colinearity with points [P] and [F], and moving [At] into colinearity with points [F] and [T].

is first "stretched" away from the net until all reactions leading to it are parallel, then replaced on the opposite side of the net with its mirror image, with reversed stabilities. In a nondegenerate chemography, the general formulation of Mohr & Stout (1980) predicts $(n+2)(n+3)+2=32$ potential solutions. Some chemographies are consistent with more than one 5-point net. These can be deduced by permutations using the operation of transposition. Thus any net may be chosen as an initial potential solution. Cases of compositional degeneracy may be treated readily by means of deformation of the nets for nondegenerate cases.

Next we consider as an example of application a real system that was studied by Stout (1985): the ternary multisystem Al_2O_3–SiO_2–H_2O, which includes the six phases kaolinite, pyrophyllite, diaspore, andalusite, quartz, H_2O. Figure 6a illustrates the chemography of this system of six phases in terms of mole fractions of the components Al_2O_3, SiO_2 and H_2O. Alternative choices of components and units will change the specific positions of phases as represented in Figure 6, but the topological arrangement will remain the same. This particular chemography involves a compositional degeneracy, namely a colinearity of quartz (Q), pyrophyllite (P), and diaspore (D), which is internal to the quadrilateral defined by the phases andalusite (A), diaspore (D), quartz (Q), and H_2O (W).

To derive the degenerate net, suppose that the phase P moves to the left (Fig. 6b) or the right (Fig. 6c), producing either the chemography III-2 or III-5 (Fig. 3), respectively. Referring to Figure 4, we may see that the corresponding nets are B-6 or C-11 and B-7 or B-7′. From the chemography of the system under study, we know that on the corresponding net the invariant points [A], [K], and [W] should be colinear, which must therefore be the line representing reaction Q + D = P. Thus to derive the degenerate net from nets B-6 and B-7 (Fig. 4), it is necessary only to move point [W] up to the line [K]-[A], making [W], [K] and [A] colinear (Fig. 7c). The Schreinemakers bundles of the three other points [Q], [P] and [D] remain the same. It is clear the resultant net is the same. To derive a new net from net C-11, move [W] up to the line [K]-[A]. This configuration is shown in Figure 7d.

Finally we consider as another example the chemography for the system involving the components MgO, SiO_2 and H_2O and the phases Antigorite (At), Brucite (B), Forsterite (F), Periclase (Pe), Talc (T) and Water (W), as shown in Figure 8a. This system shows two compositional degeneracies: an internal colinearity of B, At and T, and an external colinearity of W,B, and Pe.

As with the previous example, the corresponding initial potential net is obtained by a virtual "deformation" of the chemography. We make the degenerate chemography (Fig. 8a) nondegenerate by moving points At and B from the straight lines connecting B, At, T and W,B,P, respectively (Figs. 8b, c). The corresponding initial net is obtained from chemography II-2 (Fig. 3), giving a net with the topology C-5 (Fig. 4), illustrated in Figure 9a. Finally, in Figure 9b invariant point [W] is made colinear with points [P] and [F], and invariant point [At] colinear with points [F] and [T], without changing the rest of the invariant map.

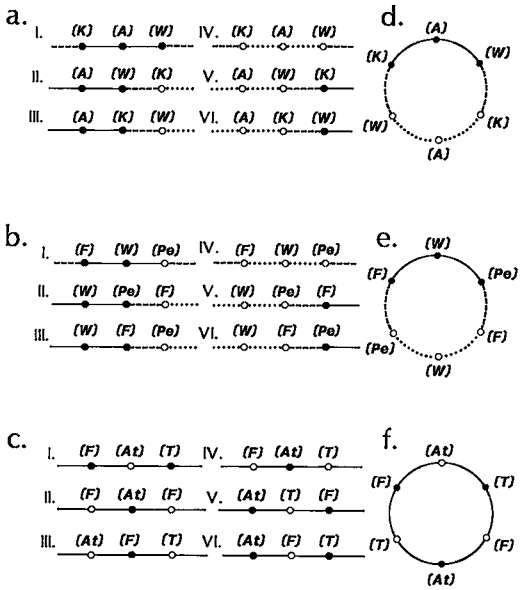


FIG. 10. Sequences of invariant points along degenerate reactions. (a) The reaction (A,K,W) in the system Al_2O_3–SiO_2–H_2O. (b) The reaction (Pe,W,F) in the system MgO–SiO_2–H_2O. (c) The reaction (F,At,T) in the system MgO–SiO_2–H_2O. Note that sequences IV, V and VI in (a), (b) and (c) are trivial conjugates (see text) of sequences I, II and III, respectively. (d), (e) and (f) are the closed loops of the degenerate reactions (A,K,W), (Pe,W,F) and (F,At,T). Note that each invariant point occurs twice, once stably and once metastably. Solid lines stable, dashed lines metastable, dotted lines doubly metastable. See text for further discussion.

SEQUENCES OF INVARIANT POINTS ALONG DEGENERATE REACTIONS

Stout (1985) gave a graphical proof that there are exactly six permissible sequences of stable and metastable invariant points along the degenerate reaction (A,K,W) in the system Al_2O_3–SiO_2–H_2O (Fig. 10a). The proof is based on projecting 3-dimensional composition – free energy relationships on a two-dimensional composition – free energy diagram to help with the recognition of the differ-

ent possible levels of stability that can be represented by the net.

Similarly, in the system $MgO–SiO_2–H_2O$, the only permissible sequences of invariant points along the degenerate reaction (Pe,W,F) are shown in Figure 10b. The degenerate reaction (F,At,T) is, however, somewhat different, having only one level of stability (Fig. 10c). This behavior is a consequence of the fact that the degeneracy of three phases, Pe, B, W, is chemographically external to the rest of the chemographic diagram (Fig. 8a); thus there are no chemically equivalent assemblages that could be more stable. The phases B, Pe, and W comprise a chemographic set that is disjoint from the set of other phases. In this case, there is no way to make any sector of the reaction (T,At,F) metastable, regardless of the sequence of invariant points along the line.

In Figures 10a, b, c, the right three lines, that is IV, V and VI, are "trivial conjugates" of the left three. In a closed net, each univariant reaction forms a closed loop, and each invariant point occurs twice, once stably and once metastably (Figs. 10d, e, f). Thus a partly closed net consisting of one set of invariant points has a trivial conjugate, which may be called its "residual net". Similarly, the two parts of a reaction loop are trivial conjugates of each other. The six permissible sequences for each case may easily be found in the three possible closed loops (Figs. 10d, e, f).

There is an exact correspondence between the sequence of three invariant points along a degenerate reaction and the relative positions of the three "absent" phases on a chemographic diagram (Day 1972). This fact is useful for construction of univariant reaction lines of degenerate systems. For example, in Figure 8a, the three phases B, At and T are chemographically colinear, and are internal to the diagram, whereas one phase, W, and two phases Pe, F, lie on opposite sides of the colinearity, respectively. Thus in Figure 10b, the point [W] on the line I (phase W absent) must be in the middle between [F] and [Pe]. Choosing successive stability levels of point [F] and [Pe] yields successively lines II and III (Fig. 10b). As for the chemographically external colinearity Pe, B, W in Figure 8a, the reaction line is stable along its entire length, but the stability level of invariant points changes by one level through each segment of the reaction line.

Consistent Nets for the System Al_2O_3 – SiO_2 – H_2O ADKPQW

In order to obtain the consistent nets for this system following the method of Stout (1985), a complete set of 28 potential solutions must first be generated from an initial solution by successive transpositions of invariant points. Some of the solutions may then be eliminated using orientation criteria. The method described below shows that it is possible to proceed directly from an initial solution to the consistent nets using slope criteria.

As an example, we choose an initial solution different from that of Stout (1985), *e.g.*, the net in Figure 7d. We can test at once whether it is a consistent solution by comparing the relative slopes of the univariant lines. This test is valid independently of whether we have chosen a left-handed, right-handed or mirror image because of the linear dependencies among the reaction slopes at any invariant point, stable or metastable. The reaction slopes are calculated from available thermodynamic data.

For all 13 reactions in the ADKPQW system, Table 1 shows values of dP/dT calculated from the internally consistent data-base of Berman (1988) under three different sets of physical conditions. These are not the values of dP/dT at points where the curves are stable, but merely the relative values of $\Delta S/\Delta V$ under the chosen conditions, but they serve to rank the slopes relative to one another. Table 2 shows the resulting sequences of slope magnitudes. It is noteworthy that the same sequence of slopes at each invariant point is found regardless of the conditions chosen for the calculation, and regardless of the fact that none of the slopes calculated apply to

TABLE 1. CALCULATED P-T SLOPES IN Al_2O_3-SiO_2-H_2O

Reaction	Symbol	B-1	B-2	B-2
K + 2Q = P + W	(A,D)	295.79	314.3	111.79
D + 4Q = P	(A,K,W)	22.27	30.8	-24.1
K = D + 2Q + W	(A,P)	- 358.4	- 808.8	1610.7
2K = D + P + 2W	(A,Q)	1965.8	1069.	117.4
P = A + 3Q + W	(D,K)	46.32	62.38	55.09
K = A + Q + 2W	(D,P)	64.10	87.15	62.66
3K = 2A + P + 5W	(D,Q)	72.08	98.02	65.34
2P = A + K + 5Q	(D,W)	25.57	32.49	41.86
D + Q = A + W	(K,P)	43.52	58.79	47.64
P + 3D = 4A + 4W	(K,Q)	44.16	59.59	49.4
D + K = 2A + 3W	(P,Q)	53.55	72.73	55.70
2D + 3Q = A + K	(P,W)	24.85	32.13	27.20
5D + 3P = 4A + 4K	(Q,W)	25.08	32.24	31.86

Slopes calculated using data from Berman (1988)
B-1: Bars/deg. Calculated at 298 K, 1 bar
B-2: Bars/deg. Calculated at 873 K, 10,000 bars
B-3: Bars/deg. Calculated at 1173 K, 15,000 bars.

TABLE 2. SLOPE SEQUENCES IN Al_2O_3-SiO_2-H_2O

Point	Slope Sequence						Compare Fig. 3d
[D]	(D,W)	> (DK)	> (D,P)	> (D,Q)	> (D,A)		Opposite
[Q]	(Q,A)	> (Q,D)	> (Q,P)	> (Q,K)	> (Q,W)		Opposite
[P]	(P,D)	> (P,Q)	> (P,K)	> (P,W)	> (P,A)		Opposite
[W]	(A,K,W)	> (W,D)	> (W,Q)	> (W,D)			Same
[K]	(K,D)	> (K,Q)	> (K,P)	> (A,K,W)			Opposite
[A]	(A,Q)	> (A,D)	> (A,K,W)	> (A,P)			Opposite

SUMMARY: [A]', [Q]', [W], [D]', [P]', [K]'

The prime ' indicates a sequence displaying the opposite handedness to the corresponding point in Fig. 3d. Thus if [A] in Fig. 3d is considered to be right-handed, then [A]' is left-handed, and is a mirror image of [A].

All three conditions of calculation (Table 1) 2981.1; 873.10,000; 1173,15000; yield the same conclusions.

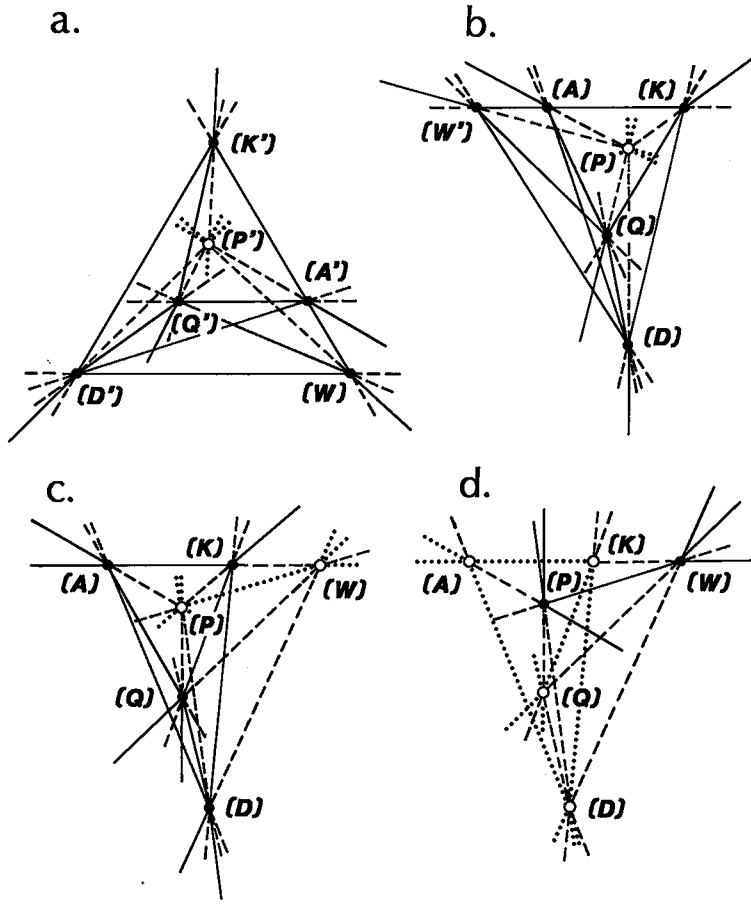


FIG. 11. (a) The initial possible net for the ADKPQW system derived from Figure 3d. Testing against the calculated sequences of slopes (Tables 1, 2) shows that points [K'], [P'], [A'], [Q'] and [D'] are not consistent with the data, because the curves occur in reverse order. (b) The mirror image of the net in Figure 7a. Only [W'] is not consistent with the data. (c) The consistent net for the ADKPQW system after transposition of [W'] from Figure 7b. (d) The mirror image of the trivial conjugate of the net in Figure 7c. Note that it has the same slope sequences as Figure 7c.

conditions of equilibrium. The results of Table 2 may be used to test the internal consistency of the initial solution (Fig. 7d). The right-hand column of Table 2 indicates whether the sequence obtained is the same as, or opposite to, the sequences shown in the assumed initial solution of Figure 7d.

For the sake of convenience, invariant points in an initial solution are defined as being "right-handed" when the clockwise sequence of reaction lines is consistent with calculated sequences of slopes, such as the point [W]. "Left-handed" invariant points have slope sequences that are the reverse of the calculated sequence, such as points [K'], [P'], [A'], [Q'] and [D']. Note that if the curves do not appear in the same order, one must infer that the thermodynamic data used to calculate the slopes are not internally consistent. We denote left-handed points with a prime. Thus, Figure 7d becomes Figure 11a. In order to obtain a consistent net, it is necessary that all left-handed points in Figure 11a be transposed to their right-handed forms.

In Figure 11a there are five left-handed points [*K'*], [P'], [A'], [Q'] and [D'], and only one right-handed point [W']. The mirror image of Figure 11a is shown in Figure 11b, which has five right-handed and one left-handed points. Transposing the point [W'] of Figure 11b yields a new configuration in Figure 11c in which all the sequences of reaction lines around all invariant points are consistent with the calculated sequences of slopes based on the internally consis-

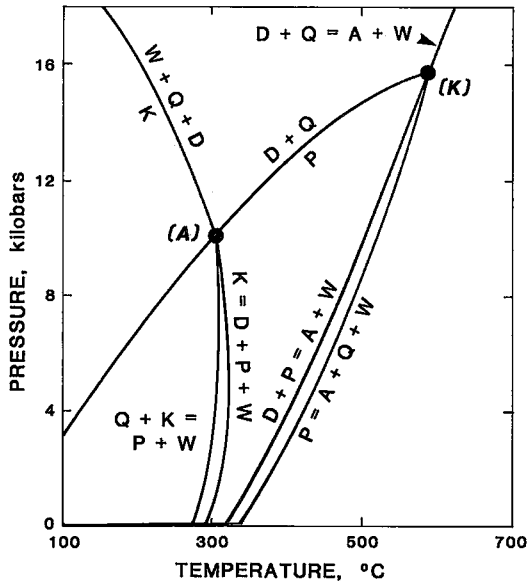


FIG. 12. Stable curves involving kaolinite, water, quartz, diaspore, pyrophyllite, and andalusite. Computed with program GE0CALC (Perkins *et al.* 1986).

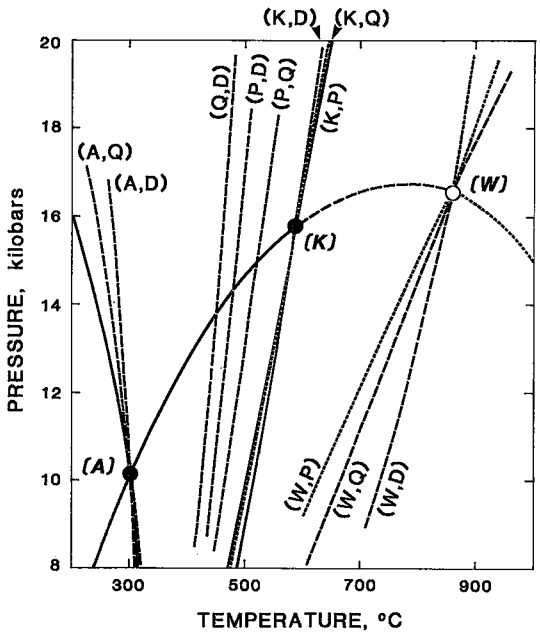


FIG. 13. Metastable and stable curves involving kaolinite, water, quartz, diaspore, pyrophyllite, and andalusite. Computed with program GE0CALC (Perkins *et al.* 1986). Invariant points [A] and [K] are stable, whereas [W] is metastable. Compare with the topology of Figure 11c.

tent data of Berman (1988). Therefore, the configuration in Figure 11c is a consistent net for the ADKPQW system. The mirror image of its trivial conjugate is also a consistent net (Fig. 11d). Thus, using the data of Berman (1988), two consistent nets are obtained by only one transposition step from the initial solution.

It is of some interest to compare the topology of the net deduced in Figure 11c with that calculated from the same fundamental data using the computer program GE0CALC (Perkins *et al.* 1986). Figure 13 shows the stable curves, from which it may be seen that the correspondence with Figure 11c is exact. Figure 12 shows the arrangement of both stable and metastable reactions and the location of the metastable invariant point [W].

If internally consistent data are used to calculate the sequences of slopes, the resulting topology will be correct in every respect. Disagreement between a deduced net and observational or experimental data can be taken as proof of inconsistency in the data.

CONSISTENT NETS IN MgO–SiO_2–H_2O WITH At, B, F, Pe, T AND W

Values of ΔS_r and ΔV_r under different conditions for all the 11 reactions of interest in the system MgO–SiO_2–H_2O among the phases At, B, F, Pe, T and W, taken from the data of Berman (1988), have been used to calculate the reaction slopes shown in Table 3. The magnitude sequences of the slopes are shown Table 4.

TABLE 3. CALCULATED P-T SLOPES IN MgO-SiO_2-H_2O

Reaction	Symbol	B_1	B_2	B_3
31T +135Pe =At +90F	(W,B)	-56.8	-56.8	-56.8
2At = 45B +17T	(W,Pe,F)	-12.3	-12.3	-12.3
T +6Pe =B + 4F	(W,At)	-45.3	-45.3	-45.3
At +51Pe =31B +34F	(W,T)	-28.6	-28.6	-28.6
At =27W +18F +4T	(B,Pe)	134.6	180.4	794.4
T +5Pe =W +4F	(B,At)	1287.5	413.7	-224.3
At +20Pe =31W +34F	(B,T)	157.5	196.6	3886.8
2At =45W +45Pe +17T	(B,F)	106.1	159.0	327.5
B = W + Pe	(At,T,F)	66.9	123.9	120.2
T +5B =6W +4F	(At,Pe)	91.2	143.6	195.1
20B +At = 51W +34F	(T,Pe)	111.0	161.1	329.6

Slopes calculated using data from Berman (1988)

B_1: Slopes calculated at 298 K, 1 bar
B_2: Slopes calculated with solids at 298 K, 1 bar, and gas at 613 K, 3 kbar
B_3: Slopes calculated with solids at 298 K, 1 bar, and with gas at 613 K, 8 kbar

TABLE 4. SLOPE SEQUENCES IN MgO-SiO_2-H_2O

Point	Slope Sequence				Ref.Tab. 3		
[W]	(W,Pe,F)	> (W,T)	> (W,At)	> (W,B)	B_1	B_2	B_3
[B]	(B,At)	> (B,T)	> (B,Pe)	> (B,F) > (B,W)	B_1	B_2	
	(B,T)	> (B,Pe)	> (B,F)	> (B,W) > B,At)			B_3
[At]	(B,At)	> (At,Pe)	> (At,T,F)	> (W,At)	B_1	B_2	
	(At,Pe)	> (At,T,F)	> (W,At)	> (B,At)			B_3
[T]	(B,T)	> (T,Pe)	> (At,T,F)	> (W,T)	B_1	B_2	B_3
[Pe]	(B,Pe)	> (T,Pe)	> (At,Pe)	> (W,Pe,F)	B_1	B_2	B_3
[F]	(B,F)	> (At,T,F)	> (W,Pe,F)		B_1	B_2	B_3

An initial solution for the system (Fig. 9b) is tested against the sequences of relative slopes in Table 4, demonstrating that there is only one left-handed point [F′] (Fig. 14a). Point [F′] can then be transposed to give the consistent net of Figure 14b. The mirror image of its trivial conjugate is also a consistent net. Figure 15 shows the sequence of stable and metastable curves computed with GE0CALC (Perkins *et al.* 1986) using the data of Berman (1988). Comparison of Figures 14 and 15 shows that the agreement is exact.

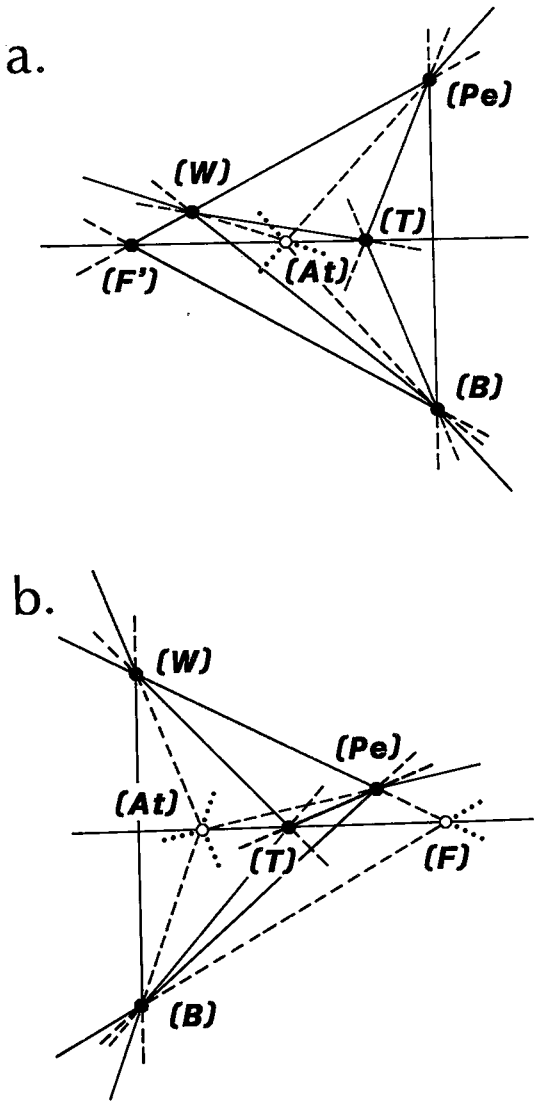


FIG. 14. (a) The initial net for the AtBFPeTW system after testing against the calculated sequences of slopes (Tables 3, 4). Only [F′] in Figure 9a is inconsistent. (b) [F′] from Figure 9a has been transposed to its right-handed form [F] making the entire net consistent with the data (Tables 3, 4).

SUMMARY AND DISCUSSION

An initial potential net for a phase diagram of any kind of ternary $(n+3)$-phase multisystem can be derived efficiently from a systematic labeling of chemographic diagrams and the corresponding univariant reaction lines. Degenerate chemographies are special cases of nondegenerate chemographies and can be derived from them by "deformation" or transposition.

The initial net is tested against the sequences of dP/dT reaction slopes calculated from thermodynamic data. All configurations of invariant points in the initial net that have slope sequences opposite to those calculated are defined as being left-handed forms, and are successively transposed to right-handed forms following the procedures of Mohr & Stout (1980). The right-handed forms are consistent with the calculated sequences of slopes. Thus nets that correspond to various sets of valid thermodynamic data may be derived directly from the initial potential net.

Commonly, a single solution set and the mirror image of its trivial conjugate correspond to a given set of thermodynamic data. These two nets can fur-

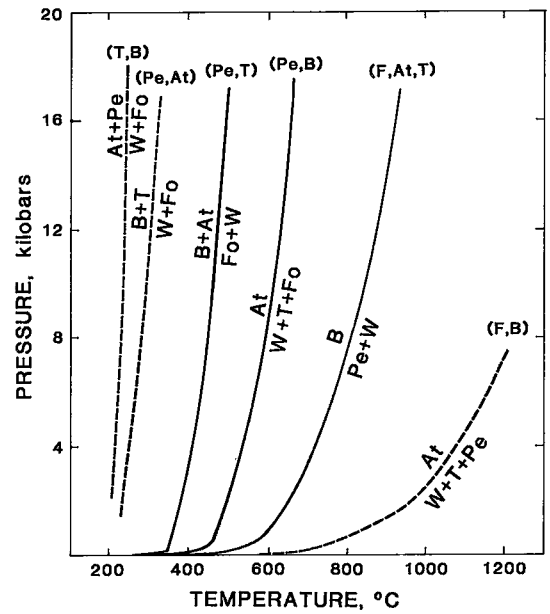


FIG. 15. Metastable and stable curves involving antigorite (At), forsterite (F), periclase (Pe), talc (T), brucite (B), and water (W). Computed with program GE0CALC (Perkins *et al.* 1986). The topology is consistent with Figure 14b.

ther be tested against experimental and observational data. Further, such a consistent net is generated from an initial net by at most three transposition steps and does not require the generation of all potential nets followed by their individual elimination.

The method outlined here makes initial use of any available thermodynamic data and proceeds directly to a consistent solution. The fact that no net can be derived using the data at hand is an indication that the data are mutually inconsistent. If the calculated slopes are too close in relative magnitudes to permit unambiguous assignment of positions of reaction curves, one may have to accept that more than one solution is possible until improved data are available.

Acknowledgements

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