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THE CONSTRUCTION OF PHASE DIAGRAMS BY MEANS OF DUAL NETWORKS

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ABSTRACT

An efficient method is developed to construct potential solutions of phase diagrams, using dual networks, which are graphs composed of divariant fields linked together by univariant lines. The assemblages observed in thin section define the chemography of the system. Once the chemography is established, the invariant points and divariant fields can be constructed, and the divariant fields are then used to construct the dual network. A potential solution for the phase diagram is obtained by inverting the dual network to obtain a basic form, and then adding the metastable equilibria to the basic form. The dual network is shown to be uniquely related to the potential solution when all of the divariant fields are placed in the dual network. Dual networks can be used in two ways. Firstly, a topologically correct potential solution of the phase diagram can be constructed from information contained in the invariant points or divariant fields. Other potential solutions can then be obtained by transposition. Secondly, given a known potential solution or phase diagram for an $(n+3)$-phase system, a new potential solution can be constructed for a system with more than $(n+3)$ phases. The method can be used with any number of components, but is illustrated with examples from two- and three-component systems. A phase diagram is constructed for serpentinites modeled by the 2-component (MgO-SiO_2, projected through H_2O), 7-phase system brucite, forsterite, lizardite, chrysotile, antigorite, enstatite and talc.

Keywords: chemographic analysis, dual networks, potential solutions, serpentinites, phase diagrams.

SOMMAIRE

On a développé une façon efficace de construire des solutions possibles d'un diagramme de phases; il s'agit de la méthode de réticules doubles où, dans un graphique, les champs bivariants sont liés par courbes univariantes. Une fois la chimiographie établie, on peut construire les points invariants et les champs bivariants. Ces derniers servent ensuite à construire le réticule double. On obtient une solution possible du diagramme de phases en invertissant le réticule double pour obtenir la forme fondamentale, et en y ajoutant ensuite les équilibres métastables. On montre que le réticule double est lié à la solution possible de façon unique quand tous les champs bivariants font partie du réticule double. On se sert de réticules doubles 1) pour construire une solution topologiquement correcte d'un diagramme de phases à partir de l'information contenue dans les points invariants ou champs bivariants (les autres solutions possibles en découlent par transposition); 2) pour trouver une nouvelle solution possible pour un système à plus de $n+3$ phases, étant donné une solution possible ou un diagramme de phases pour un système à trois phases. La méthode peut servir pour un nombre quelconque de composants; on présente des exemples choisis de systèmes à deux ou trois composants. On construit un diagramme de phases pour les serpentinites dans le système binaire MgO-SiO_2 (projection à travers H_2O) à sept phases (brucite, forstérite, lizardite, chrysotile, antigorite, enstatite et talc).

(Traduit par la Rédaction)

Mots-clés: analyse chimiographique, réticule double, solution possible, serpentinites, diagramme de phases.

INTRODUCTION

The investigation of the topologic properties of phase diagrams appears to have begun with the work of Schreinemakers (1925) on the relationships of invariant, univariant and divariant equilibria about and between invariant points. The introduction of the representation polyhedron, in which all invariant, univariant and divariant equilibria of a system were visualized as apices, edges and faces of a geometric figure, began the methodical study of the topologic properties of phase diagrams (Zen 1966, 1967). Several workers investigated the role of the representation polyhedron in determining the relationships between various nets, which are internally consistent grids of invariant points and univariant lines (Zen 1966, 1967, Zen & Roseboom 1972, Day 1972). These papers concentrated on n-component $(n+3)$-phase systems. At the same time, Kujawa *et al.* (1965) presented the relationships between the stable equilibria of unary systems with many phases. They showed that the stable equilibria of any unary system had one of a limited number of topologies. More recently, Guo (1980), Roseboom & Zen (1982) and Usdansky (1981) began research on $(n+4)$-phase systems. Roseboom & Zen (1982) used the representation polyhedron to reproduce the results of Kujawa *et al.* and extended the work to binary systems. Guo (1980), using the representation polyhedron, discovered that the phase diagrams of unary 5-phase systems belonged to one of two equivalence classes,

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based on the number of metastable invariant points in the phase diagram. This result was reproduced by Usdansky (1981), who also determined the number of equivalence classes for systems with up to four components. Usdansky worked within the restriction of the combinatorial assumption that each equilibrium appears once and only once in a phase diagram.

Chemographic analysis, formalized by Stout (1985), uses a method, developed by Mohr & Stout (1980), by which all topologically possible potential solutions for a phase diagram of an $(n+3)$-phase system can be constructed given only the phase chemography, which is the relative position of the phases in composition space. This methodology is important because available data are used to eliminate impossible solutions until the correct form of the phase diagram is found. If more than one solution is left after comparison with available data, inspection of the remaining solutions will indicate the data that must be obtained to determine the correct diagram.

To use the methodology of chemographic analysis, as given by Stout (1985), one must construct the first potential solution by connecting invariant points together. For example, there are 6 invariant points among 6 phases in a ternary system. Each invariant point can exist stably or metastably and with either a right- or left-handed parity, for a total of 24 invariant points. (Note that the stability level of an equilibrium refers to the relative Gibbs free energy of that equilibrium with respect to other equilibria of the same type. A stable equilibrium has the lowest free energy, a metastable equilibrium has the next lowest free energy, *etc.*). The 24 invariant points can be subdivided into six sets of four invariant points each. Then, one invariant point from each set must be chosen such that the six invariant points can be assembled in a consistent manner. Choosing a subset of the total number of invariant points to construct the first potential solution does not hinder the investigation of $n+3$ systems if $n \leq 3$, because the total number of invariant points that must be examined is small. For systems with more than $n+3$ phases, the initial potential solution is difficult to construct owing to the large number of invariant points to be assembled.

The purpose of this paper is to present a method by which potential solutions of phase diagrams can be more readily constructed. The method is based on dual networks, which are graphs composed of points representing divariant fields linked together by lines that represent univariant reactions. Dual networks have two uses in this context. First, dual networks can be used to construct a topologically correct potential solution of the phase diagram for an $n+3$ system from information contained in the divariant fields. Two systems will be used to illustrate this application of dual networks. The 2-component 5-phase system described by the components MgO–SiO_2–H_2O, projected through H_2O, with the phases brucite, antigorite, lizardite, chrysotile and talc (5-phase serpentine system) and the 3-component, 6-phase system described by the components Al_2O_3, SiO_2 and H_2O with the phases andalusite, diaspore, kaolinite, pyrophyllite, quartz and H_2O (alumina system). The second use for dual networks is to construct a potential solution for systems with more than $n+3$ phases where a potential solution or the phase diagram for an $(n+3)$-phase system is already known. The serpentine system will be used to illustrate this application. The potential solutions generated for the serpentine system will be discussed in a companion paper (O'Hanley 1987).

CHEMOGRAPHIC ANALYSIS

Chemographic analysis concentrates on invariant and univariant equilibria to construct potential solutions for the phase diagram of the system. Once a chemography is established, the invariant points are constructed by taking $n+2$ phases at a time until all $n+2$ combinations are used. For a nondegenerate $n+3$ system, with $n=3$, 6 combinations of $n+2$ phases are possible. As each invariant point has four forms, 24 invariant points are possible. One invariant point from each of the six subjects must be assembled in a consistent manner to construct the first potential solution. For nondegenerate systems, in which each equilibrium appears once and only once, there are exactly $[(n+2)(n+3)+2]$ constructions of this kind (Mohr & Stout 1980). Once the first potential solution is constructed, all others may be obtained from it by transposition, an operation by which the parity of external invariant points is successively changed until all permissible solutions are generated (Mohr & Stout 1980).

The combinatorial equation gives the number of each type of equilibrium (invariant points, univariant curves and divariant surfaces) in a nondegenerate system in which each equilibrium appears once and only once (Zen 1966).

$$E = P!/P_e!\ (P-P_e)!$$

where E represents the number of equilibria in the system, P is the number of phases in the system, P_e is the number of phases involved in the equilibrium, and (!) represents the factorial operation. Chemographic analysis, as developed by Mohr & Stout (1980) and Stout (1985), is based on the assumption that each equilibrium occurs exactly once.

Table 1 shows how the number of invariant points, divariant assemblages and divariant fields varies with n and P. The total number of possible forms of invariant points is also shown. Where P is greater

TABLE 1. UNIQUE EQUILIBRIA IN N-COMPONENT, P-PHASE SYSTEMS

n	P	E for P_e= n+2 Invariant points	2P(m-1)*	E for P_e= n Divariant assemblages	Number of unique divariant fields
1	3	1	2	3	3
	4	4	16	4	4
	5	10	60	5	5
2	4	1	2	6	4
	5	5	20	10	8
	6	15	90	15	16
	7	35	280	21	32
3	5	1	2	10	5
	6	6	24	20	14
	7	21	126	35	
4	6	1	2	15	6
	7	7	28	35	
	8	28	168	70	

*This equation is only appropriate for P>n+2.

than $(n+2)$, this number can be calculated by multiplying P by 2 (representing the number of parities for each invariant point) and then by $(m-1)$ [the number of stability levels in a n-component, $(n+m)$-phase system]. Thus a 3-component, 6-phase system will have $6\times 2\times (3-1)$ or 24 invariant points. The 24 invariant points can be generated from the six invariant points constructed by taking $n+2$ phases at a time. In Table 1, note how quickly the number of invariant points increases as compared to the number of divariant fields, especially for a given n as P is increased. Thus the utility of dual networks is greatest for systems for which P is greater than $(n+3)$. As the method presented here concentrates on the divariant fields rather than the invariant points as a basis for the construction of phase diagrams, the number of elements used to construct a potential solution remains manageable.

DUAL NETWORKS

Dual networks are graphs in which the stable divariant fields are represented by points and the points are connected by lines representing the reactions that relate the divariant fields to each other. Dual networks were first used in this context by Kujawa *et al.* (1965) to enumerate the stable unary equilibria; a graph of stable equilibria is called a basic form (Kujawa *et al.* 1965). Their work was extended to binary systems by Roseboom & Zen (1982), who determined that the divariant field, not the divariant assemblage, was the appropriate equilibrium to use in the dual network.

The relationship between dual networks, basic forms and potential solutions is shown in Figure 1. Figure 1a shows a topologically correct potential solution for the serpentine system modeled by the 2-component, 5-phase system consisting of brucite, antigorite, lizardite, chrysotile and talc. The solid lines represent stable univariant equilibria, the dashed and dot-dashed lines represent metastable and doubly metastable equilibria, respectively. Invariant points are represented by the symbol of the phase missing from the invariant point. If we remove all but the stable equilibria, we obtain the basic form for the potential solution in Figure 1a, represented by the heavy lines in Figure 1b. To obtain the dual network, each divariant field is represented by a point placed in that divariant field. These points are then linked with lines drawn across the respective univariant lines, which delineate the divariant fields in the basic form. Removing the basic form leaves the dual network shown in Figure 1c.

The importance of dual networks, as pointed out by Kujawa *et al.* (1965), is their unique relationship to a basic form. This uniqueness implies that the dual network contains the parity and stability information of the invariant points in the basic form. For $n+3$ systems, the dual network has all the information necessary to construct the corresponding potential solution as well as the basic form, because each invariant point is connected to every other invariant point. Thus a sufficient number of constraints are placed on invariant points not in the basic form to insure uniqueness. In general, for $n+4$ and larger systems, the dual network does not uniquely determine the potential solution because a given invariant point is not connected to all other invariant points. A proof of the nonuniqueness of the relationship between dual networks and potential solutions for $n+4$ systems is presented by Roseboom & Zen (1982). However, this author has determined that if a sufficient number of divariant fields are included in the dual network, then the potential solution is uniquely determined because the basic form has enough information in it to constrain the metastable equilibria.

CONSTRUCTION OF THE DUAL NETWORK

It is clear that the methodology of Mohr & Stout (1980) and Stout (1985) is applicable to $n+4$ and larger systems, although the details of transposition and trivial conjugates [the trivial conjugate of a potential solution is obtained by changing the stability, but not the parity of the invariant points in the solution] are more complicated (Usdansky 1961, Mohr & Stout 1980). The methodology of Stout (1985) is implicit in the rest of this paper.

A valid dual network must satisfy the following criteria:

1. No linkage lines may cross. Linkage lines join points in a dual network. Crossed linkage lines intersect at a point, and a point in a dual network represents a divariant field. As all divariant fields are already accounted for, no new ones are possible.
2. The number of sides in each polygon within the

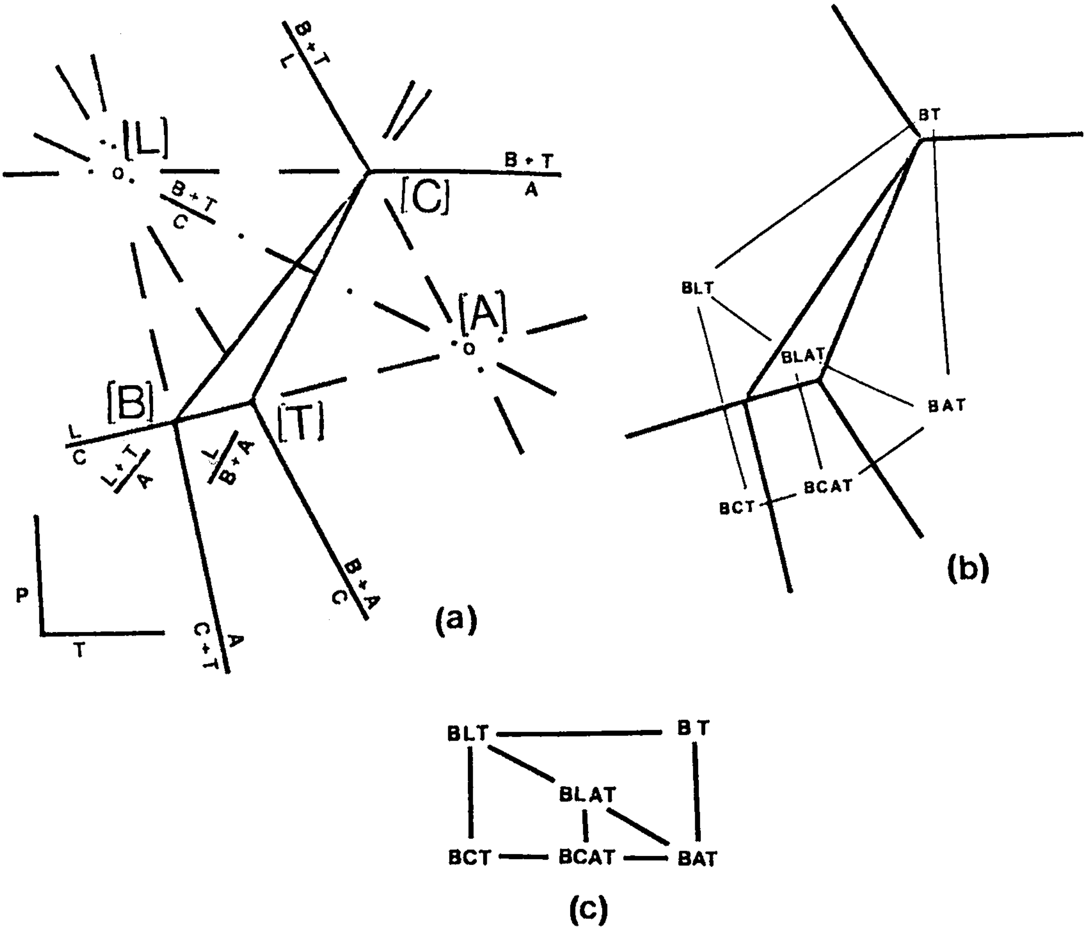


FIG. 1. Construction of a dual network from a potential solution or phase diagram. (a) An oriented potential solution or phase diagram. Solid and dashed lines represent stable and metastable reactions, respectively. Dot-dash lines represent doubly metastable reactions. (b) A binary basic form, constructed by removing the metastable and doubly metastable equilibria from the potential solution or phase diagram. The divariant fields are connected with linkage lines drawn perpendicular to the respective reaction. (c) The dual network.

dual network is equal to the number of phases at the invariant point. Each area within a polygon represents an invariant point, and the number of reactions emanating from the invariant point is related to the number of phases at the invariant point. As each linkage line is perpendicular to a stable univariant reaction, and the number of reactions is related to the number of phases at the invariant point, each polygon must have as many linkage lines as phases.

3. The dual network is composed of closed polygons only. The open side of a polygon represents a missing reaction. As each point in a dual network represents a divariant field, upon inverting the dual network the missing linkage line will juxtapose two divariant fields in the phase diagram with no reaction between them, which is impossible.

4. A dual network can only be altered by removing or adding a divariant field such that none of the criteria outlined above is violated.

Construction of the first dual network need not include all of the unique divariant fields of the system, although the more divariant fields in the dual network, the greater the constraints on the potential solution. At present, the number of divariant fields necessary to describe a phase diagram uniquely is not known for most systems. For $n+3$ systems, only two levels of stability (stable and metastable) are possible for each invariant point. As each invariant point is connected to every other invariant point, the dual network uniquely describes the potential solution because any invariant point not in the basic form is metastable and can be added to the basic form in only one way. The addition of a phase to an $(n+3)$-phase system requires a third level of stability for the invariant points and the thermodynamic constraint that every reaction pass through at least three invariant points. The constraint arises because every potential solution has a trivial conjugate, in which the relative order of the free energies for each type of equilibrium is reversed. Therefore, each reaction that passes through a sta-

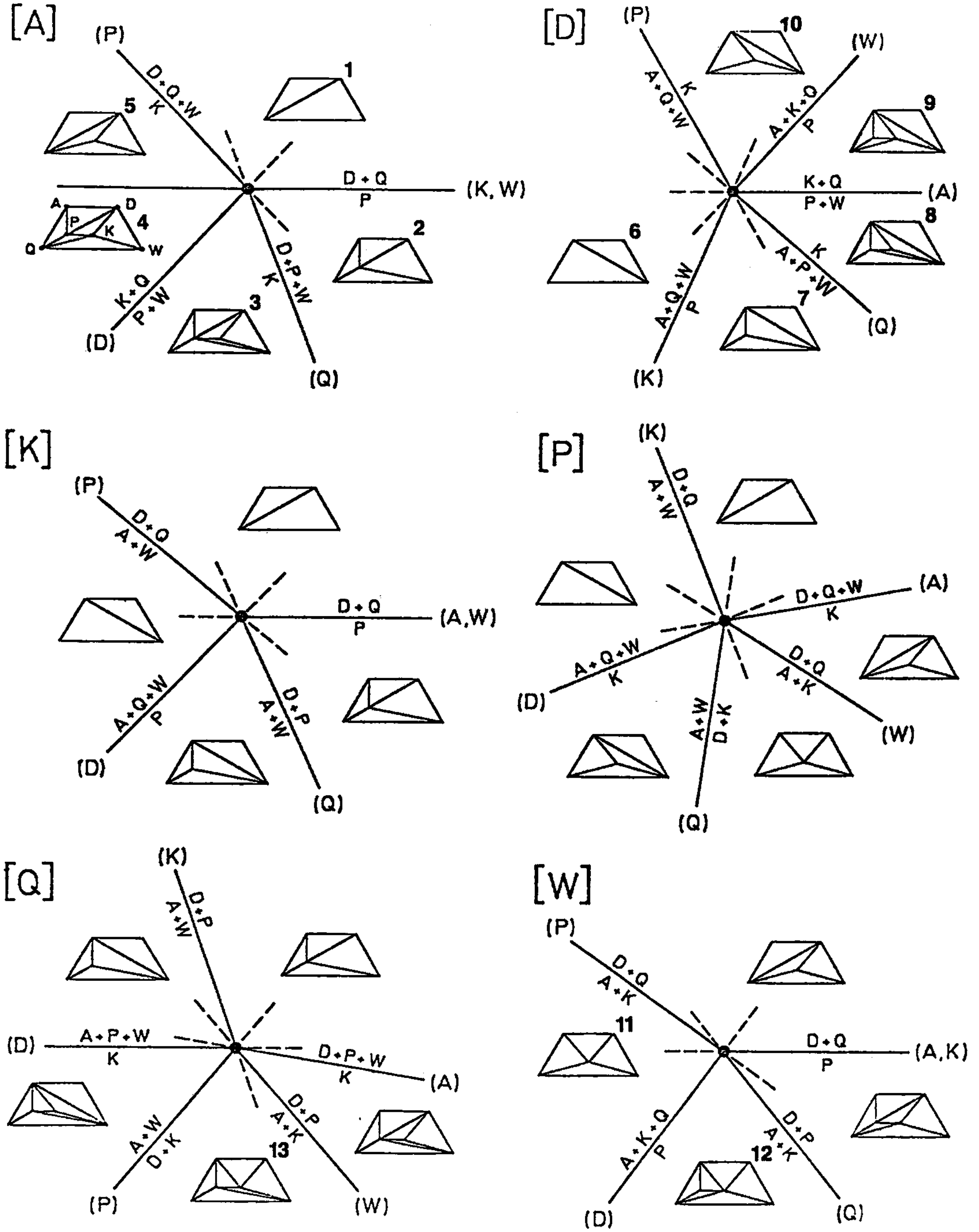


FIG. 2. Invariant points of the $n+3$ system Al_2O_3–SiO_2–H_2O. The chemography of the six phases is shown in divariant field 4 in invariant point [A].

ble invariant point must also pass through a doubly metastable invariant point. Two such invariant points must be connected by a metastable invariant point (Usdansky 1981). A necessary consequence is that some invariant points are not directly connected to others (Usdansky & Stout 1981). For unary $n+4$ systems, Guo (1980) has found that all potential solutions can be grouped into one of two equivalence classes (Usdansky 1981), based on the number of metastable invariant points in the potential solution. Of a total of ten invariant points (Table 1), unary $(n+4)$-phase potential solutions have either 4 or 6 metastable invariant points (Guo 1980) and must contain at least one stable and one doubly metastable invariant point. Therefore, a basic form containing 4 or 5 stable invariant points leads to an unique potential solution because the metastable and doubly metastable invariant points can be added to the basic form in only one way. The dual network of a basic form containing 4 or 5 stable invariant points will contain all 5 unique divariant fields. Thus constructing a dual network containing all 5 unique divariant fields in a one-component, 5-phase system will yield a unique phase-diagram.

CONSTRUCTING THE FIRST POTENTIAL SOLUTION

In principle, the method of dual networks can be used to construct the first potential solution for systems with any number of components. For the sake of clarity, examples will be from two- and three-component systems. First, the three-component alumina system will be used to illustrate the construction of potential solutions for systems for which no information is known regarding which divariant assemblages are stable. The two-component serpentine system will be used to illustrate the construction of potential solutions for systems for which information regarding stable assemblages is known. The two-component system will also be used to illustrate how new potential solutions are constructed when additional phases are added to the system's chemography.

Stout (1985) investigated the system involving the components Al_2O_3, SiO_2 and H_2O and the phases andalusite (A), diaspore (D), kaolinite (K), pyrophyllite (P), quartz (Q) and water (W) (Fig. 2). To construct the initial dual network, it is neccessary first to construct each invariant point. Thus, all the equilibria characterizing the system must be identified. In this sense, the method of dual networks is equivalent to the method of Stout (1985) because both require that all the equilibria of the system be known. For the alumina system, the invariant points, univariant lines and divariant fields are shown in Figure 2. The chemography of this system is shown as divariant field 4 within invariant point [A]. Inspection of the six invariant points in Figure 2 shows that of the 28 divariant fields present, 13 are unique. They are labeled 1–13. This number is less than that listed in Table 1 for 3-component, 6-phase systems because of the colinearity of quartz, pyrophyllite and diaspore. The unique divariant fields are used to assemble the dual network.

Assuming that nothing is known about the stability of the divariant assemblages, no advantage is gained by choosing particular divariant fields to be placed in the dual network. The divariant fields from the invariant points [A], [D], [Q] and [K] were chosen arbitrarily. A polygon is formed using the divariant fields from invariant point [A] (Fig. 3a). Another polygon can be formed by the divariant fields in [K]. Because divariant fields labeled 1 and 2 are part of [K] as well as [A] (Fig. 2), the two polygons share the points represented by the common divariant fields. Divariant fields 2 and 7 are common to [K] and [Q], so that divariant fields 2 and 7 can be used to form another polygon with the remaining divariant fields in [Q]. Note that divariant fields 2 and 9 are common to [A] and [Q], so the polygons formed by the divariant fields of [A], [K] and [Q] must have divariant field 2 in common (Fig. 3a). At this point, the dual network consists of three linked polygons. Invariant point [D] shares divariant fields 6 and 7 with [K], and fields 7 and 8 are shared with [Q]. Thus four of the five divariant fields that represent [D] are already in the dual network. Completing a new polygon with the remaining divariant field (10) from [D] makes a dual network with four polygons. These four polygons satisfy the criteria given earlier for valid dual networks.

The basic form is found by reversing the process illustrated in Figure 1. Place a point (Fig. 3b) into each polygon of the dual network and connect the points with lines drawn across the lines of the dual network (Fig. 3b). These lines represent univariant reactions, and the points are invariant points. Label the reactions using the information in Figure 2. For example, the linkage line connecting divariant field 3 to divariant field 4 represents the reaction P + W = K + Q. As expected, inspection shows that invariant points [A], [D], [K] and [Q] are stable. Once all reactions and invariant points are identified, the reactions must be oriented properly about each invariant point (Fig. 3c). Note that the reaction P + W = Q + K passes through invariant points [A] and [D] (Fig. 3b). As each equilibrium can occur once and only once, these two segments must be joined together. This will enclose [Q] in a triangle formed by invariant points [A], [K] and [D]. To construct the potential solution, metastable extensions are added to the reactions at each invariant point and made to converge at the appropriate metastable invariant point, in this case [P] and [W]. Adding doubly metastable reactions that extend away from the metastable reactions completes the potential solu-

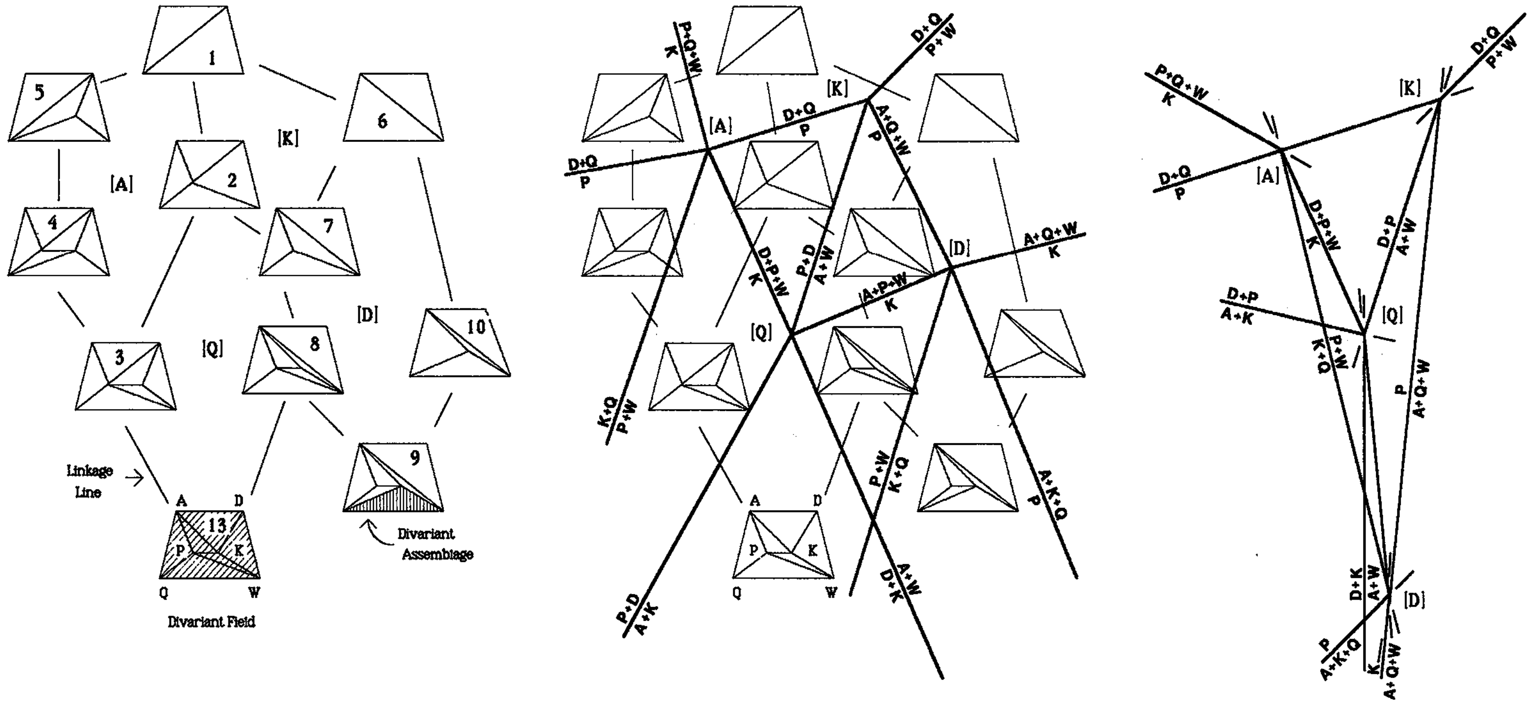


FIG. 3. Construction of a potential solution or phase diagram from a dual network. (a) The dual network. (b) The reactions are emanating from the invariant points such that each reaction crosses the linkage line to which it corresponds. (c) The reactions are oriented about the invariant points, and the metastable extensions are added to the reactions.

tion. This is potential solution 29 of this system (Stout 1985). The basic form (Fig. 3b) for potential solution 29 contains 13 divariant fields, whereas the dual network (Fig. 3a) contains 11. The other divariant fields were generated by indifferent crossings (Zen 1967). An indifferent crossing occurs when two reactions cross in P–T space but do not represent an equilibrium between all the phases in both reactions. The indifferent crossing of reactions P = A + K + Q and D + K = A + W produced divariant field 11, and the indifferent crossing of reactions D + P = A + K and K + Q = P + W generated divariant field 12.

In the previous example, it was assumed that no information was available regarding the stability of various mineral assemblages of the system. If such information is available, it suggests which divariant fields to use in the dual network. For example, the following ten assemblages have been reported for Mg serpentinites: antigorite (A) + talc (T), A + brucite (B), B + chrysotile (C), A + forsterite (F), F + T, C + T, lizardite (L) + B, L + C + B, L + C and F + E (Evans *et al.* 1976, Wicks & Whittaker 1977, Dungan 1979).

These two-phase assemblages are likely to be divariant, and thus the phases of interest can be represented by two components. Choosing the phases brucite, antigorite, lizardite, chrysotile and talc yields a 2-component system because the phases are colinear. The chemography (Fig. 4, under the top row of invariant points) consists of the two-component system MgO-SiO_2, representing the 3-component system MgO-SiO_2-H_2O, projected through water. The projection is used because forsterite and enstatite will be added to the chemography later on. The invariant points and the unique divariant fields for the *n* + 3 system are shown in the top row of Figure 4. The unique divariant fields are labeled 1–6. Lizardite and chrysotile are polymorphs in this system; they form an internal degeneracy. As

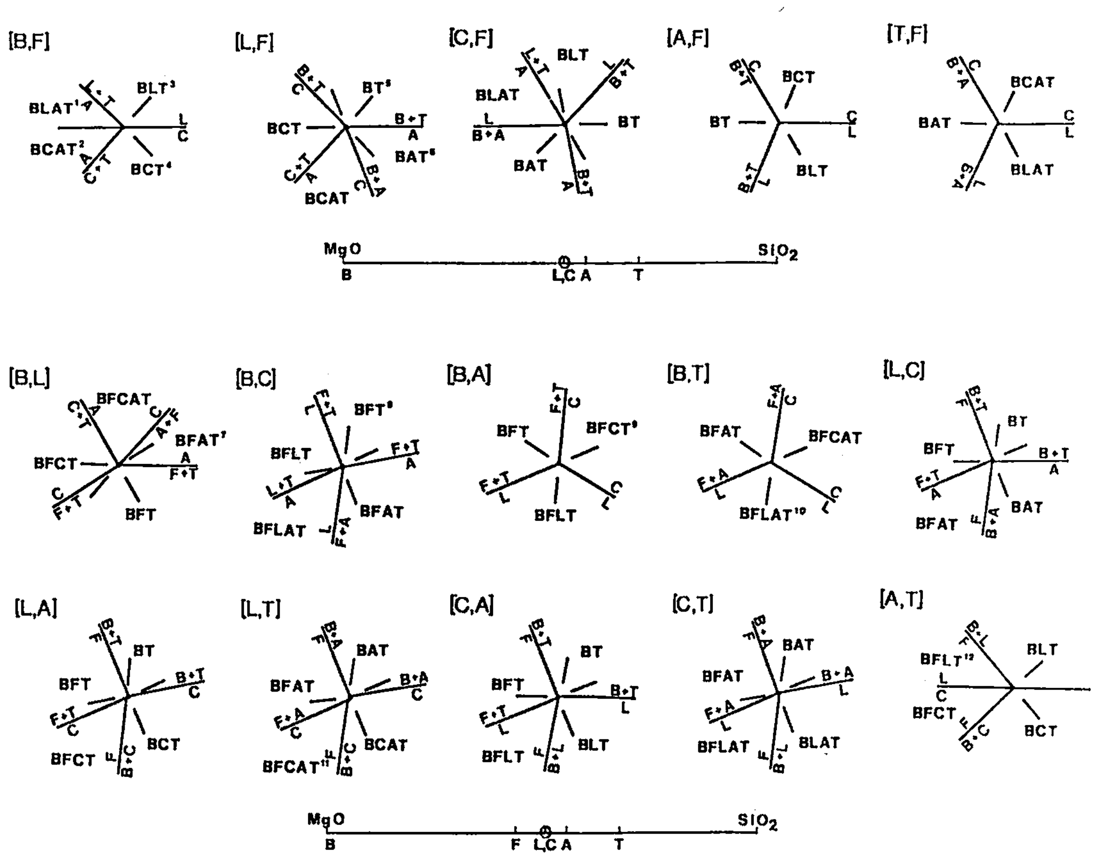


FIG. 4. Invariant points of the (*n* + 3)-phase serpentine system MgO–SiO_2–H_2O (first row) and the (*n* + 4)-phase system (first, second and third row). The solid and dashed lines represent stable and metastable reactions, respectively. [L] in the *n* + 3 system is [L,F] in the *n* + 4 system. The chemographies of the systems are shown underneath their invariant points. The phases are plotted using atom fractions.

a result the total number of divariant fields in this system will be less than that given in Table 1. The implications of assuming that lizardite and chrysotile are polymorphs will be discussed in a companion paper (O'Hanley 1987).

The six unique divariant fields for the $n + 3$ system are represented by their assemblages (*i.e.*, the divariant field containing the assemblages B + C and C + T will be represented by the symbol B–C–T). Using a divariant field of the $n + 3$ system in the dual network assumes that some assemblage in the divariant field is stable. Evans *et al.* (1976) stated that the assemblages C + T, A + B, A + F and F + T should be stabilized as temperature increases. Two of these assemblages, C + T and A + B, are in the system of interest and, therefore, the divariant fields that contain these assemblages (fields B–A–T and B–C–T) will be used to construct the dual network. The assemblage B + T has not been reported in the literature that reviewed the observed occurrences of brucite (Faust & Fahey 1962, Hostetler *et al.* 1966), and it has not been reported since then. Therefore, the divariant field B–T will not be placed in the dual network.

At this point, two divariant fields have been chosen, but no polygons have been formed. Divariant field B–C–T cannot be linked directly to B–A–T because they are not related by a single reaction. These two divariant fields can be linked if field B–C–A–T is placed between them (Fig. 5a). As no closed polygons have been formed and divariant field B–T has been excluded, fields B–L–A–T and B–L–T will be used to form closed polygons: B–L–T is linked to B–C–T, and B–L–A–T is linked to B–C–A–T. Field B–L–A–T can also be linked to B–A–T. This process yields two closed polygons (Fig. 5a). Cogitation will show that excluding B–T from the dual network, along with the need to use fields B–A–T and B–C–T, could only result in the dual network in Figure 5.

Where no information is available, constructing a dual network for a binary 5-phase system is equivalent to constructing a hierarchical diagram (Roseboom & Zen 1982). The divariant field with the greatest number of stable phases is drawn first. Interior phases are removed one at a time, generating divariant fields related to the first field until all divariant fields are accounted for.

To obtain the basic form, place an invariant point in each polygon of the dual network and connect the invariant points with reactions (Fig. 5a). Then label the reactions and the divariant fields about all sta-

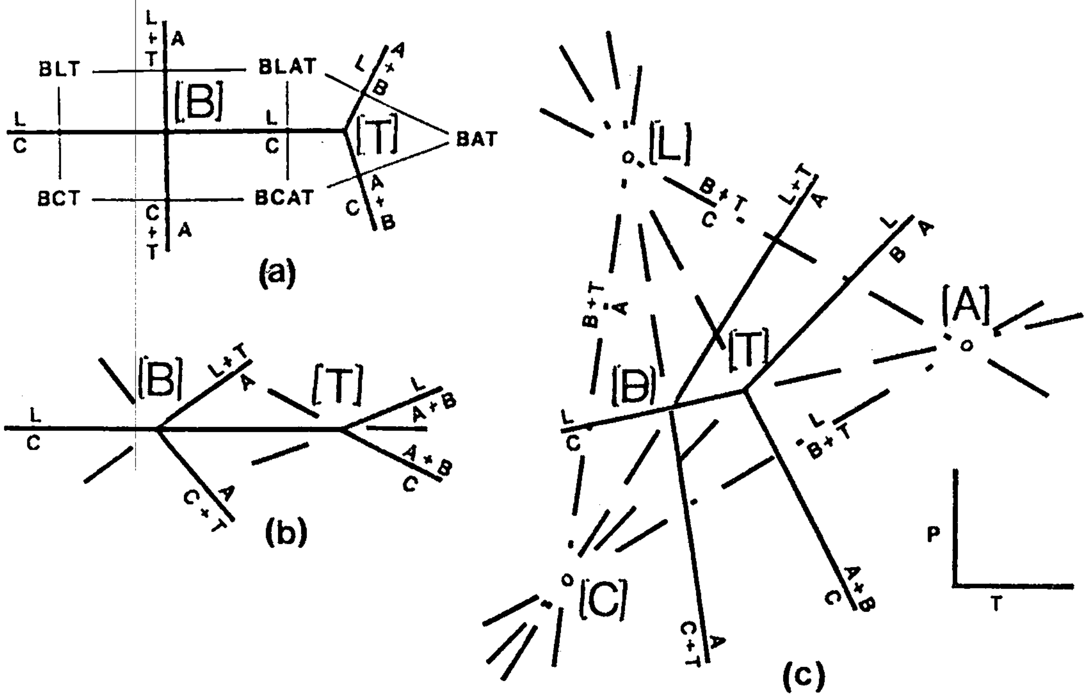


FIG. 5. Construction of a potential solution or phase diagram from a dual network. (a) The dual network is shown with the reactions drawn perpendicular to the linkage lines. [B] = [B,F] and [T] = [T,F] are stable. (b) The reactions are arranged about the invariant points, and the metastable extensions are added to the reactions. (c) Extension of the metastable reactions yields the metastable invariant points [L,F], [A,F] and [C,F], represented by an open dot.

ble invariant points. The basic form is obtained by orienting the reactions about the invariant points. The first potential solution is obtained by adding metastable extensions to the stable reactions emanating from the invariant points in the basic form (Fig. 5b) and then adding metastable invariant points at the intersection of the metastable extensions (Fig. 5c). The sequence of divariant fields (particularly B–T) that represent the invariant points [A], [C] and [L] are not in the dual network.

Eleven divariant fields were used to construct the dual network for the alumina system, whereas five divariant fields were used for the serpentine system. After the dual network has been constructed, obtaining the potential solution is straightforward. To construct a potential solution for either the serpentine or the alumina system using invariant points, six invariant points must be assembled in a consistent manner. The parity of the invariant points is determined by how they are assembled and, as a result, the assembled potential solution must be examined to insure that the stable divariant fields are generated in the proper sequence about each invariant point. Dual networks generate the proper sequence of divariant fields automatically because the parity of the stable invariant points is predetermined.

ENLARGING A SYSTEM BY ADDING A PHASE

Most, if not all, rock systems contain more than $n + 3$ phases. For example, if all of the phases given above for the serpentine system were used at once, the chemography would define an $n + 5$ system. However, chemographic analysis is understood best for $n + 3$ systems; to use the method of Stout (1985) effectively, one should use a $n + 3$ system. Dual networks can be used to construct potential solutions for $n + 3$ systems, but their advantage is brought out when they are used for larger systems. Adding a phase to the chemography increases the complexity of the analysis. For each additional phase, another level of stability is added to both the invariant points and the reactions. The number of potential solutions also increases, although the total number of potential solutions is not known for most systems; for

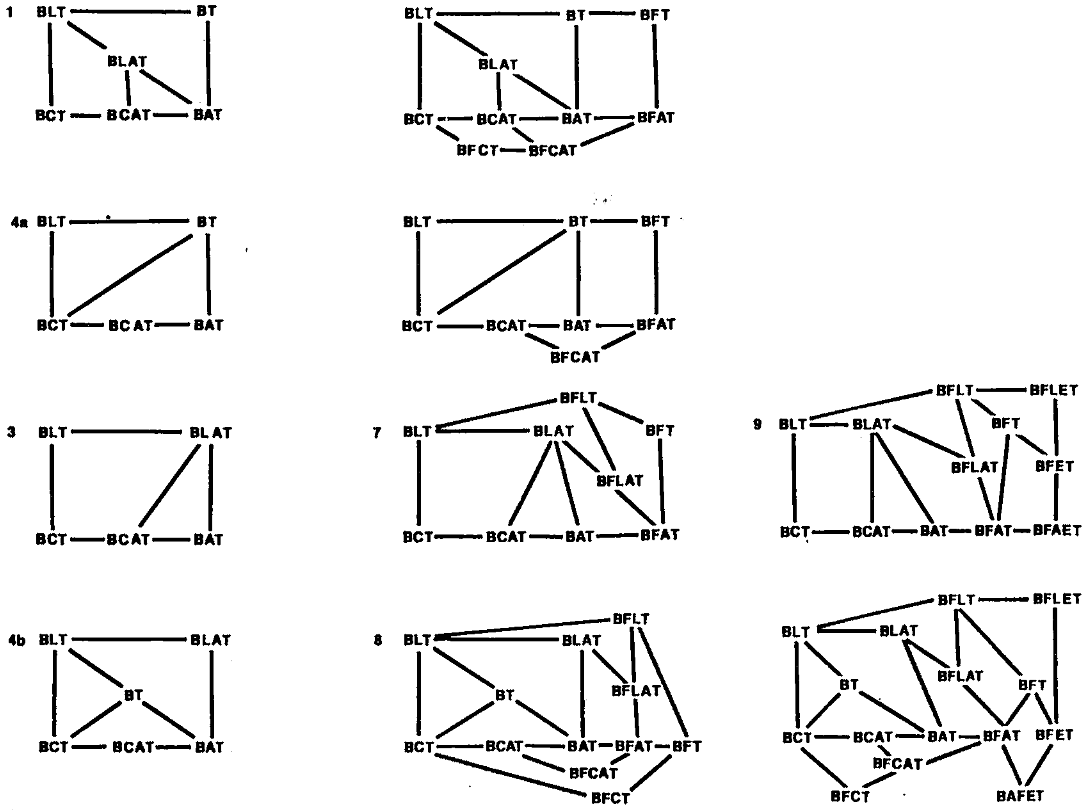


FIG. 6. Dual networks for the (n + 3)-, (n + 4)- and (n + 5)-phase serpentine systems. The number in the upper left-hand corner of each dual network is the number used when referring to the dual networks in the text.

unary $n + 4$ systems, the total number of potential solutions is 1320 (Usdansky & Stout 1981).

Given the increase in the total number of potential solutions, construction of all of them with a subsequent search is not feasible. An alternative is to use dual networks to augment the potential solutions or the phase diagrams of smaller $n + 3$ systems. Dual networks also provide a means of joining two $n + 3$ systems that describe different P–T regions of the same bulk chemistry. For example, the serpentine system, which describes the low-temperature region of hydrated ultramafic rocks, could be joined to the system containing the phases anthophyllite, enstatite, forsterite, talc, quartz and H_2O used by Chernosky *et al.* (1985) to study the behavior of Mg-anthophyllite. In either process, the dual network of an existing potential solution or phase diagram is used as a base for the larger system.

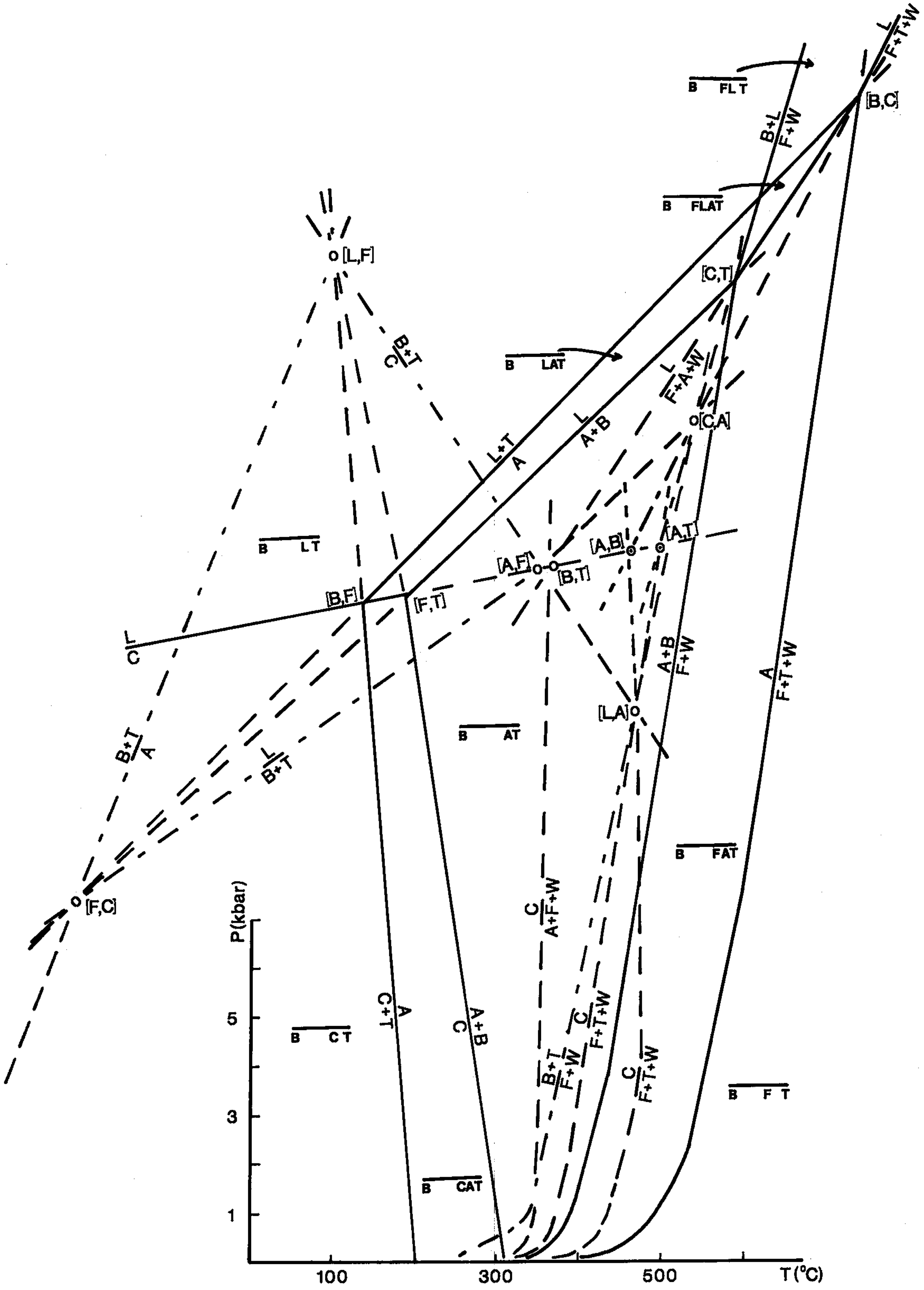
The potential solution constructed for the 5-phase serpentine system (Fig. 5c) was used to construct 19 other potential solutions. The results of examining this set to eliminate thermodynamically impossible solutions are reported in a companion paper (O'Hanley 1987). The potential solutions in Figures 1 and 5c are two of four that remain after eliminating thermodynamically impossible solutions for the $n + 3$ system. The dual networks for the four remaining potential solutions of the $n + 3$ system are shown in the first column of Figure 6.

The phases chosen to comprise the $n + 3$ system describe the low-temperature region of the phase diagram for the serpentine system. Thus the $n + 3$ system describes a small region of P–T space. To extend the area of P–T space described by the system, the chemography must be expanded by adding phases. The logical approach is to add a phase to the chemography that is stable in the region of P–T space next to the region already described by the $n + 3$ system. This way, larger regions are described by adding divariant fields containing observed assemblages to the exterior of the existing dual networks.

The extension of the 5-phase serpentine system is made by inspection of the remaining observed assemblages not included in the 5-phase system. Forsterite is stabilized during the prograde metamorphism of serpentinites and is observed in the assemblages A + F and F + T (Evans *et al.* 1976, Frost 1975). Therefore, forsterite was added to the $n + 3$ system, yielding the $(n + 4)$-phase system B–F–L–C–A–T. The additional divariant fields for this system are illustrated in rows 2 and 3 of Figure 4. The $n + 4$ system has 12 unique divariant fields (Fig. 4); six are inherited from the $n + 3$ system, and six from divariant fields containing forsterite. As forsterite is stable at higher temperatures than any of the phases in the $n + 3$ system, and the orientation of the dual networks in P–T space is known, the divariant fields containing the observed assemblages A + F and F + T have been added to the high-temperature side of the dual networks, the side on which divariant field B–A–T is located. The dual networks for the $n + 4$ system are shown in the second column of Figure 6, in the same row as the $n + 3$ dual networks from which they were made. Note that all four dual networks for the $n + 4$ system contain divariant fields with the assemblages A + F and F + T. Focus on the third row of Figure 6. A potential solution for the $n + 4$ system, that has dual network 3 as its base, is shown in Figure 7. Note that Figure 5c is contained within Figure 7. This is a result of choosing the additional phase (forsterite) such that the new potential solution of the $n + 4$ system extends the region of P–T space described by the potential solution of the $n + 3$ system.

Usdansky (1981) has determined that binary $(n + 4)$-phase potential solutions belong to one of three equivalence classes, containing 6, 7 or 10 metastable invariant points, respectively. By inspection of the dual networks for the $n + 4$ potential solutions in Figure 6, between 5 and 7 of the 15 invariant points are stable, so that the basic forms could belong to one of two equivalence classes. In these cases the dual network does not uniquely determine the potential solution because the metastable invariant points could be added to the basic form in two different ways. Dual network 8 actually contains 8 polygons, and one would expect that it would have at least 8 stable invariant points. However, the polygon represented by divariant fields B–L–T, B–F–L–T and B–F–L–A–T represents an indifferent crossing because these divariant fields do not define an invariant point.

Based on thermodynamic reasoning given by O'Hanley (1987), the potential solution shown in Figure 7 is the best one to account for the observations that apply to phases in the $n + 4$ system. Constructing an $n + 5$ system by adding enstatite to the chemography of the $n + 4$ system yields a system that includes all of the observed assemblages of magnesium serpentinites. The $n + 5$ system is B–F–L–C–A–E–T. The remaining observed assemblage is F + E. Thus a potential solution for the $n + 5$ system is constructed by adding the divariant fields containing the assemblage F + E to the dual network of the $n + 4$ system shown in the third row of Figure 6. The divariant fields generated by constructing the invariant points containing enstatite are not shown. Owing to the absence of anthophyllite in this system, the reaction F + T = E + W would generate the F + E assemblage (Evans 1977), so that the dual networks in Figure 6 have been augmented by adding the divariant field B–F–E–T to the field B–F–T. The dual networks were completed by adding divariant fields that contain the assemblage F + E. The potential solution shown in Figure 8, obtained by augmenting the dual network of the potential solution in


L / F+T+W
B FLT
B+L / F+W
[B,C]
B FLAT
[L,F]
[C,T]
B+T / C
B LAT
L / F+A+W
L+T / A
L / A+B
[C,A]
B LT
[A,B]
[A,T]
[A,F]
[B,T]
L / C
[B,F]
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A+B / F+W
A / F+T+W
[L,A]
B AT
B+T / A
L / B+T
B FAT
[F,C]
P(kbar)
C / A+F+W
A / C+T
A+B / C
B CT
C / F+T+W
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C / F+T+W
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5
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T(°C)

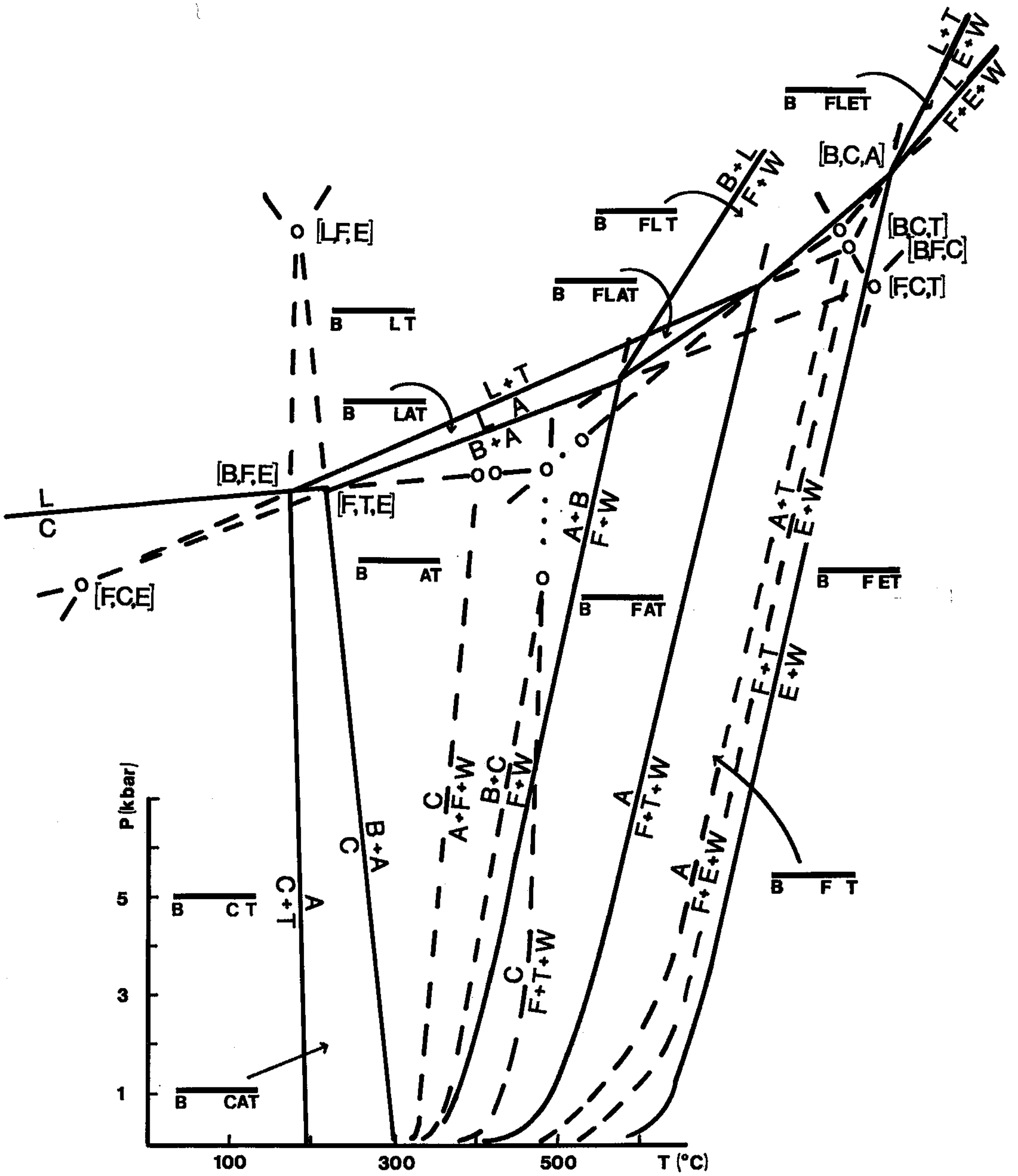

FIG. 8. Potential solution of the $n+5$ system constructed from the potential solution in Figure 7. Only stable and metastable equilibria are shown. See Figure 7 for labels of invariant points and restrictions.

FIG. 7. Potential solution of the $n+4$ system, constructed from the dual network of Figure 5c. Symbolism the same as in previous figures. Open circles with dots inside represent doubly metastable invariant points. [L,C], [B,L] and [L,T] are located below the temperature axis. The part of the phase diagram below 300°C is approximate because no experimental data are available, although the topological relationships are correct.

Figure 7, contains the summary diagram of Evans (1977) for temperatures less than 700°C.

CONCLUSION

The potential solution in Figure 8 has 35 invariant points and 31 reactions. To construct this diagram using invariant points requires finding 35 invariant points out of a possible 280 that can be connected in a consistent manner. It is much easier to use 12 divariant fields to construct such a diagram. Note that the dual network related to the potential solution in Figure 8 contains 13 divariant fields, whereas the potential solution contains 14. The 14th divariant field was generated by an indifferent crossing.

Dual networks present an opportunity to expand pre-existing systems. Starting with an $n + 3$ system allows chemographic analysis as developed by Stout (1985) to be used on a manageable number of potential solutions. Once a small number of solutions are found, the system can be expanded, and the resulting set of new potential solutions investigated. This approach also suggests that the $n + 3$ system be chosen to describe as small a region of P–T space as possible. The region described can then be increased by adding phases to the existing chemography.

The problem of uniqueness remains. However, the work of Guo (1980) and Usdansky (1981) indicates that we can have uniqueness in certain cases. At this point in our understanding, using all or a large number of the unique divariant fields in the dual network will yield a unique potential solution. The potential solution in Figure 8 is not the only possible diagram that could be generated from its basic form. It includes correctly the observations on serpentinites because the method used to construct it builds in the observations. It contains the summary diagram of Evans (1977) for serpentinites for temperatures less than 700°C.

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