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A CHEMOGRAPHIC ANALYSIS OF MAGNESIAN SERPENTINITES USING DUAL NETWORKS

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ABSTRACT

The method of dual networks is used to research the stability of lizardite and chrysotile within the simplest multisystem that describes serpentinization. The method focuses on observed assemblages as the base to construct potential solutions for the phase diagram. It allows one to include as many phases in the chemography as necessary to describe the observations. In this sense the restriction of systems to $n+3$ phases is artificial, although the new method takes advantage of the methodology developed for such systems. Potential solutions for Mg serpentinites described by $MgO–SiO_2–H_2O$ are constructed for systems of five, six and seven phases. Chemographic analysis is used to investigate the five-phase system, brucite, lizardite, chrysotile, antigorite and talc, in which lizardite and chrysotile are considered to be polymorphs. After eliminating thermodynamically impossible solutions at standard temperature and pressure, remaining potential solutions are used to construct solutions for larger systems that include forsterite and enstatite as additional phases. Using observations to construct the dual network automatically filters out many potential solutions. For example, omitting a divariant field from the dual network removes all potential solutions in which that field is stable. Equilibria occurring in the larger system that eliminate its potential solutions also eliminate potential solutions of the smaller system. (Each potential solution of the larger system contains one of the smaller system). The remaining potential solution, constructed for the seven-phase system, brucite, forsterite, lizardite, chrysotile, antigorite, enstatite and talc, describes the serpentinization of Mg peridotites. The existence of the reaction lizardite = chrysotile needs to be demonstrated. In the system used here, the stability of lizardite (L) and chrysotile (C) within Mg serpentinites depends on the location of the reaction L = C; if reaction L = C is located at pressures greater than 8 kbars, then chrysotile is the stable phase in serpentinites; if the reaction is located at low pressures, lizardite is the stable phase.

Keywords: serpentinites, chemographic analysis, networks (dual), lizardite, chrysotile.

SOMMAIRE

On emploie la méthode des réticules doubles pour établir la stabilité relative de lizardite et chrysotile dans le multisystème qui décrit la serpentinisation. Cette méthode prend comme point de départ les assemblages observés et en déduit des solutions possibles pour le diagramme des phases. Elle permet l'inclusion, dans la chimiographie, d'autant de phases qui seront nécessaires pour décrire les observations. Dans ce sens, la restriction d'un système à $n + 3$ phases est artificielle, quoique la nouvelle méthode bénéficie de la méthodologie développée pour pareils systèmes. Des solutions possibles pour serpentinites à magnesium, décrites par $MgO–SiO_2–H_2O$, sont construites pour systèmes à cinq, six et sept phases. L'analyse chimiographique sert à investiguer le système à 5 phases (brucite, lizardite, chrysotile, antigorite et talc), dans lequel on considère lizardite et chrysotile comme polymorphes. Après élimination des solutions thermodynamiquement impossibles, à température et pression normales, on se sert des solutions possibles restantes pour construire des solutions pour systèmes plus compliqués, qui comptent la forstérite et l'enstatite comme phases supplémentaires. L'emploi des observations pour construire le réticule double élimine automatiquement nombre de solutions possibles. Par exemple, l'omission d'un champ bivariant du réticule double écarte toute solution possible dans laquelle ce champ est stable. Tout équilibre d'un système qui en élimine les solutions possibles écarte aussi les solutions possibles de tout système plus petit: toute solution possible du grand système en contient une du petit. La dernière solution possible, construite pour le système à 7 phases, brucite, forstérite, lizardite, chrysotile, antigorite, enstatite et talc, décrit la serpentinisation de la péridotite à magnésium. Reste à prouver l'existence de la réaction lizardite = chrysotile. Dans le système employé, la stabilité relative de la lizardite (L) et du chrysotile (C) dépend de la pression: à haute pression (plus de 8 kbar), c'est le chrysotile, à base pression, c'est la lizardite qui est stable dans la serpentinite.

(Traduit par la Rédaction)

Mots-clés: serpentinites, analyse chimiographique, réticules doubles, lizardite, chrysotile.

INTRODUCTION

Clarifying the relationships among the serpentine minerals antigorite, lizardite and chrysotile has not been an easy matter. It is generally accepted that the alternating-wave structure of antigorite gives it a chemistry distinct from that of lizardite and chrysotile. The relationship between lizardite and chrysotile has been debated since the refinement of their crystal structures in the 1950s. Whittaker & Zussman (1956) proposed the first classification of serpentines

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based on crystal structure. This classification has withstood the test of time well, although it is not as simple as first proposed because of the numerous polytypes of lizardite and chrysotile [see Wicks & Whittaker (1975) for a discussion]. Two recently discovered minerals, balangeroite (Compagnoni *et al.* 1983) and carlosturanite (Compagnoni *et al.* 1985), will broaden the classification as well. The earliest statements on the relationship among antigorite, lizardite and chrysotile tentatively concluded that antigorite, lizardite and chrysotile are polymorphs, but that slight chemical differences conceivably could be found that would distinguish them (Deer *et al.* 1962, p. 178). Page (1968) argued, based on a statistical analysis of the available data, that the three minerals are chemically distinct and, therefore, not polymorphs. An analysis of the data available to Whittaker & Wicks (1970), many of the data being the same as used by Page, supported Page's assertion that antigorite is chemically distinct from lizardite and chrysotile. However, the data were not sufficient to justify the separation of lizardite and chrysotile on a chemical basis.

Wicks & Whittaker (1975) related the slight chemical differences noticed by Page (1968) and Whittaker & Wicks (1970) to crystal structure. Antigorite was considered chemically distinct from lizardite and chrysotile because of its structure. Wicks & Whittaker (1975) further argued that the various polytypes of lizardite and chrysotile are able to accept limited cation substitution and, therefore, lizardite and chrysotile could have overlapping chemistries. They did not think that the term polymorph should be so narrowly defined that it could not be applied to two minerals with the same chemistry but each with polytypes that allowed cation substitution.

All of the above authors stated the difficulties associated with determining the chemistry of the serpentine minerals: small size of crystals, impurities and slight chemical differences. Accepting the difficulties in determining the chemistry of serpentine minerals, it may be fruitful to attempt a different approach. Hypothesize the relationship between lizardite and chrysotile, and then construct phase diagrams from which testable assertions can be made. A program is then established for research.

The purpose of this paper is to investigate the simplest multisystem that can describe the serpentinization of ultramafic rocks, and then to investigate the properties of the potential solutions that result from the hypothesis that lizardite and chrysotile are polymorphs. Chemographic analysis (Stout 1985) is used because the properties of the phase diagram result from the chemography used to describe the system. The method of dual networks (O'Hanley 1987) will be used to construct potential solutions for the phase diagram for Mg serpentinites modeled by a 2-component, 7-phase chemography.

CHEMOGRAPHIC ANALYSIS AND DUAL NETWORKS

Many of the characteristics of potential solutions for phase diagrams, such as the number of invariant points present and the number of invariant points a univariant reaction passes through, are determined by the chemography of the phases. The method by which the relationships between the chemography and the potential solutions are investigated is called chemographic analysis (Stout 1985). An assumption basic to chemographic analysis is that each equilibrium occurs once and only once. At this point in time, the occurrence of an equilibrium more than once in a phase diagram has not been documented, although Chernosky *et al.* (1985) suggested that the system (components $MgO-SiO_2-H_2O$) composed of the phases anthophyllite, talc, enstatite, forsterite, quartz and water may have an invariant point that occurs twice. The evidence for this conclusion is based on the curvature of several reactions in the system. However, the curvature of the reactions at low pressure is a result of the co-ordinates used on the graph; for example, using log(P) instead of P for the ordinate removes the curvature.

Chemographic analysis treats potential solutions or phase diagrams topologically. That is, the geometrical properties of the potential solutions are not important to an investigation of the potential solutions. Mohr & Stout (1980) have defined a straight-line analog that is a deformation of the potential solution in which all of the reactions are considered as straight lines. This makes them easier to manipulate. No phenomena are omitted by treating the reactions as straight lines. Once a potential solution has been oriented in P–T space, the reactions can curve in any manner necessary to conform to experimentally determined reactions as long as the topology of the invariant points and univariant lines remains the same.

Dual networks are graphs in which stable divariant fields are represented by points and the points are connected by univariant lines. The univariant lines represent the univariant reactions that relate the divariant fields to each other. Inverting a dual network yields a basic form, which contains the stable equilibria of a potential solution. After orienting the stable reactions about the invariant points and adding the metastable equilibria to the basic form, a potential solution results that may correspond to the real phase-diagram.

THE FIRST POTENTIAL SOLUTION

The majority of serpentinites form by the alteration of peridotites. As both lherzolites and harzburgites contain substantial amounts of olivine, the serpentine minerals form in both altered lherzolites and harzburgites. Lherzolites, however, have sufficient

Ca and Al to stabilize diopside, tremolite, spinel and chlorite. Thus the simple system used in this paper is the first step in describing lherzolites, but the alteration of harzburgites can be described by the serpentine system using the components MgO, SiO_2 and H_2O (Mg serpentinites). The following 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). Quartz is not important in serpentinites because serpentinites form in rocks devoid of excess silica. However, quartz and anthophyllite are associated with the prograde metamorphic assemblages of serpentinites and must be accounted for in a complete chemographic analysis of these rocks. Although anthophyllite-bearing assemblages would be a more logical choice than enstatite-bearing assemblages in terms of prograde metamorphism, enstatite is more common in serpentinites than is anthophyllite.

The observed assemblages of Mg serpentinites appear to consist of various two-phase combinations, exclusive of a liquid or vapor. As these are likely to be divariant, the phases chosen to represent the $n + 3$ system are brucite, antigorite, lizardite, chrysotile and talc (Fig. 1). Note that these five phases are colinear and therefore define a 2-component system.

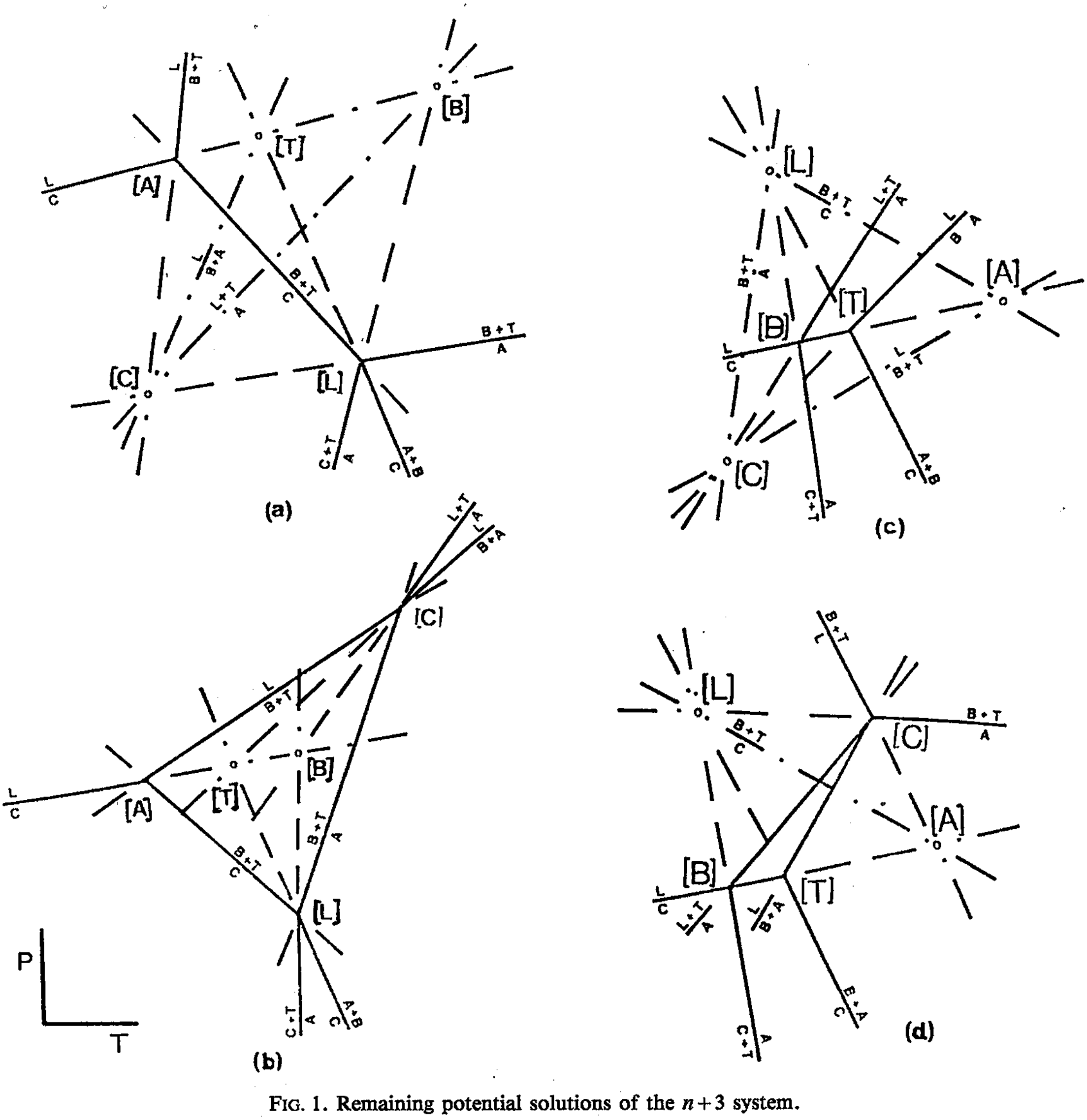

FIG. 1. Remaining potential solutions of the $n+3$ system.

The phases of interest are represented by the components $MgO-SiO_2$, projected through H_2O, because forsterite and enstatite will be added to the chemography later on, and a projection will be needed.

Lizardite and chrysotile are considered polymorphs in this system; the polymorphism makes the assemblage L + C univariant. Lizardite and chrysotile form an internal degeneracy (Zen 1967), and they can be destabilized by a chemographically external assemblage, such as forsterite + talc. Therefore, the reaction L = C will be metastable in some region of P–T space. The implication of the polymorphism will be discussed below.

The first potential solution was constructed using dual networks (O'Hanley 1987). The unique divariant fields of the $n + 3$ system were connected together to form a dual network. The process of obtaining a basic form from a dual network is called inversion. To invert a dual network, a point is placed within each polygon in the dual network. The points are connected by lines drawn perpendicular to the lines of the polygons. The points and the lines are invariant points and univariant reactions, respectively, and once labeled yield the basic form of the potential solution. Placing metastable extensions on the reactions indicates the location of the metastable invariant points. Once the doubly metastable extensions are added to the metastable reactions, the potential solution is complete. From this solution, 19 potential solutions were generated by transposition, using the method given by Stout (1985). The node diagram (Mohr & Stout 1980) for this system, which summarizes the procedure by which one potential solution is obtained from another potential solution by transposition, is shown in Figure 2.

ELIMINATION OF POTENTIAL SOLUTIONS

Thermodynamic data and observed natural assemblages are used to eliminate potential solutions (Stout 1985). Experimental phase-equilibrium data allow one to accurately locate a univariant reaction in P–T space but do not rule out the possibility that the reac-

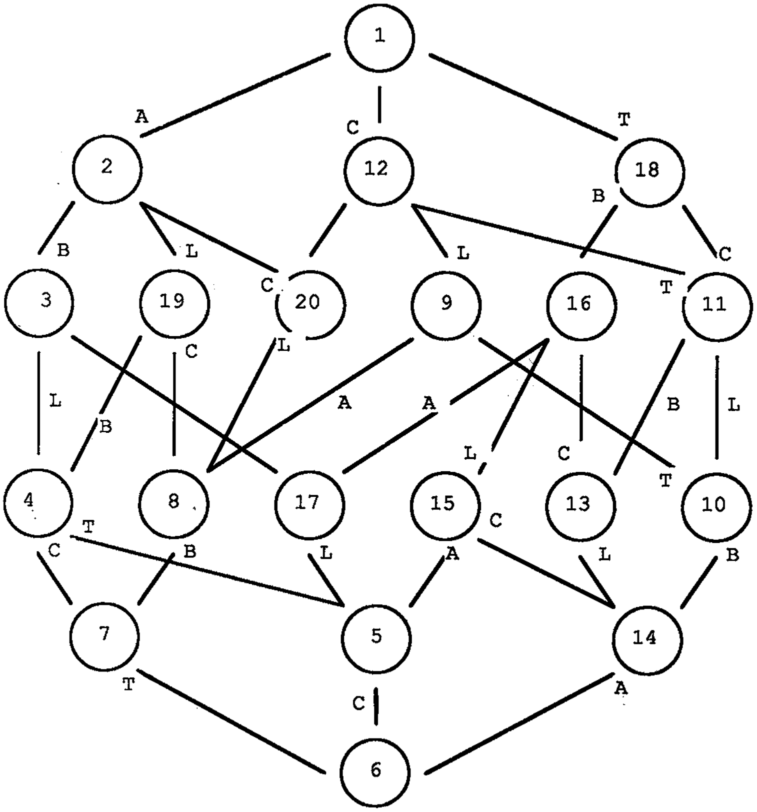

FIG. 2. Node diagram for the $n + 3$ system brucite, lizardite, chrysotile, antigorite and talc, described by $MgO-SiO_2$, projected through water. The numbers within the circles represent the various solutions. The letters represent the invariant point that must be transposed to obtain one solution from the other.

tion is metastable. This problem is less serious at high temperatures, where reaction rates are faster (Wood & Walther 1983). However, at temperatures of 100–200°C, the factors that control mass transfer within the system are important, and metastable assemblages may persist indefinitely.

Signs of entropy and volume changes associated with reactions can be used to eliminate potential solutions. Reaction triangles (Stout 1985), formed by three univariant lines that join three invariant points, are examined to insure that the three reactions indicate a consistent high-temperature and high-pressure direction (Zen 1966). An arrow is used to indicate the direction in which ΔV_R and ΔS_R are positive, where ΔV_R and ΔS_R are the volume and entropy changes of the reactions, respectively. If the arrows all point inward or outward from the triangle, the solution is thermodynamically impossible because a consistent high-temperature or high-pressure direction cannot be found.

The volume and entropy data for the phases of interest, at standard temperature and pressure, are listed in Table 1. Where possible, the data used were taken from Robie *et al.* (1978). However, inspection of Table 1 indicates that the data from the different sets agree well for forsterite, brucite, talc, water and the entropy of chrysotile. The value of 108.5 cm^3/mol for the volume of chrysotile was used because it was determined experimentally, whereas the value of 102 cm^3/mol for the volume of chrysotile was calculated from an equation proposed by Chernosky (1975). The value of 102 cm^3/mol was used for the volume of lizardite. As Chernosky was investigating the solubility of Al in lizardite, this value was thought appropriate for the Mg endmember. The standard entropy of lizardite was calculated from an entropy change of formation for an Al lizardite determined by Caruso & Chernosky (1979). As the uncertainty in the standard entropy of lizardite is large, no correction was made for the aluminum present in the lizardite sample used by Caruso & Chernosky. Data for orthoenstatite are available from only one data set.

The volume and entropy changes for the reactions were calculated at standard temperature and pressure (STP). The values for the volume and entropy changes calculated at STP may not be appropriate for higher temperatures and pressures. As a result, a potential solution eliminated by using STP data may not be eliminated by volume and entropy changes calculated at elevated temperature and pressure. The calculations to check this problem were not made for several reasons. Firstly, as the locations of the invariant points are not known, the appropriate temperatures and pressures to use in the calculations are not known either. Secondly, the necessary data are not available for lizardite. Thirdly, as the reactions in the $n + 3$ system are water-conservative reac-

TABLE 1. ENTROPY AND VOLUME DATA FOR THE MINERALS IN MAGNESIUM SERPENTINITES

Phase Chemistry	S (cal/moleK)	V (cm^3/mole)	Reference
Antigorite	51.22 ± 0.21	102.89 ± 0.51	7
$Mg_{2.85}Si_2O_5(OH)_{3.657}$	50.6 ± 0.4	102.89 ± 0.51	3
	53.3 ± 0.5[a]	104.56[a]	2
	50.66	102.89	4
Brucite	15.09 ± 0.03[a]	24.63 ± 0.07[a]	1
$Mg(OH)_2$		24.63	5
	15.09	24.63	2,4
	15.09 ± 0.05	24.63 ± 0.07	3
Chrysotile	52.89 ± 0.19[a]	108.5 ± 0.6[a]	1
$Mg_3Si_2O_5(OH)_4$		102.52	6
		107.15	5
	52.9	108.5	2,4
	52.9 ± 0.4	108.5 ± 0.6	3
Enstatite	15.84 ± 0.04[a]	31.29[a]	9
$MgSiO_3$			
Forsterite	22.75 ± 0.2[a]	43.79 ± 0.03[a]	1,3
Mg_2SiO_4	22.84	43.79 ± 0.03	6
		43.78	5
	22.75	43.79	2,4
Lizardite	42.2 ± 10.33[a]	102.5[a]	6
$Mg_3Si_2O_5(OH)_4$			
Talc	62.34 ± 0.15[a]	136.25 ± 0.26[a]	1,3
$Mg_3Si_4O_{10}(OH)_2$		136.2	5
	62.57 ± 0.02	136.25 ± 0.26	7
	62.34	136.25	4
Water (1 bar,298K)	16.72 ± 0.02[a]	18.07 ± 0.00[a]	1
H_2O			

[a] data used to calculate the entropy and volume changes of the reactions
1. Robie et al. (1978), 2. Hemley et al. (1977), 3. Evans et al. (1976), 4. Helgeson et al. (1978); 5. Zen & Chernosky (1976), 6. This study, using data from Caruso & Chernosky (1979), 7. Chernosky (1975), 8. King et al. (1967), 9. Day et al. (1985).

TABLE 2. SERPENTINITE REACTIONS AND THEIR ENTROPY AND VOLUME CHANGES

Reaction	ΔV_R (cm^3/mol)	ΔS_R(cal/molK)
Reactions in the n+3 system		
C = 0.15B + A	-1.92 ± 1.07	0.59 ± 0.69
	-1.44 ± 0.79	0.36 ± 0.4[a]
A = 0.88C + 0.06T	0.77 ± 1.06	-0.93 ± 0.6
	0.86 ± 0.74	-0.27 ± 0.53[a]
2C = 3B + T	-6.86 ± 1.61	1.81 ± 0.83
	-6.86 ± 1.24	1.81 ± 0.83[a]
2A = 2.65B + T	-4.26 ± 1.3	-0.11 ± 0.7
	-4.33 ± 1.07	1.08 ± 0.83[a]
L = 0.15B + A	4.08 ± 0.7	11.2 ± 10.5
A = 0.88L + T	-4.52 ± 0.76	-10.34 ± 9.31
2L = 3B + T	5.14 ± 0.99	23.21 ± 20.9
L = C	6.0 ± 0.86	10.66 ± 10.5

[a] Evans et al.(1976)

Reaction	ΔV_R (cm^3/mol)	ΔS_R(cal/molK)
Reactions in the n+4 and n+5 systems		
1.15C = 0.3F + A + 0.4W	-0.26 ± 1.2	7.06 ± 0.97
1.15B + A = 2.98W + 2F	10.21 ± 0.66	8.39 ± 0.97
A = 1.08F + 0.23T + 0.83W	-9.26 ± 0.79	1.62 ± 0.47
C = 1.2F + 0.2T + 1.8W	3.82 ± 0.68	17.02 ± 0.47
L = 1.2F + 0.2T + 1.8W	9.82 ± 0.08	27.71 ± 10.57
1.15L = 0.3F + A + 0.47W	6.65 ± 0.51	17.37 ± 12:11
0.5B + 0.5C = 1.5W + F	4.30 ± 0.34	13.84 ± 0.16
0.5B + 0.5L = 1.5W + F	7.33 ± 0.06	19.19 ± 5.24
1.25B + 0.25T = 1.5W + F	6.05 ± 0.19	13.32 ± 0.11
Reactions in the n+5 system only...		
A = 0.85F + 1.15E + 1.83W	3.16 ± 0.56	17.18 ± 0.28
0.3E + 0.85L = 0.17W + A	9.29 ± 0.54	13.42 ± 0.28
0.3E + 0.85C = 0.17W + A	4.29 ± 1.05	4.29 ± 0.40
A = 2E + 0.85B + 0.98W	-0.59 ± 0.63	10.07 ± 0.46
C = E + F + 2W	2.42 ± 0.66	19.34 ± 0.53
L = E + F + 2W	8.52 ± 0.06	30.03 ± 10.67
C = B + 2E + W	21.06 ± 0.61	11.00 ± 0.44
L = B + 2E + W	2.42 ± 0.13	21.69 ± 10.58
B + E = W + F	5.38 ± 0.13	8.34 ± 0.35
0.16L + 0.16T = 0.48W + E	2.32 ± 0.19	7.30 ± 1.77
0.16C + 0.16T = 0.48W + E	0.60 ± 0.29	5.59 ± 0.14
0.16T + 0.18A = 0.49W + E	-0.53 ± 0.29	4.91 ± 0.15
0.2F + 0.2T = 0.2W + E	-1.30 ± 0.21	2.32 ± 0.07
0.25B + 0.25T = 0.5W + E	0.07 ± 0.23	4.98 ± 0.12

Entropy and volume changes calculated at 1 bar and 298K tions (because of the colinearity of the phases), the behavior of water will not control the sign of the volume nor the entropy change. The last reason is that the P–T co-ordinates of many of the reactions are known in the $n + 4$ system that will be constructed later, and this knowledge can be used to eliminate potential solutions.

The reactions for the system under consideration are listed in Table 2. As the sign of ΔV_R for the reaction $A = C + T$ and ΔS_R for the reactions $C = B + A$, $A = C + T$ and $A = B + T$ are uncertain, they were not used to evaluate the consistency of reaction triangles. Using the volume and entropy changes for the other reactions to test individual reaction-triangles eliminated 14 of the 20 potential solutions in the following manner. Three reaction triangles in potential solution 1, defined by the invariant points [A], [L], [C]; [A], [B], [C], and [A], [T], [C] did not pass the consistency test using the volume changes. Thus, potential solution 1 was eliminated. Solution 12, obtained from solution 1 by transposing invariant point [T] (Fig. 2), and solution 18, obtained by transposing invariant point [C], are also eliminated because two of the three reaction triangles that eliminated solution 1 are still present in solutions 12 and 18. Volume considerations eliminated solutions 3,5,6–10, 16 and 17 as well. Entropy considerations eliminated solutions 4 and 11. As mentioned earlier, the assemblage B + T has not been reported; the two potential solutions (13 and 19) that show this assemblage as stable at 350°C at low pressure were eliminated.

Four potential solutions (numbers 2, 14, 15 and 20) remain. Solutions 2, 14, 20 and 15m, the mirror image of solution 15, are shown in Figure 1. [The mirror image of a potential solution is obtained by changing the parity of every invariant point in the solution. The potential solution and its mirror image are equivalent because the mirror image preserves the orientation criteria of the potential solution. Thus, whether the potential solution or its mirror image is used is a matter of convenience.] None of the reactions in this system has been located experimentally, so that the potential solutions cannot be placed in P–T space, although the entropy and volume changes for the reactions allow the potential solutions to be oriented in P–T space. Figure 3 shows part of the preferred solution of Evans *et al.* (1976) for the 3-component, 6-phase system brucite, forsterite, chrysotile, antigorite, talc and water. As the reaction $B + T = C$ has not been observed, all four remaining solutions are consistent

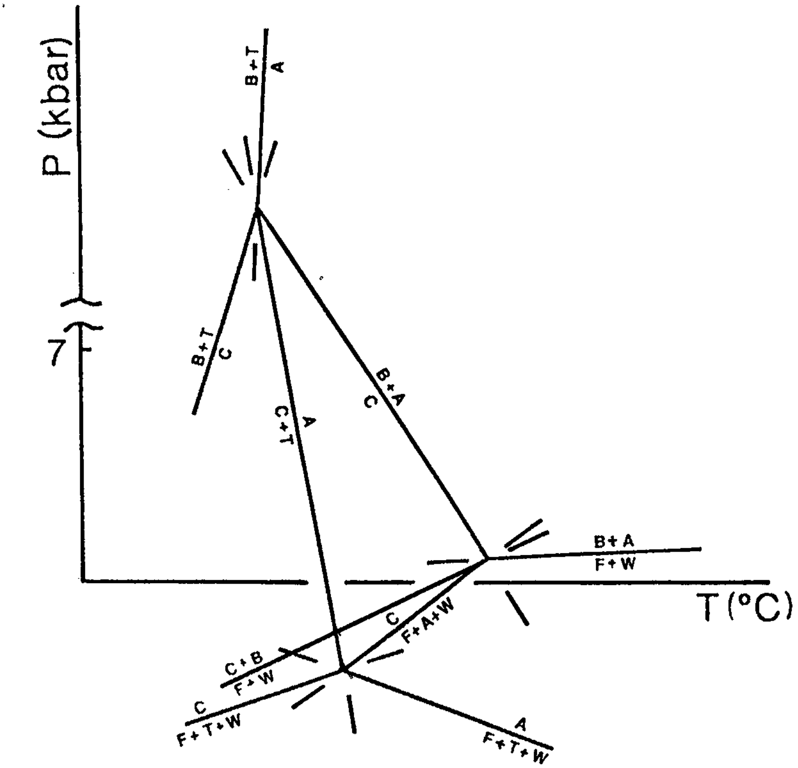

FIG. 3. The solution presented by Evans *et al.* (1976) for the system brucite, forsterite, antigorite, chrysotile, talc and water, described by $MgO–SiO_2–H_2O$.

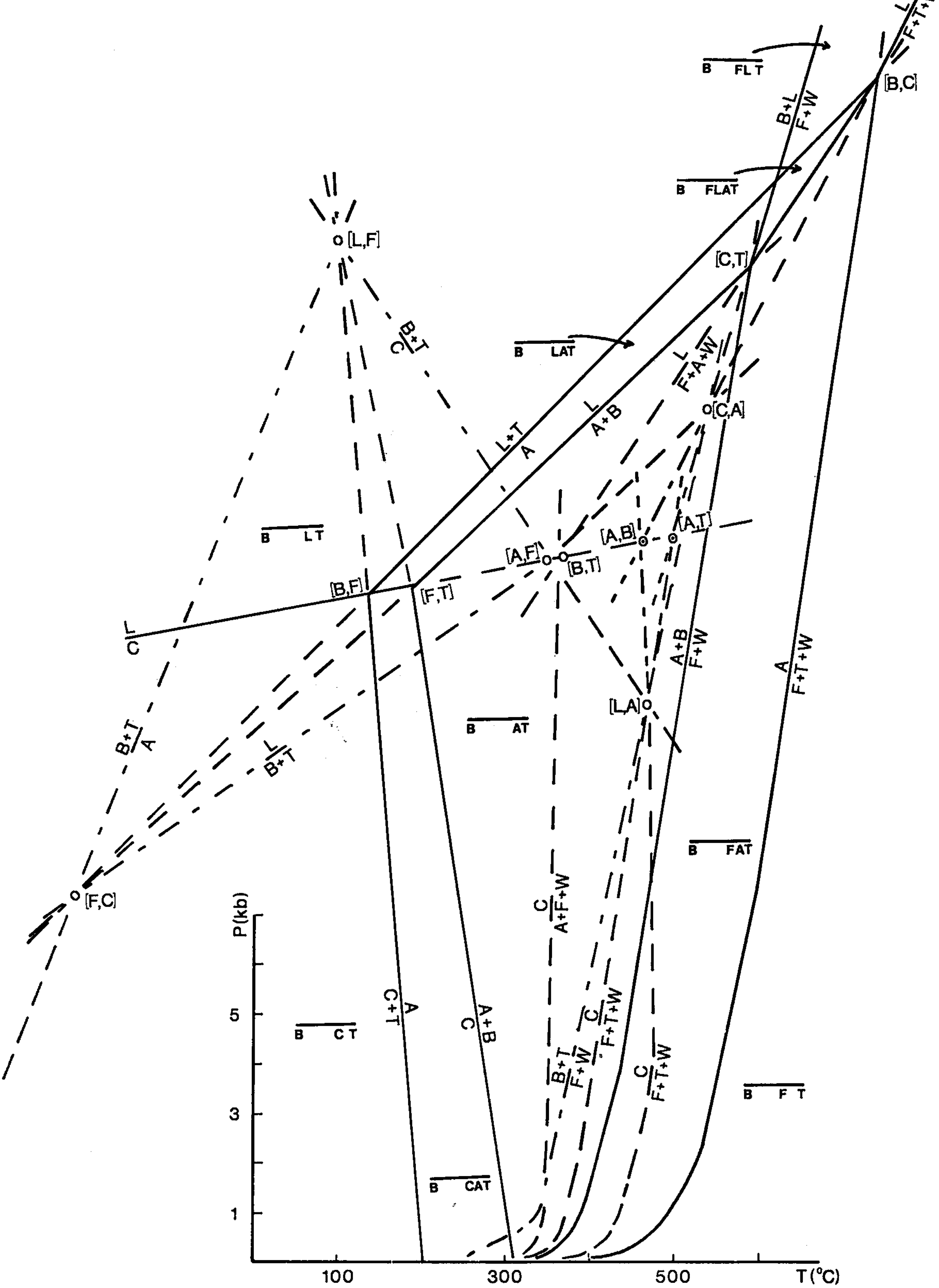

FIG. 4. Potential solution of the $n+4$ system, constructed from the dual network of Figure 1c. The symbolism is the same as in previous figures. Open circles with dots inside represent doubly metastable invariant points. [L,C], [B,L] and [L,T] are located below the temperature axis. The part of the phase diagram below 300°C is approximate because no experimental data are available, although the topological relationships are correct.

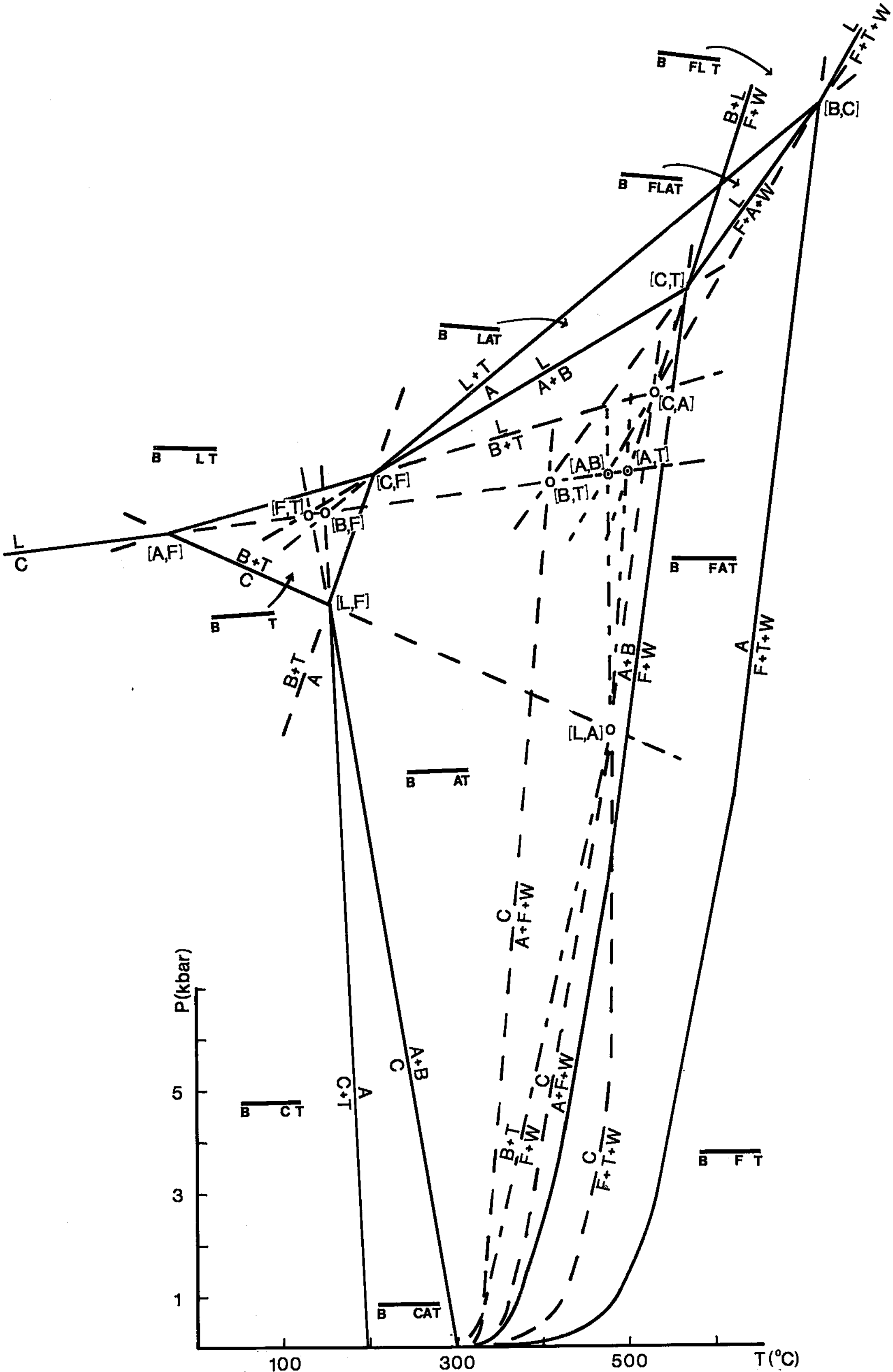

FIG. 5. Potential solution of the $n+4$ system constructed from the dual network of the phase diagram in Figure 1d. [L,C], [B,L] and [L,T] are located below the temperature axis. See caption of Figure 4 for restrictions.

with Figure 3, if the reaction L = C, or invariant point [L], is located at a pressure greater than 7 kilobars.

THE SIX- AND SEVEN-PHASE SYSTEMS

The dual networks of the four remaining potential solutions of the $n + 3$ system were used to construct dual networks for the $n + 4$ system. Forsterite was added to the 5-phase system to form a 2-component 6-phase system. The orientation of the dual networks for the remaining solutions of the $n + 3$ system is known. As the forsterite-bearing assemblages are stable at temperatures higher than those represented by the assemblages in the $n + 3$ system, the divariant fields containing the assemblages A + F and F + T were added to the high-temperature side of the dual networks (see O'Hanley 1987, Fig.

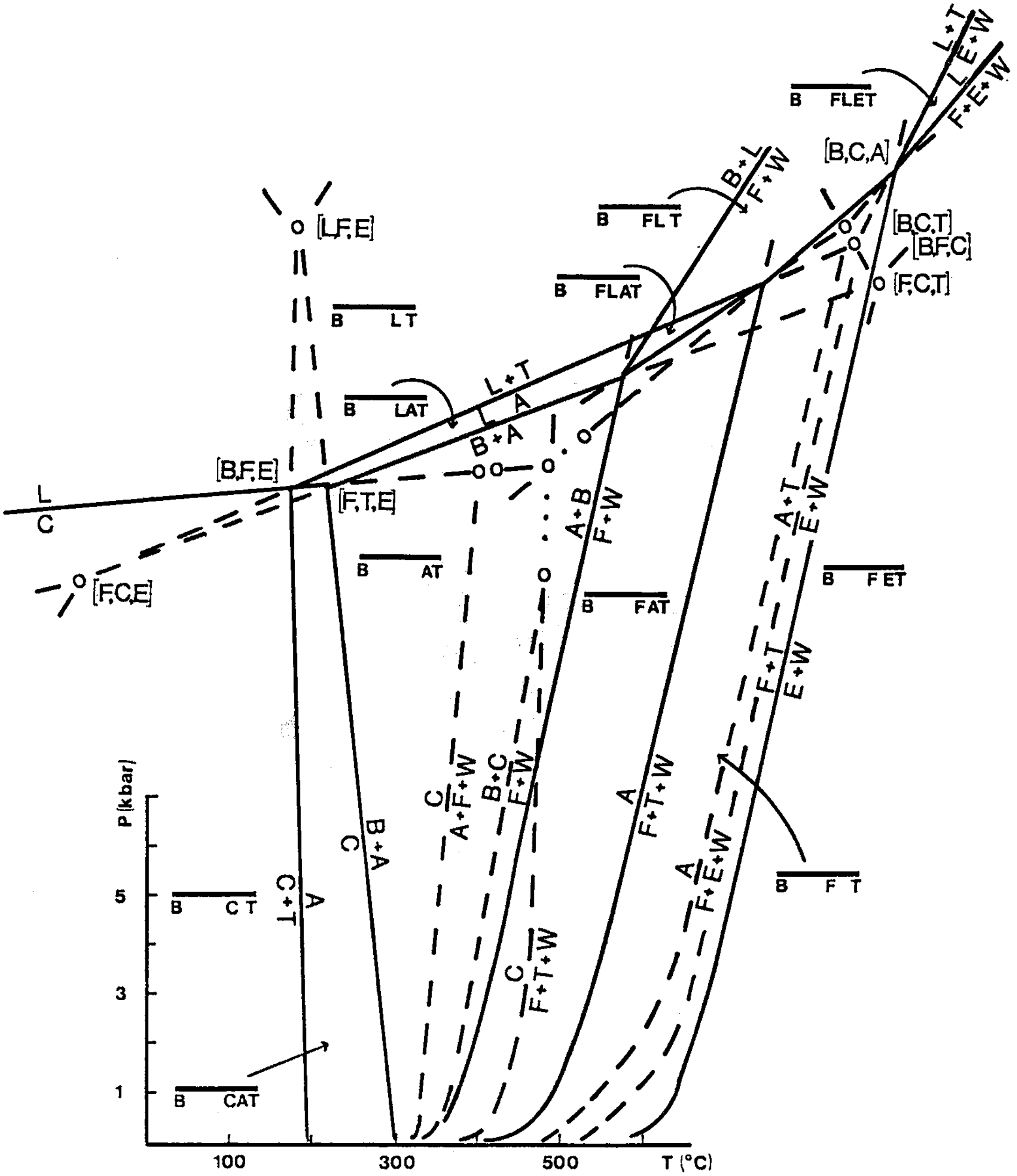

FIG. 6. Potential solution of the $n + 5$ system constructed from the phase diagram in Figure 4. Only stable and metastable equilibria are shown. See Figure 4 for labels of invariant points and restrictions.

7). Two of the potential solutions for the $n + 4$ system are shown in Figures 4 and 5.

The potential solutions for the 7-phase system are constructed by adding the divariant fields containing the F + E assemblage to the dual networks of the 6-phase system. The chemography of the 7-phase system is B–F–L–C–A–E–T. Owing to the absence of anthophyllite from this system, the reaction F + T = E + W generates the F + E assemblage (Evans 1977), so that the divariant field B–F–E–T was added to the field B–F–T of the dual networks of the 6-phase system. The potential solution shown in Figure 6 contains the summary diagram of Evans (1977) for temperatures less than 700°C. The $n + 5$ potential solution obtained by augmenting the dual network of the potential solution in Figure 5 also includes the diagram of Evans (1977) but differs from Figure 6 in not having a stability field for B + T.

DISCUSSION

The stability of the reactions C + T = A and C = B + A could not be determined in the $n + 3$ system owing to a lack of data. The $n + 4$ system contains more known information than the $n + 3$ system owing to the addition of reactions involving forsterite. The invariant point [L,F] is well constrained in the $n + 4$ system, and its parity (based on the reactions involving forsterite) dictates the stability of the reaction C = B + A.

The reaction L = C has not been investigated experimentally; thus the evidence for its existence is indirect. Lizardite and chrysotile both have been synthesized in the system MgO–SiO_2–H_2O (Chernosky 1975), and comparison of chemical compositions of natural samples has not revealed any consistent behavior of trace metals or minor elements sufficient to justify separating lizardite and chrysotile chemographically (Page 1968, Wicks & Whittaker 1977, Wicks & Plant 1979, Cressey 1979). However, no systematic comparison of the chemistry of lizardite and chrysotile from the same rock suite has been made. Most recent studies were undertaken to interpret serpentinite textures (Wicks & Whittaker 1977, Wicks & Plant 1979). These studies have concentrated on samples taken from different, widely dispersed geographic areas that would help elucidate the generation of serpentinite textures. Analytical data given by Wicks & Plant (1979) suggest that systematic differences between lizardite and chrysotile may exist in a given sample: in sample number 18538 (analysis 7, p. 806), from the Jeffrey mine, Quebec, lizardite mesh rims (7–1) are more iron-rich than chrysotile mesh centres (7–2). However, in sample 18501 (Table 7, p. 807), from the Pie Lake mine, Manitoba, chrysotile mesh rims are slightly more iron-rich than intimately mixed lizardite–chrysotile mesh cores. Knowing the chemistry of the intimately mixed lizardite and chrysotile would be useful in deciding if the polymorphic relationship is an appropriate model.

Investigating the common observation of lizardite and chrysotile within mesh textures (Cressey & Zussman 1976, Wicks & Whittaker 1977, Cressey 1979) may provide the data necessary to establish, or disprove, the polymorphic relationship used in this paper. Comparing samples from different geographic localities to illustrate that lizardite and chrysotile have overlapping chemistries may not be relevant petrologically. One needs to show that the chemistry of lizardite and chrysotile is distinct in rock samples that have the same bulk chemistry.

A detailed study of a given rock-suite would also indicate if a lizardite–chrysotile isograd exists. That is, does lizardite alter to chrysotile as pressure decreases? However, interpreting phase relationships from assemblages found in serpentinites is difficult because of the fine grain-size and intimate intergrowth of the minerals. These factors make mineral identification uncertain unless other instruments, such as an X-ray microbeam camera, are brought to bear on the problem. For example, chrysotile is observed replacing lizardite during type-5 serpentinization (Wicks & Whittaker 1977), but brucite may be produced during this process as well (Çogulu & Laurent 1984). Therefore, whether the reaction that represents the replacement of lizardite is L = C or L = B + C remains to be demonstrated.

Evans *et al.* (1976) stated that the assemblages C + T, A + B, A + F and F + T should be stabilized with increasing temperature in serpentinites. In the four solutions remaining from the $n + 3$ system, the assemblages L + T and A + B as well as C + T and A + B are in the proper sequence regardless of the location of the reaction L = C. Therefore, it is the location of the reaction L = C, not the forsterite-bearing assemblages, that determines the stability of lizardite or chrysotile.

Placing the reaction L = C at high pressure preserves the order of reactions given by Evans *et al.* (1976) in their discussion of serpentine equilibria. However, they did not consider lizardite, and their evidence for omitting it is not compelling. The serpentinites in the Oberhalbstein contain both lizardite and chrysotile (Dietrich & Peters 1971) and either phase, or both, could have participated in the reactions. If L = C is placed at low pressure, then the reactions in Figure 3 could involve lizardite rather than chrysotile. The stability of the reactions A + B = F + W and A = F + T + W is not affected by the position of L = C because L = C is metastable above 300°C.

The curvature of the reactions B + C = F + W and A = F + T + W requires the convergence of the reactions C + T = A, C = A + B, B + A = F + W and A = F + T + W at low pressure. In the $n + 4$ phase diagrams derived from Figures 1a and d, these reactions diverge at low pressure, thus eliminating these two potential solutions. In this case the larger system has placed constraints on the smaller system, reducing the number of potential solutions. Both Figures 4 and 5 contain the phase diagram generated by Evans *et al.* (1976), showing the importance of considering as many phases as possible in the multisystem.

Dungan (1979) and Evans (1977) stated that during progressive metamorphism, antigorite should disappear before enstatite appears. The sequence of divariant fields B–F–A–T, B–F–T, B–F–E–T, in the absence of anthophyllite, accounts for this observation, making the reaction F + T = E + W stable in this system. The absence of anthophyllite from the chemography reduces the use of these potential solutions for prograde metamorphism because anthophyllite is stabilized after antigorite but before enstatite with increasing temperature (Evans 1977).

Calculations by Delany & Helgeson (1978) on a number of phases in the multisystem MgO–SiO_2–H_2O, generated four invariant points that appear in the full potential solution of Figure 6: [L,A,T], [B,L,A], [B,L,C], and [L,C,T]. The work of Caruso & Chernosky (1979) postdates the work of Delany & Helgeson. Assuming that the results of Delany & Helgeson are still valid, then all of the invariant points in Figure 6 are below ~22 kbars and 500°C, which is the location of [B,L,A]. Thus the reaction L = C would be below these values as well.

At present, the discussion of the stability or metastability of lizardite and chrysotile in serpentinites is hampered by the lack of information on the reaction L = C. If one assumes that lizardite is metastable at low to moderate pressures (for example, L = C is located at >8 kilobars), a large number of reactions involving lizardite extend metastably to low pressure and to temperatures below the reactions C + T = A and C = A + B. This allows type-3 serpentinization to precede type-5 serpentinization, as observed in the Jeffrey and Lake Asbestos mines in Quebec (Wicks & Whittaker 1977, Çogulu & Laurent 1984). Petrographically, this could appear as lizardite being destabilized by replacement veins of chrysotile. This interpretation makes lizardite metastable under the P–T condition represented by these textures.

Field evidence points to the formation of serpentinites at relatively low pressures. The metamorphic facies found in the country rock surrounding serpentinites indicate that the pressure was not greater than 8 kilobars (Evans 1977). Further evidence supporting the formation of serpentinites at low pressure is the presence of fractures within serpentinites that Wicks (1984), based on the work of Rayleigh & Paterson (1965), interpreted as forming at less than 5 kbars. Thus if the reaction L = C is located at pressures greater than 8 kilobars, then chrysotile is stable in Mg serpentinites.

Another possibility is that other cations are important to the stability of lizardite, and thus lizardite and chrysotile are not polymorphs. For example, if lizardite is more aluminum-rich than the coexisting chrysotile, then lizardite is stabilized to lower-pressure and higher-temperature conditions and has a more extensive region of stability in P–T space. This explanation was proposed to explain the observation made by Frost (1975) that lizardite is found 30 metres beyond the antigorite-out isograd (Caruso & Chernosky 1979). Cressey (1979) has observed intergrowths of lizardite, chrysotile and clinochlore in mesh textures, suggesting that sufficient aluminum is present in some serpentinites to stabilize clinochlore with lizardite and chrysotile. Determining the chemistry of lizardite and chrysotile in this situation would be illuminating. Thus the compositions of coexisting lizardite and chrysotile are critical to determine the stability of lizardite and chrysotile as well as to establish the relationship between them. This problem is currently being investigated by the author.

CONCLUSION

The method of dual networks allows one to include as many phases in the chemography as necessary to describe the observations. In this sense the limitation of multisystem investigations to $n + 3$ phase systems is artificial, although the new method takes advantage of the methodology of $n + 3$ systems. Using observations to construct the dual network automatically filters out many potential solutions. This is important because it makes the investigation of large systems feasible.

The hypothesis that lizardite and chrysotile are polymorphs in Mg serpentinites has been investigated. Owing to the presence of minor elements in rock specimens, the best way to test the hypothesis would be by experiment with pure materials. As lizardite–chrysotile serpentinites appear to represent pressures less than 6 kilobars (Wicks 1984), experiments with chrysotile as the starting phase at conditions of 250°C and 3 to 6 kilobars would be appropriate. One must determine if the reaction L = C exists, and then determine which mineral, lizardite or chrysotile, is stable.

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