Stability of chrysotile and antigorite in the serpentinite multisystem

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Stability of Chrysotile and Antigorite in the Serpentinite Multisystem

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With 4 figures and 4 tables

Abstract

Consideration of the chemistry of antigorite and chrysotile, together with field evidence and available and new experimental data, permit construction and calibration of a PT-net in a MgO-SiO_2-H_2O multisystem consisting of the phases antigorite, chrysotile, brucite, forsterite, talc and water. According to this model, the upper temperature limit of stability of chrysotile and the lower temperature limit of antigorite are given by H_2O-absent reactions with negative slopes on the PT-plot. The lower stability limit of forsterite + H_2O, at most metamorphic pressures, is outside the field of stable chrysotile. Antigorite is stable relative to talc, forsterite and water to $580°C$ at 6 kb and $622°C$ at 10 kb.

Introduction

As a contribution to the problem of their relative stabilities, the consequences of differences in the compositions of the serpentine minerals are explored. One of the unique pair of P-T topologies defined by chemographic relations among six phases in the system MgO-SiO_2-H_2O will be selected on the basis of qualitative thermodynamic criteria and field relationships. This diagram will then be refined using existing experimental and thermochemical data, new experimental data on antigorite, and additional inferences from petrography.

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Chemistry of Serpentines

Although the compositional differences between the various serpentine-group minerals are small, there seems to be agreement on the following points (FAUST and FAHEY, 1962; DEER, HOWIE and ZUSSMAN, 1962; PAGE, 1968; WHITTAKER and WICKS, 1970; AUMENTO, 1970). Relative to the ideal serpentine composition $Mg_3Si_2O_5(OH)_4$, antigorite is rich in SiO_2 and poor in MgO and H_2O, although the ratio $MgO : H_2O$ is about the same. In ratio $MgO : SiO_2$, most chrysotiles and lizardites are consistent with the ideal formula, whereas both seem to contain excess H_2O[1]). Lizardite tends to be richer in Al_2O_3 and Fe_2O_3 than chrysotile, and higher in $Fe^{3+} : Fe^{2+}$ relative to antigorite. Microprobe analyses of antigorite (e.g. TROMMSDORFF and EVANS, 1972; FROST, 1973; DUNGAN, 1974) tend to confirm the SiO_2-rich and MgO-poor nature of antigorite, and almost all of these satisfy, within the limits of analytical uncertainty, the proportions of tetrahedral and octahedral cations in the formula $Mg_{2.8235}Si_2O_5(OH)_{3.647}$, a composition derived from the typical crystal structure (ZUSSMAN, 1956; KUNZE, 1956, 1961).

Of the various serpentine minerals, only chrysotile and antigorite will be considered in this study. It is possible, but not necessarily the case (CHER-NOSKY, 1975), that lizardite, which is normally very fine-grained, owes its existence to the presence of Al_2O_3 or Fe_2O_3, or to the fact that it is typically a replacement of pre-existing olivine or pyroxene. The frequent occurence of antigorite and chrysotile in fissures and veins proves that their existence is not necessarily determined by the geometry or chemistry of a pre-existing crystal structure. We therefore believe there is no reason not to assume that their relative distribution is controlled by P, T and the chemical potentials of the components. Relatively pure natural antigorites and chrysotiles do occur, and both species have been synthesized in the MgO-SiO_2-H_2O system (NOLL, 1944; BOWEN and TUTTLE, 1949; IISHI and SAITO, 1973; JOHANNES, 1975). Thus, it is reasonable to explore the stability relationships of chrysotile and antigorite in the pure three-component system.

The ideal serpentine formula will be adopted for chrysotile and the formula unit $Mg_{48}Si_{34}O_{85}(OH)_{62}$, which is exactly 17 times larger than that given above, for antigorite. These compositions plot colinear with brucite and talc in the system MgO-SiO_2-H_2O (Fig. 1), and furthermore this colinearity is independent of compositional variation resulting from variation in the super-lattice dimension of antigorite, since only more or less of $Mg(OH)_2$ is in-

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[1]) DEER, HOWIE and ZUSSMAN (1962, p. 180) suggest, on the basis of a low temperature d.t.a. peak for fine-grained serpentines, that H_2O^+ in some analyses may include surface water. In addition, some chrysotile tubes are filled with water (HUGGINS and SHELL, 1965).
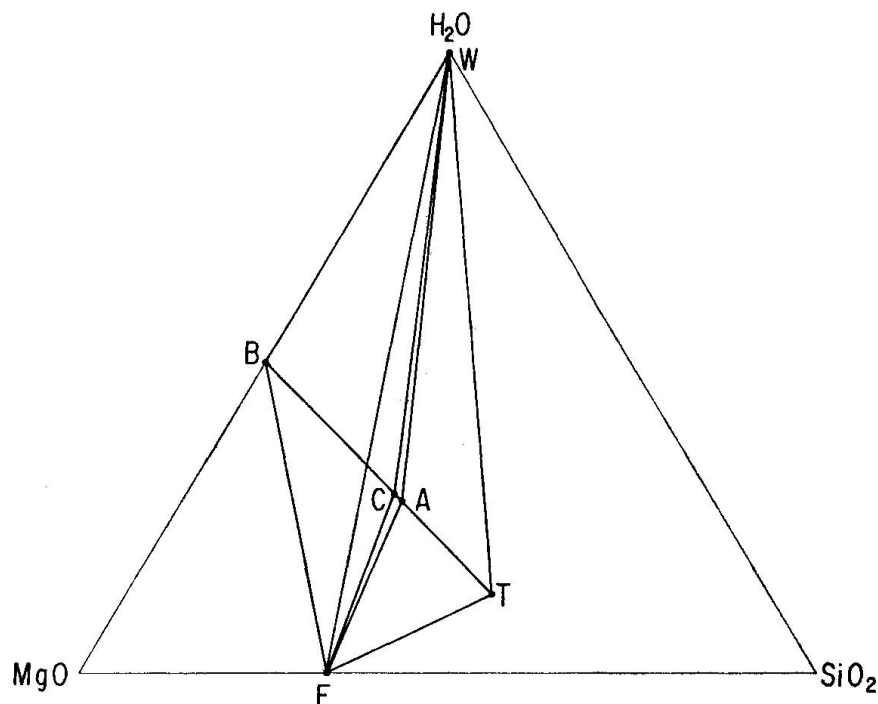
Fig. 1. Chemography of brucite B, chrysotile C, antigorite A, talc T, forsterite F and water vapor W
in the system MgO-SiO_2-H_2O.

volved. Thus, all reactions between antigorite, chrysotile, talc and brucite can
be written without the participation of H_2O as an additional phase.

Chemography and Possible Topologies

The six phases, antigorite, chrysotile, brucite, talc, forsterite, and water
vapor will be treated as a three-component multisystem. The chemography
is a quadrilateral with two interior points and a diagonal four-phase co-
linearity (Fig. 1). There are ten possible univariant reactions (Table 1), and six
possible invariant points, two of the latter, namely (W) and (F)[2], coinciding
at the same level of stability.

All phase elements (SKIPPEN and TROMMSDORFF, 1975) are contained in one
fully closed net (Fig. 2a; ZEN and ROSEBOOM, 1972). When the condition
that the univariant lines be straight is imposed, four nets of maximum closure
may be derived from this one net; in the terminology of DAY (1972), these nets
are ((F) (W)), ((B) (T)), and ((A)), which are all triangular, and ((C)), which is
quadrilateral[3]. All the nets, of course, possess an inverse net (Fig. 2b).

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[2]) Mineral abbreviations are listed in the caption to Fig. 1 and in Table 2.

[3]) Chemography Q 26 with net label ((6)) in DAY (1972, Table 3) is incorrectly stated to
correspond to topology 8. There are four reactions terminal to 6 (our C), so the topology for
this net must be quadrilateral.

Table 1. *Univariant Equilibria in the Serpentinite System*

Absent	Stoichiometry[2]	Equilibrium Constant[1]		
		A	B	C
(AB)	5 C = 6 F + T + 9 H_2O	−76500	158.31	1.726
(AC)	5 B + T = 4 F + 6 H_2O	−40095	99.54	1.014
(AFW)	2 C = 3 B + T	−6543	3.60	0.082
(AT)	B + C = 2 F + 3 H_2O	−23319	51.57	0.548
(BC)	A = 18 F + 4 T + 27 H_2O	−210330	433.89	5.002
(BFW)	15 C + T = A	−19170	41.04	0.176
(BT)	20 C = 6 F + A + 9 H_2O	−95670	199.35	1.902
(CFW)	2 A = 45 B + 17 T	−59805	−28.08	0.878
(CT)	A + 20 B = 34 F + 51 H_2O	−370710	832.05	9.058
(TFW)	17 C = A + 3 B	−25713	44.64	0.258

[1]) $\ln K = \dfrac{A}{T} + B + \dfrac{C(P-1)}{T}$ where T is °K and P is pressure in bars.

[2]) See Table 2 for abbreviations and mineral formulae. Fugacity data from BURNHAM et al. (1969); volume data from ROBIE and WALDBAUM (1968).
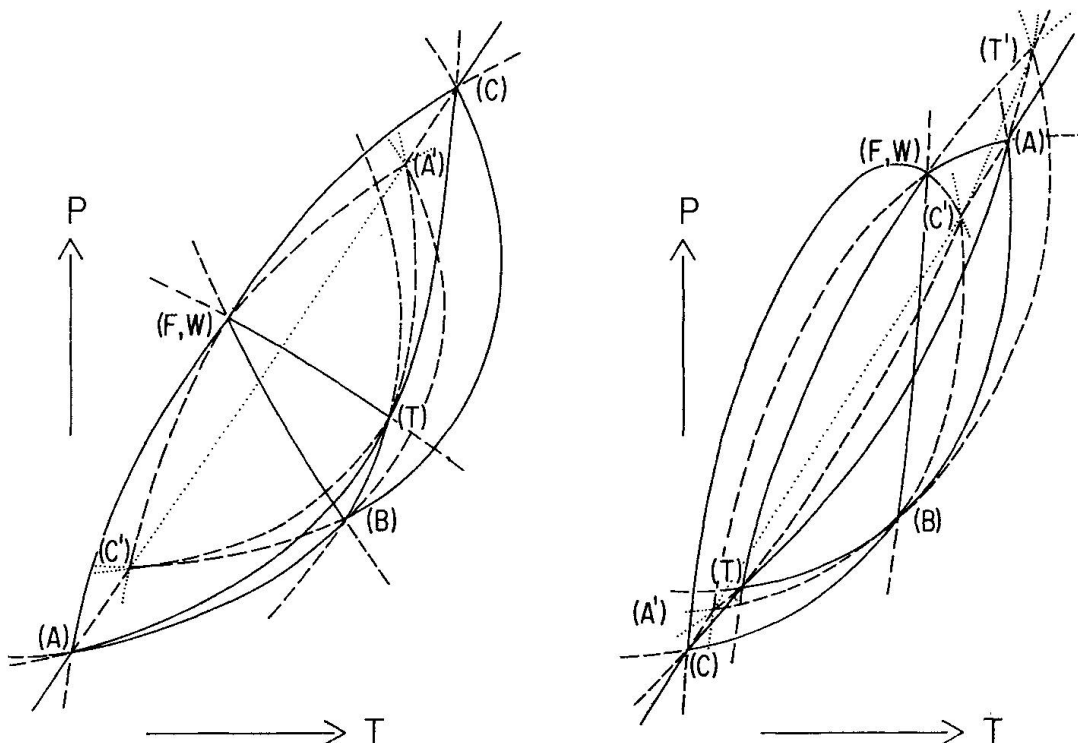
Fig. 2a.   Fig. 2b.

Fig. 2. Theoretically possible part of the multisystem net for the six phases A, B, C, F, T and W. Continuous lines are stable, dashed and dotted lines metastable. Primes indicate metastable invariant points. (F′, W′), (B′), and (T′) lie off the diagram.

The inverse nets of Fig. 2 have been drawn in such a manner that two elementary thermodynamic criteria are satisfied: (1) all W-present reactions produce water vapor with temperature increase, (2) all W-absent reactions decrease in estimated volume with pressure increase (volume data are set down in Table 2).

Table 2. *Molar Volume and Entropy Data (298 K, 1 bar)*

			$Vcm^3 . gfw^{-1}$	$S\ cal.\ deg.^{-1}\ gfw^{-1}$	
B	Brucite	$Mg(OH)_2$	24.63 ± 0.07[1])	15.09 ± 0.05[1])	
C	Chrysotile	$Mg_3Si_2O_5(OH)_4$	108.5 ± 0.6[1])	52.9 ± 0.4[2])	
A	Antigorite	$Mg_{48}Si_{34}O_{85}(OH)_{62}$	$(102.89 \pm 0.51) \times 17$[3])	$(50.6 \pm 0.4) \times 17$[2*])	
T	Talc	$Mg_3Si_4O_{10}(OH)_2$	136.25 ± 0.26[1])	$\begin{cases} 62.34 \pm 0.15[1]) \\ 57.65[4]) \end{cases}$	
F	Forsterite	Mg_2SiO_4	43.79 ± 0.03[1])	22.75 ± 0.20[1])	

Water Absent Reactions			$\Delta V\ cm^3$	$\Delta S\ cal.\ deg.^{-1}$	
(TFW)	$17\ C =$	$3\ B + A$	-24.48 ± 13.39	6.17 ± 6.80	
(AFW)	$2\ C =$	$3\ B + T$	-6.86 ± 1.24	1.81 ± 0.83	-2.88[4])
(CFW)	$2\ A =$	$45\ B + 17\ T$	-73.66 ± 18.17	18.43 ± 14.02	-61.3[4])
(BFW)	$15\ C + T =$	A	-14.62 ± 12.50	4.36 ± 9.07	9.05[4])

Sources of data:
[1]) Robie and Waldbaum (1968); [2]) King et al. (1967); [3]) Kunze (1961); [4]) Bricker et al. (1973); [2*]) Modified from S antigorite $(Mg_3Si_2O_5(OH)_4)$ given by King et al. (1967), as 53.2, by recomputing apparent impurities (as quartz and ice) with the new formula (Oterdoom, 1975).

Experimental data for three dehydration reactions in this system (Scarfe and Wyllie, 1967a, b; Johannes, 1968, 1975; Chernosky, 1973) show clearly that they occur in order of increasing temperature (over the range of experimental pressures) as follows: (AT), (AB), and (BC). New data on the upper limit of stability of antigorite, reaction (BC), obtained by Johannes, are given later in this paper. Including both stable and less stable segments of curves, this progression of curves is consistent with the topology of Fig. 2a and with its inverse, Fig. 2b; that is, the same sequence is encountered isobarically between invariant points (B) and (A') in both diagrams. Unfortunately, an experimentally unattainable precision in the Clapeyron slopes of the three curves is required to determine in which direction the curves intersect, that is, which of the two topologies is correct.

On the other hand, it can be quickly deduced from field data that only the toplogy of Fig. 2a can be correct. The assemblage A + B is common at higher metamorphic grades than C (reaction (FWT), Fig. 2), for example, Dietrich and Peters (1971), Bocquet (1974), Trommsdorff and Evans (1974). In the same areas these authors have mapped wide F-free, A-bearing zones above the upper limit of C. Both observations are only consistent with Fig. 2a and not with Fig. 2b. In Fig. 2b, the frequently described formation of A from C (e.g. Cornelius, 1912; Benson, 1918; Rost, 1949; Hess, et al., 1952; Wilkinson, 1953; Leech, 1953; Francis, 1956; Deer, Howie and Zussman, 1962; Coats, 1968; Matthes, 1971; Springer, 1975) would *only* be possible (unless there were also some mass transfer) according to the forsterite-producing reaction C = F + A + W (BT).

Reaction entropies for the W-absent reactions are of the same order of magnitude as their estimated uncertainties (Table 2). Thus, it is hazardous to use these data to predict the high temperature assemblage, or the signs of

the slopes of the univariant curves. Use of the entropy for talc from BRICKER et al. (1973), even changes the signs of the slopes of reactions (AFW) and (CFW) – such orientations are permissible in both topologies. Interestingly, however, if we take the volume and entropy data for reactions (FWT) and (BFW) at their face value, the topology of Fig. 2a is again satisfied, and that of Fig. 2b ruled out (since the slopes of these curves can only be made negative in Fig. 2b by counter-clockwise rotation, giving the wrong signs for *both* ΔS and ΔV).

Refinement of the Serpentine Phase Diagram

Having established the unique topology for the serpentine phase diagram, we must now determine what parts of the diagram pertain to metamorphic pressure-temperature conditions, and where the ten phase boundaries are located. These objectives can be realized first through the application of field and petrographic data of the following kinds: a) occurrence of assemblages for which stable equilibrium can be inferred, b) the sequences of assemblages in profiles of increasing regional and contact metamorphism, c) by calibration of these sequences with reactions in associated rocks of other bulk compositions. Secondly, the available experimental data on serpentines serve to complete the refinement.

FIELD AND PETROGRAPHIC DATA

a) Field data indicate that the following *critical* divariant assemblages have a stable existence: A + B, A + F, F + T, B + C, C + T. The criterion for stability of the first three mineral pairs is that they are found in progressive metamorphism, i.e. it can be inferred that they have formed from assemblages only one stability level lower; for example, F + T have formed directly from A (TROMMSDORFF and EVANS, 1974, Plate IC), and A + B have formed from C (DIETRICH and PETERS, 1971, Plate III; HAHN-WEINHEIMER and ROST, 1961). We infer a stability field for chrysotile (hence for B + C and C + T) because chrysotile has been observed to have formed *directly* from antigorite (CHIDESTER, 1962, Fig. 20; JAHNS, 1967, Table 5.3; COLEMAN, 1971, p. 901; KEUSEN, 1972, p. 418, PAGE and NOCKLEBERG, 1972, p. 140). We have, in addition, found chrysotile replacing the antigorite schist of Val Malenco in Val Scerscen, Italy. Therefore our diagram must encompass at least parts of the following divariant regions (see Fig. 2a): (CBA), (CBT), (CFWT), (BFWT) and (ABFW). This implies that the W-absent reactions (BFW), i.e. C + T = A and (TWF), i.e. C = A + B must occur on the diagram. To our knowledge, the paragenesis B + T has not been reported. Hence the P–T conditions of the divariant

field (ACFW) and the bounding W-absent reactions (CFW) and (AFW) may not be realized in nature.

b) The observed sequence of reactions in progressive metamorphism is:

I. (BFW) $C + T \to A$. For example, antigorite first appears as veins in lizardite-chrysotile serpentinites in the northern Oberhalbstein (DIETRICH and PETERS, 1971).

II. (FWT) $C \to A + B$. For example, $A + B$ have a first appearance in the southern Oberhalbstein (CORNELIUS, 1912; DIETRICH and PETERS, 1971).

III. (CT) $A + B \to F + W$. For example, at higher grades than (II.) in Val Malenco, the assemblage $A + B + F$ is common (TROMMSDORFF and EVANS, 1972; BUCHER and PFEIFER, 1973).

IV. (BC) $A \to F + T + W$. For example, the Bergell tonalite contact aureole and the Lepontine regional metamorphism (TROMMSDORFF and EVANS, 1974), Erbendorf, Bavaria (MATTHES, 1971), Mt. Stuart, Washington (FROST, 1975).

Although this complete sequence has not been fully described from contact metamorphism, the sequence is consistent with the first appearance of antigorite at the expense of chrysotile *before* the first appearance of forsterite + antigorite, which in turn precedes forsterite + talc (MATTHES, 1971; SPRINGER, 1974; FROST, 1975). Our diagram should therefore permit this sequence to occur isobarically as well as along a regional metamorphic P–T gradient. This, combined with the volume data, requires that reactions (BFW) and (FWT) have negative slopes on the P–T diagram. It also requires that the pressures of both invariant points (B) and (F) are located below common metamorphic P–T gradients.

c) The first appearance of antigorite in the Oberhalbstein (in veins with T but not B) coincides with the transition from the prehnite-pumpellyite to the pure pumpellyite zone (DIETRICH and PETERS, 1971). Unfortunately the P–T conditions for this transition are not yet known. In the southern Oberhalbstein, the reaction (FWT) is coincident with the beginning of the greenschist facies as indicated by the pumpellyite-out isograd (DIETRICH and PETERS, 1971; DIETRICH et al., 1974, Fig. 1). The reaction pumpellyite + chlorite + quartz → actinolite + epidote + H_2O is believed to take place at temperatures very approximately of 300° to 350°C (NITSCH, 1971). In the Western Alps, the distribution of rock-forming antigorite, often with B but not with F, overlaps widely with that of lawsonite (BOCQUET, 1974). This requires a stability field for $A + B$ at least as low as 350°C (CRAWFORD and FYFE, 1965; NEWTON, 1966; NITSCH, 1973).

EXPERIMENTAL

Theoretically, the P, T, f_{H_2O} relations of only three equilibria suffice to define all ten equilibria in Table 1. Three dehydration curves have been determined experimentally.

Table 3. *Experimental run data on the reaction (BC): A = F + T + W*

Runs with synthetic talc (T) + synthetic forsterite (F) + 10% natural antigorite (A) from Piz Lunghin

Run No.	Pressure (kb) Piston-cylinder runs	Temperature (°C)	Run duration (days)	Result
72	15	670	13	only T + F
109	15	660	28	only T + F
84	15	650	12	+ A
117	15	650	10	− A
111	15	650	21	only T + F
127	15	640	7	+ A
101	15	630	6	+ A
94	15	610	6	+ A
64	10	650	16	only T + F
115	10	630	7	− A
67	10	630	22	− A
110	10	625	10	no change
108	10	620	25	no change
112	10	615	19	+ A
54	10	610	22	+ A
87	10	610	20	+ A

Hydrothermal runs

Run No.	Pressure (kb)	Temperature (°C)	Run duration (days)	Result
42a	6	640	34	− A *)
42b	6	620	34	− A *)
48a	6	610	96	only T + F
40	6	605	82	only T + F
45a	6	600	136	only T + F
51a	6	595	195	only T + F
48b	6	590	96	only T + F
49a	6	580	156	no change
45b	6	580	136	no change
51b	6	575	195	no change
43b	6	570	60	no change
58a	6	565	195	no change
49b	6	560	156	+ A
58b	6	550	195	+ A
41a	4	580	162	T + F + trace A
56a	4	570	210	− A
41b	4	560	162	no change
53a	4	555	255	no change
44	4	550	186	no change
57a	4	540	255	no change
57b	4	530	255	no change
57c	4	520	255	+ A
46a	2	570	245	only T + F
47a	2	560	408	only T + F
60	2	550	413	no change
47b	2	540	408	only T + F
52a	2	520	270	no change
52b	2	500	270	no change
55a	2	480	210	+ A
55b	2	460	210	+ A

*) In these runs reactants were 100% antigorite.

Runs with talc + forsterite + antigorite (10%), all synthetic, piston-cylinder runs

Run No.	Pressure (kb) Piston-cylinder runs	Temperature (°C)	Run duration (days)	Result
122	10	630	7	only T + F
123	10	610	11	+ A

We report here new experimental brackets for the reaction (BC) A = F + T + W (Table 3; see also JOHANNES, 1975), determined at water pressures from 2 to 15 kilobars. The runs at 2, 4 and 6 kilobars were done in carefully calibrated "Tuttle-type" hydrothermal bombs, with both temperature and pressure estimated accurate to $\pm 1\%$. A piston-cylinder apparatus was used for the runs at 10 and 15 kilobars; pressures in this apparatus are accurate to $\pm 5\%$, temperatures to $\pm 5°C$ (JOHANNES, 1973). Reactants consisted of synthetic talc and synthetic forsterite mixed with 10% natural antigorite from Piz Lunghin, Graubünden (analysis Table 4). Two runs were made with all synthetic material (Table 3). Run products and relative gains and losses were determined in x-ray diffractograms. Bracketing runs have been plotted as $\ln f_{H_2O}$ vs. $1/T$ in Fig. 3 at a total pressure of 1 bar. Because the breakdown of antigorite is much faster than its formation, the equilibrium curve (BC) has been drawn not exactly in the middle of the brackets but slightly towards the higher temperature limits, namely 622°C at 10 kb, 580°C at 6 kb, 551°C at 4 kb, and 513°C at 2 kb. The bracket obtained at 10 kb with synthetic antigorite is identical to that obtained with natural antigorite.

In order to use the dehydration curves (AT), (AB) and (BC) to determine simply by difference the locations of the W-absent curves (BFW) and (FWT) and the invariant points (B) and (T) with an accuracy of $\pm 30°C$, an experimental accuracy and precision of $\pm 1°C$ is required. Similarly, an accuracy of better than ± 10 calories per mole for the ΔG_f of the participating phases is required to do the same from thermochemical data. Therefore, we have derived the log K expression in Table 1 by a combination of experimental and field information as follows. A best-fit line (Fig. 3) was fitted through

Table 4. *Composition of antigorite, Piz Lunghin*

	(1)	(2)	(3)
SiO_2	40.85	42.37	43.0
Al_2O_3	1.23	1.28	0.70
Fe_2O_3	1.62	1.68	–
FeO	0.93	0.96	1.23*)
MgO	37.84	39.25	41.5
CaO	1.31	0.00	0.00
MnO	0.13	0.13	0.07
Na_2O	0.008	0.008	–
K_2O	0.005	0.005	–
H_2O^+	13.44	13.94	–
H_2O^-	1.25	0.00	–
CO_2	1.08	0.00	–
Cr_2O_3	–	–	0.01
NiO	–	–	0.04
	99.69	99.62	86.55

(1) Bulk analysis, Bundesanstalt für Geowissenschaft und Rohstoffe.
(2) Corrected for carbonate impurity and adsorbed water.
(3) Microprobe analysis, B. R. FROST, University of Washington.
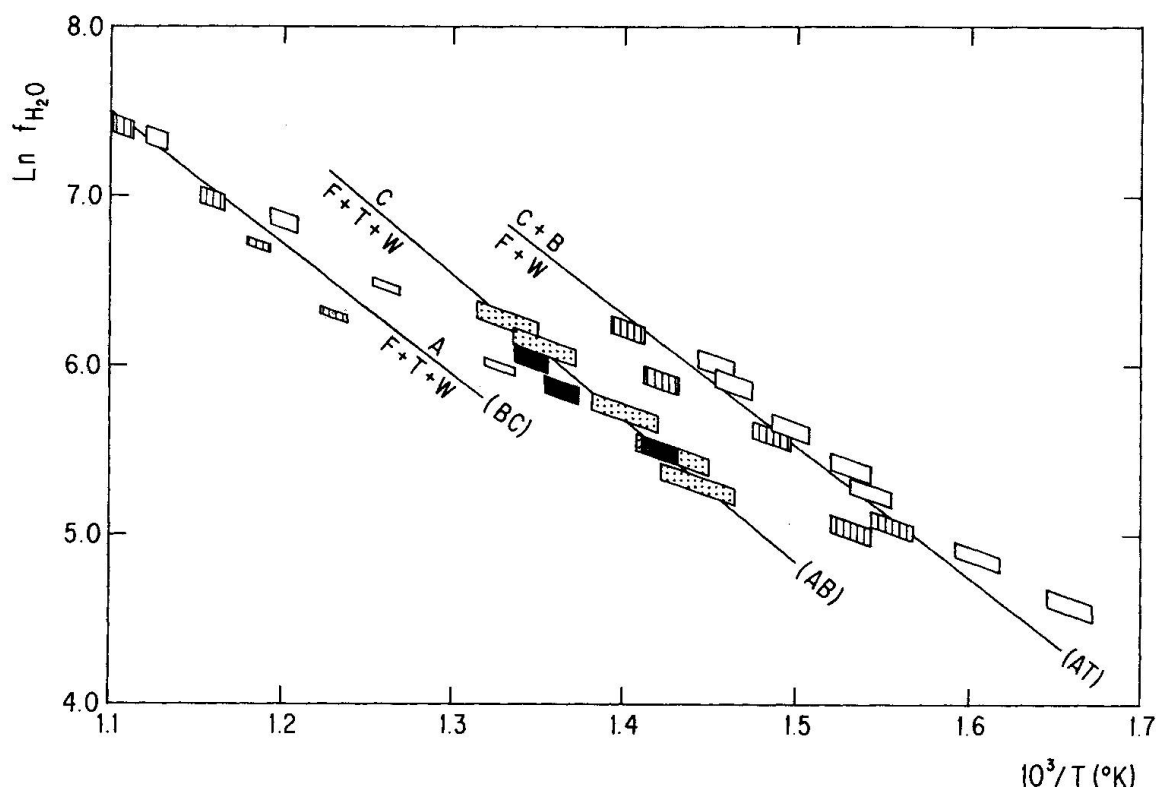*) Total Fe as FeO.

Fig. 3. Van't Hoff plot of experimental data for reactions (BC), (AB) and (AT). Total pressure 1 bar. For (AB), authors estimate of the equilibrium curve is plotted; filled boxes, SCARFE and WYLLIE (1967a), dotted, CHERNOSKY (1973). For (AT) and (BC), individual reaction reversals are plotted (JOHANNES, 1968, this paper Table 3). Experimental uncertainties have been taken to be $\pm 5°$C for all curves, $\pm 5\%$P for (AB), (AT) and the piston-cylinder runs of (BC), and $\pm 1\%$P for the hydrothermal runs on (BC).

the reversal points for reaction (AT) as determined by JOHANNES (1968). The details of experimental runs are not available for (AB), and, despite good agreement between SCARFE and WYLLIE (1967 a, b) and CHERNOSKY (1973) for (AB), the slope of the equilibrium line in the Van't Hoff plot (Fig. 3) is quite uncertain. With the line for (BC) drawn through the values given above, a slope for (AB) was chosen so that the intersection of (AB) and (BC) (invariant point (B)) was at 195°C ($P_{H_2O} = P_t$). Curve (BT) was then calculated by combination of (AB) and (BC). The resulting intersection of (BT) and (AT), i.e. invariant point (T), was a few degrees above 300°C, a temperature which enables (FWT) to be drawn consistent with the field data cited above. The line adopted for (AB) – with the help of field data – fits within quoted error limits all but one of the data of SCARFE and WYLLIE and CHERNOSKY (Fig. 3), although it is slightly steeper than the best-fit curve. Its slope corresponds to $\Delta H° = 16.892$ kcal/mole H_2O, which may be compared with $\Delta H° = 16.900$ (± 0.340) kcal at 500 K and 15.418 (± 0.340) at 800 K, using enthalpy data for talc, forsterite and H_2O from ROBIE and WALDBAUM (1968) and chrysotile from KING et al. (1967). A flatter line for (AB), or conversely a steeper curve

for (BC)[4], would place invariant points (B) and (T) at lower temperatures, inconsistent with the field evidence. Curvilinear Van't Hoff plots, while more in agreement with high temperature heat capacities, are not justified by the temperature spread of the experimental data.

Serpentine Phase Diagram

The locations of internally consistent reaction boundaries in the P_{H_2O} ($= P_{total}$)-T section are shown in Fig. 4. The dehydration reactions, located essentially by experiment, are probably good to at least $\pm 20°C$, whereas the positions of the W-absent reactions, located indirectly as described above, must be regarded as very approximate. These low-entropy reactions are clearly sluggish in the field, for example lizardite and chrysotile in Upper Engadine serpentinites survive several kilometers beyond the first appearance of antigorite + brucite (DIETRICH and PETERS, 1971; TROMMSDORFF, unpublished). Similarly, chrysotile coexists with talc well above the first appear-
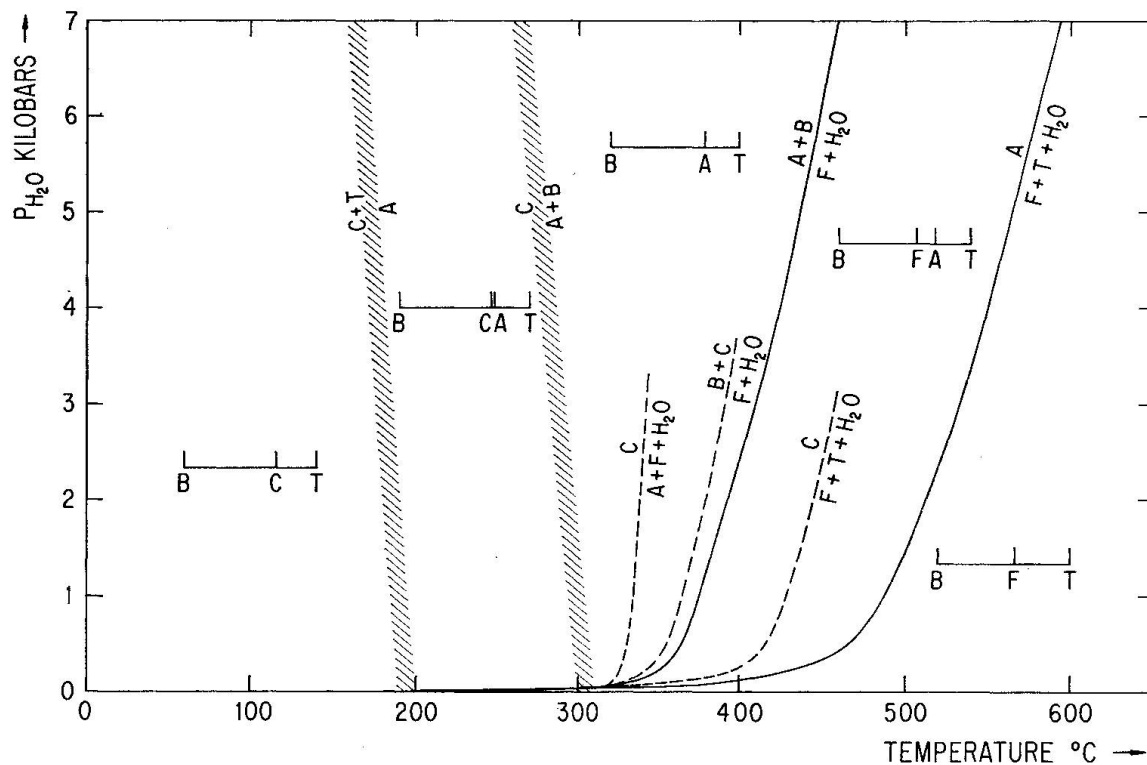

Fig. 4. Temperature-pressure ($P_{H_2O} = P_{total}$) diagram for stable (continuous lines) and metastable (dashed lines) equilibria in the multisystem A, B, C, F, T and H_2O.

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[4] A steeper curve for (BC) would agree better with ΔS from tabulated data, but it is clear that S (talc) and S (antigorite) are really not well known.

ance of vein-antigorite in the Oberhalbstein (DIETRICH and PETERS, 1971, Plate 3). This also provides a probable explanation for the differences of opinion as to where, in relation to the metamorphic facies, the transformation of chrysotile to antigorite serpentinites takes place (HESS et al., 1952; WILKINSON, 1953).

The main consequences of the diagram are the following: The curves (AT) and (AB) are metastable over their experimentally determined range, and the stable lower limit of forsterite + H_2O is given by (CT). The stable formation of chrysotile + brucite from forsterite + H_2O, and the converse (perhaps LEECH, 1953, p. 33) is only possible at extremely low pressures. The diagram permits a substantial field of coexistence of antigorite and chrysotile. It also provides a more than 100°C wide field for forsterite + antigorite. This agrees with the occurrence of this pair in the Lepontine Alps from the chloritoid zone up to the calcite + diopside isograd, more than half-way between the staurolite and sillimanite isograds (TROMMSDORFF and EVANS, 1974, Fig. 9). On the other hand, the forsterite + talc field is narrowed down considerably and is now in much better agreement with estimates of its width from regional and contact metamorphic environments (TROMMSDORFF and EVANS, 1972, 1974; SPRINGER, 1975; FORST, 1975).

The temperatures obtained by oxygen isotope studies on lizardite and chrysotile serpentinites (below 200°C) and on antigorite serpentinites (220° to 460°C, WENNER and TAYLOR, 1971) are in excellent agreement with the diagram. The diagram is also consistent with the rather strong evidence that low temperature meteoric waters are involved in the serpentinization process in some chrysotile-lizardite serpentinites (BARNES and O'NEIL, 1969; WENNER and TAYLOR, 1973).

The dehydration reactions on the diagram may be used with confidence as limiting conditions for assemblages in metamorphic, impure ultramafic rocks (EVANS and TROMMSDORFF, 1975). The effect of solid solution on the locations of the W-absent reactions may, on the other hand, be very considerable. Similarly, for mineral species which do not occur in the simple system considered in this paper, for example Al-lizardite, the configuration of the diagram might be quite different.

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