Zeitschrift:	Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie
Band:	56 (1976)
Heft:	1
Artikel:	Stability of chrysotile and antigorite in the serpentinite multisystem
Autor:	Evans, Bernard W. / Johannes, W. / Oterdoom, Heiko
DOI:	https://doi.org/10.5169/seals-43677

## Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. <u>Mehr erfahren</u>

## **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. <u>En savoir plus</u>

## Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. <u>Find out more</u>

# Download PDF: 18.08.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

# Stability of Chrysotile and Antigorite in the Serpentinite Multisystem

By Bernard W. Evans\*), W. Johannes\*\*), Heiko Oterdoom\*\*\*) and Volkmar Trommsdorff\*\*\*)

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<sub>2</sub>-H<sub>2</sub>O multisystem consisting of the phases antigorite, chrysotile, brucite, forsterite, tale 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<sub>2</sub>O-absent reactions with negative slopes on the PT-plot. The lower stability limit of forsterite + H<sub>2</sub>O, at most metamorphic pressures, is outside the field of stable chrysotile. Antigorite is stable relative to tale, 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<sub>2</sub>-H<sub>2</sub>O 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.

<sup>\*)</sup> Department of Geological Sciences, University of Washington, Seattle, Washington 98195, U.S.A.

<sup>\*\*)</sup> Mineralogisches Institut, T. U. Hannover, D-3000 Hannover, Welfengarten 1, West Germany.

<sup>\*\*\*)</sup> Institut für Kristallographie und Petrographie, ETH-Zentrum, CH-8092 Zürich, Switzerland.

## **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<sub>2</sub>-H<sub>2</sub>O 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 collinear with brucite and talc in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O (Fig. 1), and furthermore this collinearity is independent of compositional variation resulting from variation in the super-lattice dimension of antigorite, since only more or less of Mg (OH)<sub>2</sub> is in-

<sup>&</sup>lt;sup>1</sup>) 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, tale T, forsterite F and water vapor W in the system MgO-SiO<sub>2</sub>-H<sub>2</sub>O.

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 colinearity (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<sup>3</sup>). All the nets, of course, possess an inverse net (Fig. 2b).

<sup>&</sup>lt;sup>2</sup>) Mineral abbreviations are listed in the caption to Fig. 1 and in Table 2.

<sup>&</sup>lt;sup>3</sup>) 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.

		Equilibrium Constant <sup>1</sup> )		
Absent	Stoichiometry <sup>2</sup> )	$\boldsymbol{A}$	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)	$2 \mathrm{C} = 3 \mathrm{B} + \mathrm{T}$	-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)	$15 \mathrm{C} + \mathrm{T} = \mathrm{A}$	-19170	<b>41.04</b>	0.176
(BT)	$20 \text{ C} = 6 \text{ F} + \text{A} + 9 \text{ H}_2\text{O}$	-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

Table 1. Uni	variant E	quilibria	in the	Serp	entinite	System
--------------	-----------	-----------	--------	------	----------	--------

<sup>1</sup>) ln K =  $\frac{A}{T}$  + B +  $\frac{C(P-1)}{T}$  where T is °K and P is pressure in bars.

<sup>2</sup>) See Table 2 for abbreviations and mineral formulae. Fugacity data from BURNHAM et al. (1969); volume data from ROBIE and WALDBAUM (1968).



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.

<sup>1</sup> 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).

#### Serpentinite Multisystem

			$Vcm^3$ . $gfw^{-1}$	$S \ cal. \ deg.^{-1} \ gfw^{-1}$
B C A	Brucite Chrysotile Antigorite	$\begin{array}{l} Mg(OH)_2 \\ Mg_3Si_2O_5(OH)_4 \\ Mg_{48}Si_{34}O_{85}(OH)_{62} \end{array}$	$\begin{array}{c} 24.63 \pm 0.07^{1} \\ 108.5 \pm 0.6^{1} \\ (102.89 \pm 0.51) \times 17^{3} ) \end{array}$	$\begin{array}{c} 15.09 \pm 0.05^{1}) \\ 52.9 \pm 0.4^{2}) \\ (50.6 \pm 0.4) \times 17^{2*}) \\ (62.34 \pm 0.15^{1}) \end{array}$
T F Water	Forsterite Absent React	Mg <sub>3</sub> Sl <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> Mg <sub>2</sub> SiO <sub>4</sub> ions	$\frac{130.25 \pm 0.26^{2}}{43.79 \pm 0.03^{1}}$ $\Delta V \ cm^{3}$	$(57.65^{4})$ 22.75 $\pm$ 0.20 <sup>1</sup> ) $\Delta S \ cal. \ deg.^{-1}$
(TFW (AFW (CFW (BFW	() () ()	17 C = 3 B+A 2 C = 3 B+T 2A = 45 B+17 T 15 C + T = A	$\begin{array}{r} -24.48 \pm 13.39 \\ - \ \ 6.86 \pm 1.24 \\ - \ \ 73.66 \pm 18.17 \\ - \ \ 14.62 \pm 12.50 \end{array}$	$\begin{array}{rrrr} 6.17 \pm 6.80 \\ 1.81 \pm 0.83 & - 2.88^{4}) \\ 18.43 \pm 14.02 & -61.3^{4}) \\ 4.36 \pm \ 9.07 & 9.05^{4}) \end{array}$

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

Sources of data:

<sup>1</sup>) ROBLE and WALDBAUM (1968); <sup>2</sup>) KING et al. (1967); <sup>3</sup>) KUNZE (1961); <sup>4</sup>) BRICKER et al. (1973); <sup>2</sup>\*) Modified from S antigorite (Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) 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  $\Delta$ S and  $\Delta$ V).

## **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 (CHI-DESTER, 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)  $C+T \rightarrow A$ . For example, antigorite first appears as veins in lizardite-chrysotile serpentinites in the northern Oberhalbstein (DIETRICH and PETERS, 1971).

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

III. (CT)  $A + B \rightarrow F + W$ . 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)  $A \rightarrow F + T + W$ . 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 + tale (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  $\rightarrow$  actinolite + epidote + H<sub>2</sub>O 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

	Pressure (kb)	Temperature (°C)	Run duration	
Run No.	Piston-cy	linder runs	(days)	Result
72	15	670	13	only $\mathbf{T} + \mathbf{F}$
109	15	660	28	only $T + F$
84	15	650	12	+Å
117	15	650	10	- A
111	15	650	21	only $\mathbf{T} + \mathbf{F}$
127	15	640	7	$+\mathbf{A}$
101	15	630	6	$+\mathbf{A}$
94	15	610	6	$+\mathbf{A}$
64	10	650	16	only $\mathbf{T} + \mathbf{F}$
115	10	630	7	$-\mathbf{A}$
67	10	630	22	-A
110	10	625	10	no change
108	10	620	<b>25</b>	no change
112	10	615	19	$+\mathbf{A}$
54	10	610	<b>22</b>	$+\mathbf{A}$
87	10	610	20	$+\mathbf{A}$
	Hydroth	ermal runs		
42a	6	640	34	A *)
42 b	6	620	34	-A*)
48a	6	610	96	only $\mathbf{T} + \mathbf{F}$
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
51 b	6	575	195	no change
43 b	6	570	60	no change
58a	6	565	195	no change
49b	6	560	156	+A
58b	6	550	195	$+\mathbf{A}$
41a	4	580	162	$\mathbf{T} + \mathbf{F} + \mathbf{trace} \mathbf{A}$
56 a	4	570	210	-A
41b	4	560	162	no change
53a	4	555	$\boldsymbol{255}$	no change
44	4	550	186	no change
57a	4	540	255	no change
$57 \mathrm{b}$	4	530	255	no change
57 c	4	520	<b>255</b>	+A
46a	2	570	<b>245</b>	only $T + F$
47 a	<b>2</b>	560	408	only $\mathbf{T} + \mathbf{F}$
60	<b>2</b>	550	413	no change
47 b	2	<b>540</b>	408	only $\mathbf{T} + \mathbf{F}$
52a	2	<b>520</b>	<b>270</b>	no change
$52\mathrm{b}$	<b>2</b>	500	<b>270</b>	no change
55a	2	480	210	$+\mathbf{A}$
$55 \mathrm{b}$	<b>2</b>	<b>46</b> 0	210	$+\mathbf{A}$

\*) In these runs reactants were 100% antigorite.

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

	Pressure (kb)	Temperature (°C)	Run duration	
Run No.	Piston-cy	ylinder runs	(days)	Result
122	10	630	7	only $\mathbf{T} + \mathbf{F}$
123	10	610	11	$+\mathbf{A}$

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  $\pm 5^{\circ}$ 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  $\ln f_{H_0O}$  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  $\pm 30^{\circ}$ C, an experimental accuracy and precision of  $\pm 1^{\circ}$ C is required. Similarly, an accuracy of better than  $\pm 10$  calories per mole for the  $\Delta G_{f}$  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

$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(1)	(2)	(3)
$\begin{array}{c ccccccccccc} \mathrm{Al}_2 \tilde{\mathrm{O}}_3 & 1.23 & 1.28 & 0.70 \\ \mathrm{Fe}_2 \mathrm{O}_3 & 1.62 & 1.68 & - \\ \mathrm{FeO} & 0.93 & 0.96 & 1.23 \\ \mathrm{MgO} & 37.84 & 39.25 & 41.5 \\ \mathrm{CaO} & 1.31 & 0.00 & 0.00 \\ \mathrm{MnO} & 0.13 & 0.13 & 0.07 \\ \mathrm{Na}_2 \mathrm{O} & 0.008 & 0.008 & - \\ \mathrm{K}_2 \mathrm{O} & 0.005 & 0.005 & - \\ \mathrm{H}_2 \mathrm{O}^+ & 13.44 & 13.94 & - \\ \mathrm{H}_2 \mathrm{O}^- & 1.25 & 0.00 & - \\ \mathrm{CO}_2 & 1.08 & 0.00 & - \\ \mathrm{Cr}_2 \mathrm{O}_3 & - & - & 0.01 \\ \mathrm{NiO} & - & - & 0.04 \\ \hline & 99.69 & 99.62 & 86.55 \\ \end{array}$	SiO,	40.85	42.37	43.0
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Al <sub>2</sub> Õ <sub>3</sub>	1.23	1.28	0.70
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Fe <sub>2</sub> O <sub>3</sub>	1.62	1.68	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	FeO	0.93	0.96	1.23*
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	MgO	37.84	39.25	41.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CaO	1.31	0.00	0.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	MnO	0.13	0.13	0.07
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Na <sub>2</sub> O	0.008	0.008	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	K,Ō	0.005	0.005	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	H,0+	13.44	13.94	_
$\begin{array}{cccccccc} \dot{\text{CO}}_2 & 1.08 & 0.00 & -\\ \dot{\text{Cr}}_2 \dot{\text{O}}_3 & - & - & 0.01\\ \dot{\text{NiO}} & - & - & 0.04\\ \hline & 99.69 & 99.62 & 86.55\\ \end{array}$	H,0-	1.25	0.00	
$\begin{array}{cccc} \operatorname{Cr}_2 O_3 & - & - & 0.01 \\ \operatorname{NiO} & - & - & 0.04 \\ \hline & 99.69 & 99.62 & 86.55 \end{array}$	CŌ,	1.08	0.00	_
NiO $  0.04$ 99.69 99.62 86.55	$Cr_2O_3$			0.01
99.69 99.62 86.55	NiŌ	-	-	0.04
		99.69	99.62	86.55

#### Table 4. Composition of antigorite, Piz Lunghin

(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  $\pm 5^{\circ}$ C for all curves,  $\pm 5^{\circ}$ P for (AB), (AT) and the piston-cylinder runs of (BC), and  $\pm 1^{\circ}$ 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  $195^{\circ}$ C ( $P_{H_{2}O} = P_{t}$ ). 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  $\Delta H^{\circ} = 16.892$  kcal/mole H<sub>2</sub>O, which may be compared with  $\Delta H^{\circ} = 16.900$  $(\pm 0.340)$  kcal at 500 K and 15.418 ( $\pm 0.340$ ) at 800 K, using enthalpy data for talc, forsterite and H<sub>2</sub>O 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  $\pm 20^{\circ}$ 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 appearance



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<sub>2</sub>O.

<sup>4</sup>) A steeper curve for (BC) would agree better with  $\Delta S$  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<sub>2</sub>O is given by (CT). The stable formation of chrysotile + brucite from forsterite + H<sub>2</sub>O, 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 + tale 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.

#### Acknowledgements

We wish to acknowledge the support of the U.S. National Science Foundation (Grant # GA 29767), the Deutsche Forschungsgemeinschaft (Az. Jo 63/6), and the Schweizerischer Nationalfonds 2.249.074.

#### REFERENCES

#### SMPM = Schweiz. Mineral. Petrogr. Mitt.

- AUMENTO, F. (1970): Serpentine mineralogy of ultrabasic intrusions in Canada and on the mid-Atlantic ridge. Geol. Survey Canada Paper 69–53, 51 p.
- BARNES, I. and O'NEIL, J. R. (1969): The relationship between fluids in some fresh alpine-type ultramafics and possible modern serpentinization, western United States. Geol. Soc. Amer. Bull., 80, 1947–1960.
- BENSON, W. N. (1918): The origin of serpentine. Amer. J. Sci., 46, 693-731.
- BOCQUET, J. (1974): Etudes minéralogiques et petrologiques sur les metamorphismes d'âge alpin dans les alpes françaises. Univ. Scientifique et Médicale de Grenoble.
- BOWEN, N. L. and TUTTLE, O. F. (1949): The system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. Geol. Soc. Amer. Bull., 80, 1947–1960.
- BRICKER, O., NESBITT, W. and GUNTER, W. (1973): The stability of talc. Amer. Mineral., 58, 64-72.
- BUCHER, K. and PFEIFER, H. R. (1973): Über Metamorphose und Deformation der östlichen Malenco-Ultramafitite und deren Rahmengesteine (Prov. Sondrio, N-Italien). SMPM, 53, 231-241.
- BURNHAM, C. W., HOLLOWAY, J. R. and DAVIS, N. F. (1969): Thermodynamic properties of water to 1000°C and 10,000 bars. Geol. Soc. Amer. Spec. Paper 132, 96 p.
- CHERNOSKY, J. V. (1973): The stability of chrysotile, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> and the free energy of formation of talc, Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>. Geol. Soc. Amer. Annual Meeting, Dallas, Texas, p. 575 (abstr.).
- CHERNOSKY, J. V. (1975): Aggregate refractive indices and unit cell parameters of synthetic serpentine in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Amer. Mineral., 60, 200-208.
- CHIDESTER, A. H. (1962): Petrology and geochemistry of selected talc-bearing ultramafic rocks and adjacent country rocks in north-central Vermont. Prof. Paper U.S. Geol. Survey 345, 207 p.
- COATS, C. J. A. (1968): Serpentine Minerals from Manitoba. Canad. Mineral., 9, 321-347.
- COLEMAN, R. G. (1971): Petrologic and geophysical nature of serpentinites. Geol. Soc. Amer. Bull., 82, 897-918.
- CORNELIUS, H. P. (1912): Petrographische Untersuchungen in den Bergen zwischen Septimer- und Julierpass. N. Jb. Miner. Beilage Bd. 35, 374–498.
- CRAWFORD, W. A. and FYFE, W. S. (1965): Lawsonite equilibria. Amer. J. Sci., 263, 262–270.
- DAY, H. D. (1972): Geometrical analysis of phase equilibria in ternary systems of six phases. Amer. J. Sci., 272, 711–734.
- DEER, W. A., HOWIE, R. A. and ZUSSMAN, J. (1962): Rock-forming Minerals, vol. 3, sheet silicates. Longmans, Green & Co. Ltd., London, 270 p.
- DIETRICH, V. and PETERS, T. (1971): Regionale Verteilung der Mg-Phyllosilikate in den Serpentiniten des Oberhalbsteins. SMPM, 51, 329-348.
- DIETRICH, V., VUAGNAT, M., and BERTRAND, J. (1974): Alpine metamorphism of mafic rocks. SMPM, 54, 291-332.
- DUNGAN, M. A. (1974): The origin, emplacement, and metamorphism of the Sultan Mafic-Ultramafic Complex, North Cascades, Snohomish County, Washington. Ph. D. thesis, University of Washington, Seattle.
- EVANS, B. W. and TROMMSDORFF, V. (1975): Der Einfluss von Kationenersatz auf die Hydratisierung von Duniten – Korrekturen und Kommentare. SMPM, 55, 457–459.
- FAUST, G. T. and FAHEY, J. J. (1962): The serpentine-group minerals. U. S. Geol. Survey Prof. Paper 384A, 92 p.

- FROST, B. R. (1973): Contact metamorphism of the Ingalls Complex at Paddy-Go-Easy Pass, Central Cascades, Washington. Ph. D. thesis, University of Washington, Seattle.
- FROST, B. R. (1975): Contact metamorphism of serpentinite, chloritic blackwall and rodingite at Paddy-Go-Easy Pass, Central Cascades, Washington. J. Petrol., 16, 272–313.
- FRANCIS, G. H. (1956): The serpentine mass in Glen Urquhart, Inverness-shire, Scotland. Amer. J. Sci., 254, 201–226.
- HAHN-WEINHEIMER, P. and Rost, F. (1961): Akzessorische Mineralien und Elemente im Serpentinit von Leupoldsgrün (Münchberger Gneismasse). Ein Beitrag zur Geochemie ultrabasischer Gesteine. Geochim. Cosmochim. Acta, 21, 165–181.
- HESS, H. H., SMITH, R. J. and DENGO, G. (1952): Antigorite from the vicinity of Caracas, Venezuela. Amer. Mineral., 37, 68-75.
- HUGGINS, C. W. and SHELL, H. R. (1965): Density of bulk chrysotile and massive serpentinite. Amer. Mineral., 50, 1058-1067.
- IISHI, K. and SAITO, M. (1973): Synthesis of antigorite. Amer. Mineral., 58, 915–919.
- JAHNS, R. H. (1967): Serpentinites of the Roxbury district, Vermont, p. 137–160, in Wyllie, P. J., ed., Ultramafic and Related Rocks. John Wiley & Sons, Inc., New York, 464 p.
- JOHANNES, W. (1968): Experimental investigation of the reaction forsterite + H<sub>2</sub>O = serpentine + brucite. Contr. Mineral. Petrol., 19, 309–315.
- JOHANNES, W. (1973): Eine vereinfachte Piston-Zylinder-Apparatur hoher Genauigkeit. N. Jb. Miner. Mh., 7/8, 337-351.
- JOHANNES, W. (1975): Zur Synthese und thermischen Stabilität von Antigorit. Fortschr. Mineral., 53, 36.
- KEUSEN, H. R. (1972): Mineralogie und Petrographie des metamorphen Ultramafitit-Komplexes vom Geisspfad (Penninische Alpen). SMPM, 52, 385-478.
- KING, E. G., BARANY, R., WELLER, W. W., and PANKRATZ, L. B. (1967): Thermodynamic properties of forsterite and serpentine. U.S. Bureau of Mines, Report of Investigations 6962, 19 p.
- KLINKHAMMER, B. and ROST, F. (1967): Die Serpentinite des Oberpfälzer Waldes. VGMG Sonderheft, 16, 112–136.
- KUNZE, G. (1956): Die gewellte Struktur des Antigorits, I. Zeit. Krist., 108, 82-107.
- KUNZE, G. (1961): Antigorit. Strukturtheoretische Grundlagen und ihre praktische Bedeutung für die weitere Serpentin-Forschung. Fortschr. Mineral., 39, 206–324.
- LEECH, G. B. (1953): Geology and mineral deposits of the Shulaps Range, Southwestern British Columbia. British Columbia Dept. Mines, Bull. 32.
- MATTHES, S. (1971): Die ultramafischen Hornfelse, insbesondere ihre Phasenpetrologie. Fortschr. Mineral., 48, 109–127.
- NEWTON, R. C. (1966): Some calc-silicate equilibrium relations. Amer. J. Sci., 264, 204-222.
- NITSCH, K. H. (1971): Stabilitätsbeziehungen von Prehnit- und Pumpellyit-haltigen Paragenesen. Contr. Mineral. Petrol., 30, 240–260.
- NITSCH, K. H. (1973): Neue Erkenntnisse zur Stabilität von Lawsonit. Fortschr. Mineral., 51, Beiheft 1, 34–35.
- NOLL, W. (1944): Anwendung der Elektronenmikroskopie beim Studium hydrothermaler Silikatreaktionen. Kolloid. Zeits., 107, 181–190.
- OTERDOOM, W. H. (1975): Geologisch-petrographische Untersuchungen des Malencoserpentins in Val Scerscen. Diplomarbeit, ETH, Zürich.
- PAGE, N. J. (1968): Chemical differences among the serpentine "polymorphs": Amer. Mineral., 53, 201-215.

- PAGE, N. J. and NOCKLEBERG, W. J. (1972): Genesis of Mesozonal granitic rocks below the base of the Stillwater Complex, in the Beartooth Mountains, Montana. U.S. Geol. Survey Prof. Paper 800-D, D 127-D 141.
- ROBIE, R. A. and WALDBAUM, D. R. (1968): Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. U.S. Geol. Survey Bull, 1259, 256 p.
- Rost, F. (1949): Das Serpentinit-Gabbro-Vorkommen von Wurlitz und seine Mineralien. Heidelberger Beiträge zur Mineralogie und Petrographie, 1, 626–688.
- SCARFE, C. M. and WYLLIE, P. J. (1967a): Experimental redetermination of the upper stability limit of serpentine up to 3 kb pressure. Trans. Amer. Geophys. Union, 48, 225.
- SCARFE, C. M. and WYLLIE, P. M. (1967b): Serpentine dehydration curves and their bearing on serpentine deformation in orogenesis. Nature, 215, 945–946.
- SKIPPEN, G. B. and TROMMSDORFF, V. (1975): Invariant phase relations among minerals on T-X fluid sections. Amer. J. Sci., 275, 561-572.
- SPRINGER, R. K. (1974): Contact metamorphosed ultramafic rocks in the Western Sierra Nevada Foothills, California. J. Petrol., 15, part 1, 160–195.
- TROMMSDORFF, V. and EVANS, B. W. (1972): Progressive metamorphism of antigorite schist in the Bergell tonalite aureole (Italy). Amer. J. Sci., 272, 423-437.
- TROMMSDORFF, V. and EVANS, B. W. (1974): Alpine metamorphism of peridotitic rocks. SMPM, 54, 333-352.
- WENNER, D. B. and TAYLOR, H. P. (1971): Temperatures of serpentinization of ultramafic rocks based on O<sup>18</sup>/O<sup>16</sup> fractionation between coexisting serpentine and magnetite. Contr. Mineral. Petrol., 32, 165–185.
- WENNER, D. B. and TAYLOR, H. P. (1973): Oxygen and hydrogen isotope studies of the serpentinization of ultramafic rocks in oceanic environments and continental ophiolite complexes. Amer. J. Sci., 272, 207–239.
- WHITTAKER, E. J. W. and WICKS, F. J. (1970): Chemical differences among the serpentine "polymorphs", a discussion. Amer. Mineral., 55, 1025–1047.
- WILKINSON, J. F. G. (1953): Some aspects of the alpine-type serpentinites of Queensland. Geol. Mag., 90, 305-321.
- ZEN, E-AN and ROSEBOOM, E. H., Jr. (1972): Some topological relationships in multisystems of n+3 phases, III. Ternary systems. Amer. J. Sci., 272, 677-710.
- ZUSSMAN, J. (1956): Antigorite: Superlattice and structural formula. Amer. Mineral., 41, 148-151.

Manuscript received January 31, 1976.