PETROLOGIC ASPECTS OF SERPENTINITE METAMORPHISM

Volkmar Trommsdorff

Institut für Kristallographie und Petrographie, ETH-Zentrum, 8092 Zürich (Svizzera)

ABSTRACT. — The sequence of dehydration reactions observed during progressive metamorphism of serpentinite rocks agrees with that calculated from experiments plus thermodynamic data. The relative stabilities of minerals and mineral assemblages in the serpentinite multisystem, however, are deter-mined by H_2O -absent equilibria, which are only known approximately in P-T space. Using the available thermodynamic data of minerals in the serpentinite system the experimental data are used to calculate standard enthalpies of reaction at 298 K and 1 bar. By combination of these data, all reactions in the system can be recalculated. As a result, no stability field for chrysotile assemblages can be established which contrasts with published and new field evidence. It is also shown that previous serpentinite phase diagrams are thermodynamically inconsistent. The varying structural state of anti-gorite at different *P*-*T* conditions is the most likely explanation rather than the influence of additional components in serpentinites.

RIASSUNTO. - La sequenza delle reazioni di deitratazione nel metamorfismo progressivo delle serpentiniti corrisponde a quella che risulta da reazioni sperimentali e anche a quella calcolata dai dati termodinamici. I rapporti relativi della stabilità tra minerali o paragenesi nel sistema delle serpentiniti vengono determinati da reazioni con assenza di H2O. La posizione di queste reazioni nello spazio pressione-temperatura è conosciuta solo molto ap-prossimativamente. Con l'aiuto dei dati termodinamici dei minerali nel sistema delle serpentiniti possono essere calcolate le entalpie standard di 298 K e 1 bar dei punti d'equilibrio sperimentale. La combinazione di questi dati permette la ricalcolazione di tutte le reazioni nel sistema. Risulta così dai dati a disposizione che per paragenesi del crisotilo non nasce un campo di stabilità e ciò è in netto contrasto coi fatti concreti sul terreno. Soprattutto, dal punto di vista termodinamico, i diagrammi di fase preesistenti sul metamorfismo delle serpentiniti non sono consistenti. Lo strato strutturale dell'antigorite varia come funzione della temperatura e pressione, e queste, più che l'influenza delle componenti addizionali, serve come spiegazione per le discrepanze tra natura, esperimenti e la base termodinamica.

Introduction

In recent attempts to compare experimental and field evidence on the progressive metamorphism of serpentinite (Evans and TROMMSDORFF, 1970; TROMMSDORFF and Evans, 1972, 1974; Evans, Johannes, OTERDOOM and TROMMSDORFF, 1976; FROST, 1975; HEMLEY, MONTOYA, CHRIST and HOSTETLER, 1977; HEMLEY, MONTOYA, SHAW and LUCE, 1977; OTERDOOM, 1978; CORTESOGNO, LUCCHETTI, MASSA, 1981) agreement has largely been reached about the sequence of reactions occurring along low to medium pressure geothermal gradients up to the breakdown of antigorite. The corresponding P-T diagram for the system MgO-SiO₂-CaO-H₂O is given in fig. 1. The dehydration equilibria are known to approximately \pm 30° and \pm 500 bars and are not sensitive to chemical variations in the minerals as occurring in metaperidotites. The H₂O-free equilibria are known to a much less degree and depend strongly on mineral composition. Fig. 2 is an isobaric $T-X_{MgO}$ section at 2 kb across fig. 1, for the system MgO-SiO₂-H₂O with the coexisting Ca-phases projected onto the diagram. The typical serpentinite assemblages are at $MgO/(MgO + SiO_2) \cdot 59$ on the diagram. Because of the sluggishness of the H2O-free reactions, experimental data have only been derived for some of the dehydration reactions. The P-T position of the H₂O-free equilibria has been constructed from the intersection points of the dehydration reactions plus entropy and volume data of the minerals involved. Because of the large uncertainties, field information was used to



Fig. 1. — Phase diagram for reactions involving serpentine minerals in the system CaO-MgO-SiO₂-CO₂-H₂O after EVANS and TROMMSDORFF (1970); EVANS, JOHANNES, OTERDOOM and TROMMSDORFF (1976) and OTERDOOM (1978). Stable dehydration equilibria: solid lines, metastable dashed. H₂O free equilibria shaded. Abbreviations: A = antigorite; B = brucite; C = chrysotile; Di = diopside; F = forsterite; T = talc; Tr = tremolite; W = H₂O.

further constrain the H2O-free equilibria (EVANS, JOHANNES, OTERDOOM and TROMMS-DORFF, 1976; OTERDOOM, 1978). This field information was derived from presently the best known profile of progressively metamorphosed serpentinites which is located along the boundary of the Austroalpine and the Penninic nappes between Arosa and Val Malenco. Serpentinite assemblages along this profile have been studied by amongst others CORNELIUS (1912), DIETRICH and PETERS (1971), TROMMSDORFF and EVANS (1972, 1974), Oterdoom (1978), Green (1982) and KÜNDIG (1982). Disregarding lizardite, which is always aluminous, the critical assemblages of the H2O-free reactions are compiled for this profile in the map fig. 3. In the order of increasing grade chrysotile and chrysotile + talc, antigorite, antigorite + diopside and antigorite+brucite occur, in agreement with fig. 1 and with the isobaric section in fig. 2.

The *P*-*T* diagram in fig. 1 was constructed by intersecting straight line fits of the known dehydration reactions plotted in log f_{H_2O} versus 1/T space in such a way that the H₂O equilibria which were assumed to occur stably in the field, were also stable in the phase diagram. The straight line fit method



Fig. 2. — Isobaric *T-X* section across the diagram fig. 1 at $P_{H_2^0} = 2$ kb. The progressive sequence of assemblages for typical serpentinite compositions may be read off at MgO/(MgO + SiO₂) = .59. See text.

assumes $\Delta c^{\circ} p_{\rightarrow}(T)$ to be constant. This can introduce large errors and from a thermodynamic point of view such phase diagrams are not satisfying.

DELANEY and HELGESON (1978) and HEL-GESON, DELANEY, NESBITT and BIRD (1978) point out that there is a number of ambiguities in the serpentinite system and that they were unable to create a stability field for chrysotile from the existing experiments and thermodynamic data of the minerals involved. Whereas these authors were fitting clapeyron slopes to the experiments, we have chosen a different approach to check consistency of the experimental data with the thermodynamic data base. This kind of approach was proposed by SKIPPEN and CARMICHAEL (1977) and uses a plot of $\Delta H^{\circ}_{\rightarrow}$ (298.1) versus temperature. For symbols see table 1. The free energy change of a reaction at equilibrium may be written as:

$$\Delta G^{O}_{+}(T_{E},P_{E}) = \Delta G^{O}_{+}(T_{E},1) + RTlnK + \Delta V_{S_{+}} \cdot (P_{E}-1) = 0 \quad (1)$$

Making use of the fundamental relationships

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H_{T_2}^{o} = \Delta H_{T_1}^{o} + \int_{T_1}^{T_2} e^{o} p dT \qquad (3)$$

$$\Delta S^{O}(T_{2}) = \Delta S^{O}(T_{1}) + \int_{T_{1}}^{T_{2}} \frac{c^{O}p}{T} dT \qquad (4)$$

we can rewrite equation (1)

$$\Delta G^{O}_{+}(T_{E'}) = \Delta H^{O}_{+}(T_{R'}, 1) + \int_{T_{R}}^{T_{E}} \Delta c^{O} p_{+} dT$$

$$- T_{E}(\Delta S^{O}_{+}(T_{R'}, 1) + \int_{T_{R}}^{T_{E}} \frac{\Delta c^{O} p_{+}}{T} dT)$$

$$+ \Delta V_{S} \cdot (P_{E'}-1) + RTlnK \qquad (5)$$

Thus, at equilibrium ΔH^0_{\perp} can be calculated:

$$\Delta H^{O}_{*}(T_{R}, 1) = - \int_{T_{R}}^{T_{E}} \Delta c^{O} p_{*} dT + T_{E} \Delta S^{O}_{*}(T_{R}, 1)$$

$$+ T_{E} \int_{T_{R}}^{E} \frac{\Delta c^{O} p_{*}}{T} dT - RT_{E} lnK - \Delta V_{S_{*}} \cdot (P_{E}-1)$$
(5a)

To fit the c⁰p function up to five terms have been used:

$$c^{o}p = a + bT + cT^{-2} + dT^{2} + eT^{-1/2}$$
 (6)

TABLE 1List of symbols used

(2)	a, b, c, d, e	- Standard molal heat capacity coefficients for the power function $a + bT + cT^{-2} + dT + cT^{-V2}$					
(3)		First three terms also known as Maier Kelley power function.					
	e ^o p	- Standard molal heat capacity at constant pressure.					
(4)	∆c ^o p,	- Standard molal heat capacity of reaction.					
	G	- Gibbs free energy.					
	ΔG^{O}_{a} (T,P)	- Apparent standard molal Gibbs free energy of reaction at temperature T and pressure P.					
	н	- Enthalpy.					
	$\Delta H^{O}_{+}(T,P)$	- Apparent standard molal enthalpy of reaction at temperature T and pressure P.					
	∆H ^o f	- Standard molal enthalpy of formation from the elements at 298,15 K and 1 bar.					
(5)	к	- Equilibrium constant.					
(5)	PE	- Equilibrium pressure.					
	PR	- Reference pressure.					
	s	- Entropy.					
	s°	'- Standard molal entropy at 298 K and 1 bar.					
5a)	$\Delta S^{O}_{+}(T,P)$	- Standard molal entropy of reaction at temperature T and pressure P.					
	TE	- Equilibrium temperature.					
	TR	- Reference temperature.					
	vo	- Standard molal volume at 298 K and 1 bar.					
(6)	∆V _{s+}	- Standard molal volume of reaction for the solid phases.					

TABLE 2 Thermodynamic data base

	s ^o	vo	c ^O coefficients					source
			а	b x 10 ³	c	d x 10 ⁶	e	
Antigorite	861,36	1749,13	1241,1	517,25	-2877600	0	0	(a,b,c)
Brucite	15,10	24,63	24,431	3,6107	- 625530	0	0	(d)
Clinochrysotile	52,89	108,50	149,3	-4,964	- 411520	0	-1343,1	(d)
Diopside	34,2	66,09	78,44	0,45127	- 344890	Ö	- 602,1	(d,e)
Forstérite	22,75	43,79	54,489	0,81594	- 213660	0	- 416,97	(e)
Talc	62,34	136,25	127,7	8,9426	-2104500	0	- 514,63	(d,e)
Tremolite	131,19	272,92	290,25	6,3403	-2954600	0	-1765,9	(d,e)
H ₂ 0	16,718	-	1,761	6,565	- 53337	1.15	- 86,48	(e)

 s^{o} : cal mol⁻¹ κ^{-1} ; v^{o} : cm³ mol⁻¹; c_{p}^{o} : cal mol⁻¹ κ^{-1} ; a to e: see equation (6).

(a) Helgeson, Delany, Nesbitt and Bird (1978)

(b) Evans, Johannes, Oterdoom and Trommsdorff (1976)

(c) King, Barany, Weller and Pankratz (1967)

(d) Holland (1981)

(e) Robie, Hemingway and Fisher (1978)

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The first three terms are known as «Maier-Kelley» equation; up to five terms are used in the tables of ROBIE, HEMINGWAY and FISHER (1978).

Substituting equation (6) into equation (5 *a*), integrating and rearranging gives:

$$\begin{split} \Delta H^{\circ}_{+}(T_{R'}1) &= T_{E} \Delta S^{\circ}_{+}(T_{R'}1) - RT_{E} lnK - \Delta V_{s_{+}} \times (P_{E}^{-1}) \\ &+ \Delta a_{*} [-T_{E} + T_{R}^{-} + T_{E} ln(T_{E}^{\prime}/T_{R}^{-})] \\ &+ \Delta b_{*} [T_{E}^{2}/2 + T_{R}^{2}/2 - T_{E}^{T}T_{R}^{-}] \\ &+ \Delta c_{*} [V2T_{E} - 1/T_{R} + T_{E}^{\prime}/2T_{R}^{2}] \\ &+ \Delta d_{*} [T_{E}^{3}/6 + T_{R}^{3}/3 - T_{R}^{2}T_{E}^{\prime}/2] \\ &+ \Delta e_{*} [-2(\sqrt{T_{E}} - \sqrt{T_{R}}) - 2(\sqrt{T_{E}} - T_{E}^{\prime}/\sqrt{T_{R}})] \end{split}$$
(7)

Thus, knowing lnK, the S^o , the V^o and the *a*, *b*, *c*, *d* and *e* terms, experimental equilibrium points can be recalculated and plotted in a diagram of ΔH^o_{-} , (298.1) versus temperature. This kind of diagram has a number of advantages as compared to *P*-*T* or *logK* versus 1/T diagrams when comparing experimental data with the thermodynamic data.

Three cases may be distinguished (fig. 4): Case (a): experimental brackets and thermodvnamic data base are consistent.

- Case (b): experimental brackets and thermodynamic data base are inconsistent. A slope in the « equilibrium » trend line implies a systematic derivation of at least one of the thermodynamic parameters (S° , V° , a, b, c, d, e) or of the activity of at least one mineral in the system as compared to the corresponding mineral used in the experiment.
- Case (c): in the experiments, no equilibrium situation was attained that can be interpreted with the chosen thermodynamic parameters and activities of the phases.

In case (a) the resulting ΔH°_{-} (298,1) may be compared with the corresponding value as calculated from the $\Delta H^{\circ}_{\rm f}$ of the participating phases using tabulations like those of ROBIE, HEMINGWAY and FISHER (1978) or of HELGESON, DELANEY, NESBITT and BIRD (1978). If all but one of the $\Delta H^{\circ}_{\rm f}$ values of the reactants and products are known, an apparent enthalpy of

formation may be calculated from the $\Delta H^{\circ}_{\rightarrow}$ (298,1) value.

Table 2 summarizes the thermodynamic data base used in the calculation of experimental ultramafic equilibria.

Serpentinite reactions, experiment and theory

The breakdown of chrysotile according to

$$5Mg_{2}Si_{3}O_{5}(OH)_{4} = \\chrysotile \\= 6Mg_{2}SiO_{4} + Mg_{3}Si_{4}O_{10}(OH)_{2} + 9H_{2}O \quad (8) \\forsterite talc$$

has been repeatedly studied experimentally (BOWEN and TUTTLE, 1949; PISTORIUS, 1963; KITAHARA, TAKENOUCHI and KEN-NEDY, 1966; YODER, 1967) but reversibility of the reaction has only been « obtained » recently (SCARFE and WYLLIE, 1967; CHER-NOSKY, 1973 and 1982; HEMLEY, MON-TOYA, CHRIST and HOSTETLER, 1977). The results of the last four studies are shown in the ΔH°_{+} (298.1) versus T diagram of fig. 5 using the thermodynamic data base of table 1, equation (7) and fugacity data for H2O from BURNHAM, HOLLOWAY and DAVIS (1969). A value of 165,600 ± 2,000 cal. for the ΔH°_{\perp} (298.1) was adopted to fit the data set of CHERNOSKY (1973), HEM-LEY, MONTOYA, CHRIST and HOSTETLER (1977) and the 1000 bar point of SCARFE and WYLLIE (1967) within the limits of quoted uncertainty. This value may be compared with 165,826 cal. using the tables of ROBIE, HEMINGWAY and FISHER (1978) and of 164,531 cal. using the values tabulated in Helgeson, Delany, Nesbitt and Bird (1978). The new data of CHERNOSKY (1982) plot with a slope of about 50 cal. deg⁻¹ which is, other than claimed by the author clearly inconsistent with the thermodynamic data base used. If, for example the entropy of chrysotile used was in error, an adjustment of the So (298.1) of chrysotile by 10 cal. deg⁻¹ mole⁻¹ would be necessary to obtain consistency. Of all the experimentalists, only CHERNOSKY (1973, 1982) and HEMLEY, MONTOYA, CHRIST and HOSTETLER (1977) have characterized their serpentine mineral. It is, however probable that also the synthetic serpentine of SCARFE and WYLLIE



Fig. 3. — Parageneses of metamorphosed serpentinites in the profile Arosa-Malenco (Eastern Switzerland and Northern Italy). Data after DIETRICH and PETERS (1971), PETERS (1963), GREEN (1982), KÜNDIG (1982), and the author. Sample locations are approximate.



Fig. 4. — Three cases of data points on diagrams of experimental temperature versus ΔH^{α} , (298.1). See text for explanation.

(1967) was clinochrysotile (CHERNOSKY, 1982).

From the experiments of HEMLEY, MON-TOYA, CHRIST and HOSTETLER (1977), it seems that differences, caused by the use of natural instead of synthetic chrysotile, are trivial compared to those of the different studies.

JOHANNES (1968) has bracketed the reaction:

$$\begin{array}{rl} Mg_{3}Si_{2}O_{5}(OH)_{4} &+ Mg(OH)_{2} = \\ chrysotile & brucite \\ &= 2Mg_{2}SiO_{4} + 3H_{2}O \\ forsterite \end{array} \tag{9}$$

at H₂O pressures from 500 to 7000 bars. His brackets can be fitted with a value for ΔH°_{+} (298.1) of 51,680 ± 600 cal. which compares with 52,582 cal. using the tables of ROBIE, HEMINGWAY and FISHER and with 51,125 cal. using the compilation of HELGESON, DELANY, NESBITT and BIRD (1978) (fig. 6). The X-ray pattern of the synthetic chrysotile used by JOHANNES indicates clinochrysotile.

JOHANNES (in EVANS, JOHANNES, OTER-DOOM and TROMMSDORFF, 1976) and HEM-LEY, MONTOYA, SHAW and LUCE (1977) have experimentally investigated the breakdown of antigorite modelled by the reaction:

$$\begin{array}{rl} Mg_{48}Si_{34}O_{85}(OH)_{62} &= \\ & antigorite \\ = & 18Mg_2SiO_4 + & 4Mg_3Si_4O_{10}(OH)_2 + \\ & forsterite & talc \\ & + & 27H_2O \end{array} \tag{10}$$

The value adopted for the apparent ΔH°_{\pm} (298.1) is 516,000 \pm 3,000 and fits all the data within the quoted experimental uncertainty (fig. 7). The best fit curves of EVANS, JOHANNES, OTERDOOM and TROMMS-DORFF (1976) and of HEMLEY, MONTOYA, SHAW and LUCE (1977) are presented in fig. 7, both display a slope of 70 cal. deg⁻¹ which is far higher than the uncertainty in the entropy of the reaction. The fit of HEL-GESON, DELANY, NESBITT and BIRD (1978) is outside of all but two of the experimental brackets. Also shown in the diagram is a point derived from the field (see later). In order to obtain information about the stability relations of serpentine reactions the ΔH°_{+} values for equations (8), (9) and

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Fig. 5. — ΔH°_{\cdot} (298.1) versus temperature of experiment for reaction (8). Experimental data points are considered equilibrium by the investigators. Sloping uncertainty bars refer to temperature. *RHF* refers to ΔH°_{\cdot} (298.1) calculated from the tables of ROBIE, HEMINGWAY and FISHER (1978). HELGESON refers to ΔH°_{\cdot} (298.1) calculated from the tables of HELGESON, DELANY, NESBITT and BIRD (1978).







Fig. 7. — ΔH_{-}^{u} (298.1) versus temperature of experiments for reaction (10). Experimental data points are brackets (JOHANNES), the experimental 1000 bar point of HEMLEY, MONTOYA, SHAW and LUCE (1977) is considered experimental equilibrium. Other points refer to the *P*-*T* fit for this reaction by HEMLEY, MONTOYA, SHAW and LUCE (1977) and by EVANS, JOHANNES, OTERDOOM and TROMMSDORFF (1976). The line HELGESON indicates the fit by HELGESON, DELANY, NESBITT and BIRD (1978) for this equilibrium.

(10) may be combined to calculate the H₂O-missing equilibria:

$$17Mg_{3}Si_{2}O_{5}(OH)_{4} =$$
chrysotile
$$= 3Mg(OH)_{2} + Mg_{48}Si_{34}O_{85}(OH)_{62} (11)$$
brucite antigorite

and

$$15Mg_{3}Si_{2}O_{5}(OH)_{4} + Mg_{3}Si_{4}O_{10}(OH)_{2} = chrysotile talc = Mg_{48}Si_{34}O_{85}(OH)_{62} (12) antigorite$$

that delimit the stability fields of chrysotile and antigorite:

 $\Delta H^{\circ}_{\rightarrow (11)}(298.1) = - 8,640 \text{ cal.} \pm 12,800$ $\Delta H^{\circ}_{\rightarrow (12)}(298.1) = - 19,200 \text{ cal.} \pm 9,000$

Using the entropies of reactions (11) and (12) (tabulated in Evans, JOHANNES, OTER-DOOM and TROMMSDORFF, 1976) from our basic data set no geologically reasonable stability fields for chrysotile or chrysotile + talc arise. Consideration of CaO as a component leads to an additional dehydration reaction which has been observed (EVANS and TROMMSDORFF, 1970) and mapped (TROMMSDORFF and EVANS, 1972) in regionally and contact metamorphosed terraines:

$$8CaMgSi_{2}O_{6} + Mg_{48}Si_{34}O_{85}(OH)_{62} = diopside antigorite = 18Mg_{2}SiO_{4} + 4Ca_{2}Mg_{5}Si_{8}O_{22}(OH)_{2} + forsterite tremolite + 27H_{2}O (13)$$

This reaction has not yet been studied experimentally, but it has been calculated by combination of reaction (10) with the H₂O missing reaction:

$$2CaMgSi_2O_6 + Mg_3Si_4O_{10}(OH)_2 = diopside talc = Ca_2Mg_5Si_8O_{22}(OH)_2 (14) tremolite$$

and

Fig. 8. - Parageneses in contact-metamorphosed serpentinites from Val Sissone, Malenco area, Northern Italy. Data from TROMMSDORFF and EVANS (1972, 1980). Reactions (10) and (13) are indicated by broken lines. Reaction (15) coincides with (13).

using Skippens (1974) estimate of the free energy of reaction (14) (Evans, 1977; TROMMSDORFF and EVANS, 1977). It may alternatively be located by using more recent information from the field. In Val Ventina (Malenco), in the contact aureole of the Bergell tonalite (fig. 8) reaction (13) coincides with the breakdown of titanian clinohumite (TROMMSDORFF and EVANS, 1980) according to

$$M_{16}Si_8O_{32}(OH)_2TiO_2 =$$

titanian clinohumite
$$= 8M_2SiO_4 + MTiO_3 + H_2O$$
(15)
forsterite ilmenite/geikielite

where M refers to Mg, Fe, Mn and Ni. This reaction has been reversed experimentally by ENGI and LINDSLEY (1980) using titanian clinohumites from Val Malenco.

With a pressure estimate of $3,000 \pm 500$ bar based upon fission track investigations in the Bergell-Malenco area by MILLER, WAGNER and JÄGER (1979), equation (14) has an equilibrium temperature of $430 \pm 10^{\circ}$ and correspondingly reaction (1). This field data together with the P-T curve from EVANS, JOHANNES, OTERDOOM and TROMMSDORFF (1976) and OTERDOOM (1978) are shown in fig. 3. Again, the P-T curve has a slope of > 50 cal. deg⁻¹ in the ΔH° (298.1) versus temperature diagram. Taking a value of ΔH°_{-} (298.1) of 499,500 cal. and combining reaction (1) with reactions (8) and (10) results in an H₂O-absent reaction which delimits the stability of diopside and tremolite in low grade serpentinite systems:

$$15Mg_{3}Si_{2}O_{5}(OH)_{4} + Ca_{2}Mg_{5}Si_{8}O_{22}(OH)_{2} = chrysotile tremolite = Mg_{48}Si_{34}O_{85}(OH)_{62} + 2CaMgSi_{2}O_{6} (16) antigorite diopside (16)$$

$$\Delta H^{\circ}_{(16)}(298.1) = -15.075$$
 cal.

together with entropy and volume data from table 1, this leaves no stability in the pure serpentinite system for reaction (16).

Discussion

The apparent metastability of reactions (11), (12) and (16) contrasts with the sequence of critical assemblages found in the field (fig. 3). Several possible explanations may be considered to take care of this discrepancy. For example clinochrysotile could be metastable in metamorphic terraines and form metastably at low temperatures. Its survival up to upper greenschist facies then could be due to the sluggishness of its breakdown reaction. In fact, the reacting chrysotile assemblages overlap with their products, the antigorite assemblages, over a distance of more than 50 km in the Arosa-Malenco profile (fig. 3). Antigorite occurs first at prehnite-pumpellyite grade at Arosa (GREEN, 1982) and rock-forming clinochrysotile lasts up into the biotite zone (KÜNDIG, 1982). Whereas antigorite is frequently observed to form from chrysotile assemblages, the opposite has never been demonstrated conclusi-





Fig. 9. $\Delta H^{\circ}_{\bullet}$ (298.1) versus temperature diagram for reaction (15). Sloping curve calculated from the *P-T* curve of OTERDOOM (1978). The data point was derived from the field, see text. Uncertainty bars refer to pressure (vertical) and temperature (sloping).

veley. As long as no proof can be presented that chrysotile can form from antigorite (see also WICKS and WHITTAKER, 1977) metastability of chrysotile cannot be excluded. Another possibility for the discrepancy is that natural serpentinites are compositionally different from their experimental counterparts. These differences however, seem to have relatively little influence to the experimental behaviour of serpentines (HEMLEY, MONTOYA, CHRIST and HOSTETLER, 1977; EVANS, JOHANNES, OTERDOOM and TROMMS-DORFF, 1976). Although many analyses of serpentines have been made (PAGE, 1968; WHITTAKER and WICKS, 1970) partitioning data amongst coexisting serpentines for Fe and Al, the main impurities, are rare. In order to calculate a possible shift of reactions (11), (12) and (16) such data are badly needed.

Finally, combined crystal structural and compositional reasons may be responsible for the discrepancy. KUNTZE (1961) described antigorites with widely varying superstructures of their structural wave ranging from 2×10 to 2×20 SiO₄ tetrahedra wavelengths. The accompanying variation in composition must according to Kuntzes model be along a vector between talc and brucite, Mg3H10Si4. For natural antigorites this seems more or less to be the case (WHIT-TAKER and WICKS, 1970). Recalculation of the structure of the antigorite used by KING, BARANY, WELLER and PANKRATZ (1967) in their cp measurements reveals a nearly ideal Kuntze formula that corresponds to a superstructure wave with a period of 2×17 SiO₄ tetrahedra. The same holds for the antigorite that was used by HEMLEY, MONTOYA, SHAW and LUCE (1977) in their experiments. The antigorite from Piz Lunghin, used by JOHAN-NES in his experiments (EVANS, JOHANNES, OTERDOOM and TROMMSDORFF, 1976) has a more magnesium-rich composition and, according to KUNTZES (1961) model a longer superstructure period. In order to solve the discrepancy between field and experiment on the relative stability of chrysotile versus antigorite assemblages, a systematic chemical and crystal-structural study of serpentine minerals along a profile of progressive metamorphism is needed.

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