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THE STABILITY OF CLINOCHRYSOTILE

JOSEPH V. CHERNOSKY, Jr.
Department of Geological Sciences, University of Maine at Orono, Orono, Maine 04469, U.S.A.

Abstract

The univariant reaction that defines the maximum thermal stability of clinochrysotile,

$$\underset{\text{clinochrysotile}}{5Mg_3Si_2O_5(OH)_4} = \underset{\text{forsterite}}{6Mg_2SiO_4} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + \underset{\text{vapor}}{9H_2O},$$

has been bracketed with reversed experiments. Midpoints of the experimental brackets are located at 2 kbar, 437 ± 12°C; 4 kbar, 486 ± 18°C; 5 kbar, 504 ± 13°C; 6.5 kbar, 524 ± 18°C. The starting material consisted of synthetic clinochrysotile, synthetic forsterite + talc or a mixture of all three phases. The reaction was considered to be reversed if a 20% change in the intensities of X-ray reflections (relative to a pattern of the starting material) could be observed after the completion of an experiment. Simultaneous correlation of calorimetric data for a number of phases in the system $MgO-SiO_2-H_2O$, together with bracketing data obtained in this study and for the reaction chrysotile + brucite = 2 forsterite + $3H_2O$ (Johannes 1968), are used to evaluate free energy, entropy and heat capacity for clinochrysotile, talc, forsterite and brucite.

Keywords: chrysotile, asbestos, thermodynamic parameters.

Sommaire

La réaction univariante qui détermine la stabilité thermique maximum du clinochrysotile,

$$\underset{\text{clinochrysotile}}{5Mg_3Si_2O_5(OH)_4} = \underset{\text{forstérite}}{6Mg_2SiO_4} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + \underset{\text{vapeur}}{9H_2O}$$

a été encadrée au moyen d'expériences renversées. Les points centraux des fourchettes expérimentales sont situés à 2 kbar: 437 ± 12°C, 4 kbar: 486 ± 18°C, 5 kbar: 504 ± 13°C, 6.5 kbar: 524 ± 18°C. Le matériau de départ était du clinochrysotile synthétique ou de la forstérite synthétique et du talc ou un mélange de ces trois phases. On considère que la réaction est renversée s'il se produit un changement de 20% dans l'intensité des raies de diffraction X des phases dans le produit par rapport au diagramme de départ. La corrélation simultanée des données calorimétriques de plusieurs phases du système $MgO-SiO_2-H_2O$ ainsi que des données expérimentales provenant de cette étude et de celle de Johannes (1968) sur l'équilibre chrysotile + brucite = 2 forstérite + $3H_2O$ permettent d'évaluer l'énergie libre, l'entropie et la capacité calorifique du clinochrysotile, du talc, de la forstérite et de la brucite.

(Traduit par la Rédaction)

Mots-clés: chrysotile, asbeste, paramètres thermodynamiques.

Introduction

Since the pioneering study of phase equilibria in the system $MgO-SiO_2-H_2O$ by Bowen & Tuttle (1949), numerous workers (Yoder 1952, 1967, Pistorius 1963, Kitahara *et al.* 1966, Johannes 1968, Scarfe & Wyllie 1967, Hemley *et al.* 1977) have reinvestigated the stabilities of chrysotile and chrysotile + brucite, which were thought to be defined by the reactions

$$\underset{\text{chrysotile}}{5Mg_3Si_2O_5(OH)_4} = \underset{\text{forsterite}}{6Mg_2SiO_4} + \underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + \underset{\text{vapor}}{9H_2O} \quad \text{.....(1)}$$

and

$$\underset{\text{chrysotile}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{brucite}}{Mg(OH)_2} = \underset{\text{forsterite}}{2Mg_2SiO_4} + \underset{\text{vapor}}{3H_2O} \quad \text{.....(2)}$$

These reactions were studied at water pressures ranging from 0.5 to 60 kbar. However, only the phase boundaries determined by Scarfe & Wyllie (1967), Johannes (1968) and Hemley *et al.* (1977) were reversed. On the basis of recent experimental data for antigorite (Johannes 1975) and careful analysis of mineral compatibilities found in metamorphosed serpentinites, Evans *et al.* (1976) suggested that reactions (1) and (2) are metastable; they argued convincingly that these reactions should be written with antigorite rather than chrysotile as the stable serpentine. On the basis of thermodynamic calculations, Delany & Helgeson (1978) suggested that pure Mg-chrysotile is metastable at all temperatures and pressures. It is, however, clear that chrysotile of unspecified composition does have a stability field because it has been observed to form directly from antigorite (Evans *et al.* 1976 and references cited therein, Wicks & Plant 1979). Although it is beyond the scope of this paper to speculate on the role that variable Fe^{2+}, Fe^{3+}, Al and Cr contents play in determining the thermal stability of chrysotile, it is important to note that the compositional fields of chrysotile, lizardite and antigorite overlap (Wicks & Plant 1979). It is reasonable, therefore, to consider that chrysotile solid solutions may very well coexist stably with lizardite and antigorite solid solutions over a finite and, perhaps, rather wide temperature interval (Caruso & Chernosky 1979).

As part of a broader investigation of serpentine stability, the dehydration curve for clinochrysotile $Mg_3Si_2O_5(OH)_4$, represented by reaction (1), was determined at water pressures up to 7 kbar. Although reaction (1) is probably metastable, the experimental data allow us to place constraints on the thermodynamic properties of phases involved in this reaction.

Preliminary results of this investigation were reported orally (Chernosky 1973) and are superseded by the data presented in this paper.

Experimental Methods

Starting materials

Mixtures having the bulk compositions $2MgO \cdot SiO_2$, $3MgO \cdot 4SiO_2$ and $3MgO \cdot 2SiO_2$ were prepared by drying, weighing and mixing appropriate proportions of MgO (Fisher, lot 787699) and SiO_2 glass (Corning lump cullet 7940, lot 62221). SiO_2 glass and MgO were fired at 1000°C for two hours to drive off adsorbed water. Forsterite, talc and clinochrysotile were hydrothermally synthesized from the oxide mixes. Purity and crystallinity of the synthetic phases were confirmed by examination with a petrographic microscope and X-ray diffraction; chrysotile was examined with a TEM.

Starting materials used for the experiments consisted of pure clinochrysotile, a mixture of talc, forsterite and clinochrysotile synthesized simultaneously from a starting material having the composition $3MgO \cdot 2SiO_2$, or a mixture of all three phases, each of which was synthesized separately. The latter starting material was prepared by mixing clinochrysotile with stoichiometric proportions of talc and forsterite and grinding for half an hour to ensure homogeneity. Charges were prepared by sealing approximately 10 mg of starting material together with excess distilled, deionized water in 1.25-cm-long gold or platinum capsules.

Procedure

Experiments were performed using conventional cold-seal hydrothermal equipment at the Geophysical Laboratory, at the Massachusetts Institute of Technology and at the University of Maine at Orono; experiments performed in these laboratories are identified in Table 1 by the letters, g, t and m, respectively.

Experiments at the Geophysical Laboratory were conducted in 25.4-cm-long, vertically mounted test-tube bombs. Temperatures were regulated with on–off-type controllers. The emf across unsheathed chromel–alumel thermocouples, which were replaced after each experiment, was measured with a calibrated multipoint recorder. The temperatures reported are probably accurate to within ± 10°C of the stated value. Pressures were measured with a 25.4 cm bourdon-tube gauge and are probably accurate to ± 2% of the stated value.

Experiments at MIT and at the University of Maine were conducted in 30.5-cm-long, horizontally mounted test-tube bombs. Pressures were measured with factory-calibrated 40.6 cm Heise gauges. In order to conserve valve stems

TABLE 1. EXPERIMENTS BRACKETING THE REACTION $5C = 6F + T + 9H_2O$

Experiment number	T (°C)	P_{H_2O} (kbar)	Duration (hours)	Results	Extent of Reaction
55m	409(3)	0.5	6888	C(-)F(+)T(+)	M
53m	427(5)	0.5	5328	C(-)F(+)T(+)	W
321t	399(7)	1.0	1176	C(+)F(-)T(-)	W
297t	422(7)	2.0	1512	C(+)F(-)T(-)	S
289t	431(7)	2.0	1992	C(+)F(-)T(-)	M
212t	431(7)	2.0	1400	C(+)F(-)T(-)	W
287t	442(7)	2.0	2522	C(-)F(+)T(?)	W
215t	458(7)	2.0	1572	C(-)F(+)T(?)	W
355t	445(7)	4.0	1512	C(+)F(-)T(-)	S
300t	462(7)	4.0	3960	C(+)F(-)T(-)	S
356t	476(7)	4.0	2908	C(+)F(-)T(-)	W
298t	474(7)	4.0	1512	C(+)F(-)T(-)	S
51m	497(7)	4.0	5066	C(-)F(+)T(+)	S
448g	465(10)	5.0	1152	C(+)F(-)T(-)	S
447g	480(10)	5.0	1128	C(+)F(-)T(-)	S
54m	496(5)	5.0	7824	C(+)F(-)T(-)	M
49m	511(6)	5.0	5090	C(-)F(+)T(+)	M
42m	499(2)	6.5	1340	C(+)F(-)T(-)	S
43m	508(5)	6.5	3240	C(+)F(-)T(-)	S
44m	536(6)	6.5	1680	C(-)F(+)T(+)	M
446g	500(10)	6.9	784	C(+)F(-)T(-)	S

Growth or diminution of a phase is indicated by a (+) or (-), respectively. Symbols S, M, and W are qualitative estimates of the extent of reaction and represent greater than 75 percent, 75 to 25 percent, and less than 25 percent, respectively. All assemblages include H_2O. Starting materials for experiments 215t and 287t consisted of chrysotile (C), starting material for 212t contained chrysotile and a trace of forsterite; all other starting materials contained chrysotile, forsterite (F), and talc (T). Experiments were performed at the Geophysical Laboratory (g), at MIT (t), and at the University of Maine (m). See text for discussion of temperature uncertainty.

and packings, pressures were monitored carefully at the initiation of each experiment to guard against possible leaks, and were then monitored on a weekly or biweekly basis. Minor fluctuations in pressure resulting from temperature drift did occur; however, experiments that suffered pressure drops of greater than 50 bars were discarded. Pressures are believed to be accurate to within ± 1% of the stated values. Errors in reported temperatures that were due to temperature gradients across the sample-containing capsules and to inaccurately calibrated thermocouples were evaluated. Temperature gradients in the pressure vessels were measured at room pressure and found to be less than 1°C over a working distance of 3.0 cm. Because the sample capsules were 1.25 cm long, errors arising from temperatures gradients in the pressure vessels were assumed to be negligible. Temperature measurements in both laboratories were made using sheathed, chromel-alumel thermocouples, each of which was calibrated against a previously standardized thermocouple in order to ensure internal consistency among experiments performed in different pressure vessels. For experiments performed at the University of Maine, the temperature calibration for each shielded thermocouple was checked after every experiment, whereas this procedure was not followed for experiments performed earlier at MIT. Consequently, errors in the reported temperatures for experiments conducted at MIT are estimated to be ± 7°C, whereas errors for experiments performed at the University of Maine are reported as ± 2 standard deviations about the mean temperature and represent error due solely to temperature drift.

Owing to sluggish reaction rates at temperatures and pressures close to the phase boundary, complete reaction was never obtained. Determination of reaction direction at a given temperature and pressure was based on a comparison of an X-ray-diffraction pattern of an experimental product with a pattern of the starting material over the interval 5 to 40° ($CuK\alpha$ radiation). The 002, 020 and 006 reflections of talc and all of the forsterite reflections within this interval were compared with the 002 and 004 reflections of clinochrysotile in order to judge direction of reaction. A reaction was considered to be reversed if at least 20% change in the intensities of X-ray reflections of an experimental product relative to those of the starting material could be observed. Microscopic observation of the experimental products did not reveal textural criteria that could be used to judge direction of reaction.

Unit-cell parameters for clinochrysotile were obtained by refining a powder pattern obtained with an 11.46 cm Debye-Scherrer camera. CaF_2 (Baker Lot 91548, *a* 5.4620 ± 0.0005 Å) standardized against gem diamond (*a* 3.56703 Å: Robie *et al.* 1967) was used as an internal standard. The unit-cell parameters of clinochrysotile were refined using a computer program written by Burnham (1962).

RESULTS

Synthesis and characterization of phases

Clinochrysotile $Mg_3Si_2O_5(OH)_4$ is readily synthesized from an oxide mix at temperatures and pressures to the left of the dehydration curve shown in Figure 1. Although the synthetic phase is extremely fine-grained, observation with a transmission electron-microscope revealed the long, slender, hollow-tube morphology characteristic of chrysotile. The powder pattern for synthetic clinochrysotile published by Chernosky (1975, Table 2) is representative of the powder patterns of clinochrysotile encountered in the bracketing experiments. Unit-cell parameters for clinochrysotile used in the bracketing experiments are *a* 5.306(6), *b* 9.174 (12), *c* 14.650(8) Å, *β* 93.34° and *V* 712.13 (9.77) Å^3; the numbers in parentheses represent the estimated standard deviation in terms of the least units cited for the value to their immediate left. The uncertainties only represent precision in measuring the X-ray reflections.

Chernosky (1975) observed that chrysotiles synthesized 20 or 30°C below the phase boundary (Fig. 1) are interspersed with 5–10% Mg-lizardite. Hydrothermal treatment (Chernosky 1975) of such a mixture at 413°C and $P(H_2O) = 2$ kbar produced 100% tubular serpentine, suggesting that clinochrysotile is more stable than pure Mg-lizardite at the conditions of the experiment. Care was taken to avoid using chrysotile contaminated with lizardite for starting material.

Forsterite Mg_2SiO_4 was synthesized hydrothermally at 800°C and $P(H_2O) = 1$ kbar in experiments ranging from four days to two weeks in duration. Crystals are fine grained (0.009 mm) and anhedral. The position of the 130 reflection at $d = 2.764$ Å coincides with d_{130} of synthetic forsterite (Fisher & Medaris 1969).

Talc $Mg_3Si_4O_{10}(OH)_2$ was synthesized hydrothermally at 680°C, $P(H_2O) = 2$ kbar in experiments lasting from three days to three weeks. Talc typically crystallized in aggregates of fine grained (0.012 mm) plates. The unit-cell para-

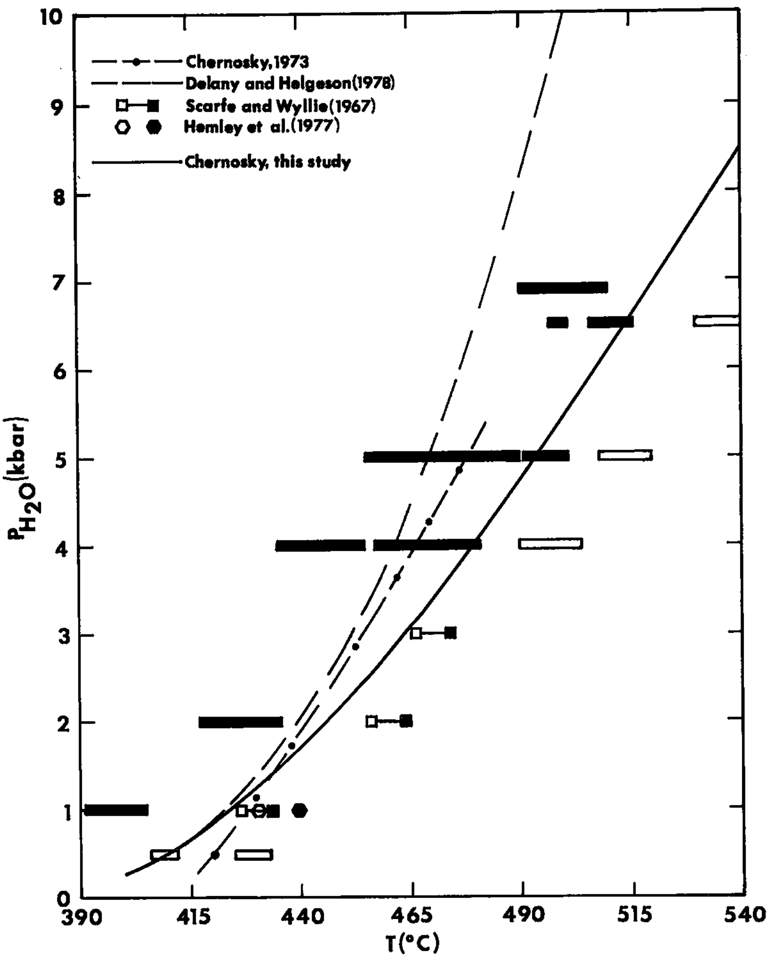

FIG. 1. Dehydration curve for the reaction 5C = 6F + T + $9H_2O$. Solid symbols represent growth of chrysotile; open symbols represent growth of the high-temperature assemblage. Size of symbols represents uncertainty in the measurement of temperature and pressure. Dashed curve was calculated by Helgeson *et al.* (1978); dash–dot curve is based on preliminary data reported by Chernosky (1973); the solid curve was calculated (Table 4, run C) using the experimental data in Table 1 and the thermochemical values in Tables 2 and 3.

meters agree with those of natural (PDF 13–558) and synthetic talc (Forbes 1969).

The reaction 5C = 6F + T + $9H_2O$

The upper thermal stability of clinochrysotile may be defined by the reaction clinochrysotile = forsterite + talc + vapor (reaction 1). Critical experiments bracketing the position of the dehydration curve for this reaction at $P_{\text{fluid}} \approx P(H_2O)$ are summarized in Table 1 and plotted on Figure 1. Because the bracket at $P(H_2O)$ = 2 kbar was established in part by optical examination of the charge, it merits additional discussion. Two experiments, 212t and 289t, were used to establish the low temperature end of the bracket at 431 ± 7°C. After hydrothermal treatment, the small amount of modal forsterite (~ 1%) present in the starting material (talc was not observed but was presumed to be present) for experiment 212t had been converted to clinochrysotile. The result of experiment 289t, which was performed with a starting material containing all three phases, confirmed the result of experiment 212t. Experiment 287t was used to establish the high-temperature end of the bracket at 442 ± 7°C. After hydrothermal treatment, the starting material that contained only clinochrysotile had been converted to clinochrysotile plus about 5% modal forsterite; again, talc was not observed in the products but was presumed to be present.

The stability of chrysotile has also been investigated by Bowen & Tuttle (1949), Pistorius (1963), Kitahara *et al.* (1966) and Yoder (1967); however, the dehydration curves they obtained lie as much as 70°C higher than the curve determined in the present study. Reversibility was not demonstrated by these investigators, and their curves doubtless represent metastable synthesis rather than stability boundaries.

Reversibility is claimed in two recent investigations (Scarfe & Wyllie 1967, Hemley *et al.* 1977) pertaining to the stability of chrysotile. The data obtained during these two studies are plotted on Figure 1 where they may be compared with the data obtained in the present study. Although the dehydration curve obtained during the present study lies at lower temperatures than the curve of Scarfe and Wyllie and the bracket of Hemley *et al.* at $P(H_2O) = 1$ kbar, the agreement among the three data sets is remarkable considering that three very different experimental techniques were employed to reverse this highly sluggish reaction. Although the results of all three studies are reasonably close, it is worthwhile to critically evaluate all three data sets, because accurate location of dehydration curves in P–T space is required for thermochemical calculations.

Scarfe & Wyllie (1967) did not identify the serpentine mineral formed in their experiments. However, experiments conducted on the same composition $Mg_3Si_2O_5(OH)_4$ at similar pressures and temperatures during this study suggest that it was clinochrysotile. Scarfe and Wyllie used textural criteria (topotactic crystallization) to determine that the back reaction had occurred; they stated that 200 hours were required to establish the forward reaction, and 600 hours to establish the back reaction.

The discrepancy between the results obtained in the present study and those of Scarfe and Wyllie is probably due to the difficulty of establishing the direction of reaction, although the lack of adequate calibration of experimental equipment may be a contributing factor. The results obtained in the present study are judged to be more reliable because the experiments were conducted for periods of up to 6888 hours in calibrated hydrothermal apparatus; Scarfe & Wyllie (1967) did not discuss calibration of their equipment.

Hemley *et al.* (1977) monitored phase changes of the solids and compositions of the aqueous solutions in equilibrium with the solids to reverse the reactions

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 5H_2O = \underset{\text{chrysotile}}{Mg_3Si_2O_5(OH)_4} + 2H_4SiO_4$$

and

$$\underset{\text{talc}}{Mg_3Si_4O_{10}(OH)_2} + 4H_2O = \underset{\text{forsterite}}{1.5Mg_2SiO_4} + 2.5H_4SiO_4$$

at $P(H_2O) = 1$ kbar. The intersection of these two reactions in log $m(SiO_2)$ *versus* $1/T$ space yields the equilibrium temperature 435 ± 6°C for the dehydration of chrysotile to forsterite and talc at $P(H_2O) = 1$ kbar (Fig. 1). The bracket shown on Figure 1 was obtained using synthetic phases; use of natural minerals in the starting material resulted in a higher equilibrium temperature (441 ± 6°C).

With natural mineral pairs as starting materials, both talc–chrysotile and talc–forsterite equilibria were reversed by approaching the equilibrium concentration of dissolved silica from both directions. However, only two of the four experiments using *synthetic* talc–chrysotile pairs were reversals, and both of these approached the "equilibrium" concentration of silica from the same direction. In other words, only the high-temperature side of the synthetic talc–chrysotile equilibrium was defined by reversed experiments. In addition to possible errors due to lack of calibration [Hemley *et al.* (1977) did not mention calibration of their apparatus], it is conceivable that these workers did not define the low-temperature side of the bracket for experiments involving synthetic pairs. Hence, the polybaric reversals for synthetic phases presented in this paper are deemed to be superior to the 1 kbar reversal reported by Hemley *et al.* (1977).

DISCUSSION

Thermodynamic considerations

Several sets of "internally consistent" thermodynamic parameters for chrysotile and related minerals in the system $MgO–SiO_2–H_2O$ have been proposed recently (Zen & Chernosky 1976, Hemley *et al.* 1977, Helgeson *et al.* 1978, Robie *et al.* 1978). The latter two compilations are the most comprehensive, although there are disagreements in the reported thermochemical values for a number of minerals. For example, the values of Gibbs free energy reported for forsterite and talc differ by more than four and twelve kilojoules, respectively. Discrepancies arise because the compilation of Helgeson *et al.* (1978) is based primarily on phase-equilibrium measurements, whereas that of Robie *et al.* (1978) is based primarily on calorimetric measurements.

Helgeson *et al.* (1978) used preliminary experimental data establishing the location of reaction (1), 5C = 6F + T + $9H_2O$, in P–T space (Chernosky 1973) to calculate thermodynamic properties for chrysotile. These authors noted a discrepancy between their calculated thermodynamic parameters for chrysotile and the experimental data of Johannes (1968) for reaction (2), C + B = 2F + $3H_2O$. They suggested that the discrepancy arose because "Johannes' experimental reactants and products were not comparable to those in Chernosky's experiments". Hence, it is appropriate to re-evaluate the thermodynamic values for chrysotile, forsterite, talc and brucite in the light of the new experimental data presented in this paper.

TABLE 2. SOURCES OF THERMOCHEMICAL DATA FOR REFERENCE PHASES USED IN THE EVALUATION

Phase	$\overset{\circ}{C}p(T)$	S°(298), H°_f(298), G°_f(298)
H_2 (ideal gas)	1	2
O_2 (ideal gas)	1	2
Si (crystal, liquid)	1	2
Mg	4	3
H_2O (gas)	4	2,5
SiO_2 (α- and β-quartz)	4	2
MgO	4	3

(1) Hultgren et al. (1973); (2) CODATA Task Group (1978); (3) CODATA Task Group (1973); (4) Stull & Prophet (1971) and Chase et al. (1974, 1975); (5) Fisher & Zen (1971).

TABLE 3. THERMOCHEMICAL VALUES ALLOWED TO VARY DURING THE EVALUATION

Thermodynamic Property	Reference	Number of Observations
Brucite		
Heat of formation	Robie et al. (1978)	1
Free energy of formation	King et al. (1975)	1
Entropy	Robie et al. (1978)	1
Relative heat content	King et al. (1975)	13
Low temp. heat capacity	Giauque & Archibald (1937)	23
Clinochrysotile		
Heat of formation	King et al. (1967)	
Low temp. heat capacity	King et al. (1967)	10
Entropy	King et al. (1967)	1
Forsterite		
Heat of formation	King et al. (1967)	1
Free energy of formation	King et al. (1967)	1
Entropy	Stull & Prophet (1971)	18
Relative heat content	Orr (1953)	16
Talc		
Heat of formation	Barany (1963)	1
Free energy of formation	Bricker et al. (1973)	1
Entropy	Robie & Stout (1963)	1
Low temp. heat capacity	Robie & Stout (1963)	12

The computer program PHAS 20 (Haas 1974) was used to simultaneously evaluate and correlate a large body of calorimetric data for selected phases in the system $MgO–SiO_2–H_2O$ (Tables 2, 3) with phase-equilibrium data for reactions (1) and (2). Descriptions of the mathematical model, the standard-state conventions as well as the computer program used to perform the calculations are published elsewhere (Haas 1974, Haas & Fisher 1976) and need not be repeated here. Sources of the thermodynamic data for the elements and oxides Mg, Si, H_2, O_2, MgO, H_2O, α-quartz and β-quartz, used as reference phases in the evaluation, are given in Table 2. Thermodynamic values for reference phases were held constant, whereas thermodymanic values for brucite, clinochrysotile, forsterite and talc (Table 3) as well as the phase-equilibrium data were allowed to vary during the evaluation.

Experimental phase-equilibrium data were supplied as values of log *K* for a reaction at the pressure and temperature of each limiting experiment. Log *K* values for reactions (1) and (2) were calculated at the pressure and temperature corresponding to that end of each limiting experiment farthest from the equilibrium curve, in order to account for uncertainty in the measurement of temperature and pressure. Calculating log *K* for each experiment amounted to determining log $f(H_2O)$ at the pressure and temperature of the experiment, using the tables of Burnham *et al.* (1969). This simplification was possible because it was assumed that the compositions of the solid phases had remained unchanged during the course of the experiments. Since the thermochemical correlations were performed at a total pressure of 1 atmosphere, experimental data collected at variable total pressures were all corrected for the effect of pressure on the volume change of the solid phases (Eugster & Wones 1962). The correction amounted to adjusting experiments conducted at different total pressures so that they "appear" as if they were performed at the same constant total pressure. Log *K* values at 1 atm were calculated using the expression $\log K = \eta(H_2O) \log f(H_2O, P_{exp}) - \Delta V_s(P - P_{exp}) / 2.303\ RT$, where $\eta(H_2O)$ is the stoichiometric coefficient for H_2O in the reaction, ΔV_s is the volume change for the solid phases participating

TABLE 4. COMPARISON OF THERMOCHEMICAL VALUES FOR BRUCITE, CHRYSOTILE, FORSTERITE AND TALC AT 298K, 1 BAR

	Helgeson et al. (1978)	Robie et al. (1978)	A All thermo. data no reactions	B All thermo. data C=F+T+H_2O	C All thermo. data C=F+T+H_2O C+B=F+H_2O
Brucite					
S°(298K,1) j mol^{-1}K^{-1}	63.14	63.18±0.13	63.194	63.194	63.194
G°(298K,1) j mol^{-1}	-835319	-833506±440	-834122	-834122	-834122
Cp(298K,1) j mol^{-1}K^{-1}		77.28	77.406	77.406	77.391
Chrysotile					
S°(298K,1) j mol^{-1}K^{-1}	221.3	221.3±0.8	221.334	221.265	221.271
G°(298K,1) j mol^{-1}	-4037020	-4034024±3500	-4034212	-4030410	-4030419
Cp(298K,1) j mol^{-1}K^{-1}		273.70	273.632	273.632	273.632
Forsterite					
S°(298K,1) j mol^{-1}K^{-1}	95.19	95.19±0.84	95.75	95.75	95.75
G°(298K,1) j mol^{-1}	-2056704	-2051325±1345	-2051284	-2051873	-2051941
Cp(298K,1) j mol^{-1}K^{-1}		117.90	110.603	110.603	110.603
Talc					
S°(298K,1) j mol^{-1}K^{-1}	260.8	260.83±0.63	260.745	260.754	260.751
G°(298K,1) j mol^{-1}	-5523633	-5536048±4350	-5529925	-5530823	-5530663
Cp(298K,1) j mol^{-1}K^{-1}	334.30	321.7	322.212	322.196	322.192

Column A was calculated using the data in Tables 2 and 3; column B was calculated using the data in Tables 1, 2, and 3; column C was calculated using the data in Tables 1, 2, 3 and Johannes (1968, Table 1).

in the reaction, P_{exp} is the pressure at which the experiments were performed and P is the pressure to which all experiments were corrected (1 atm). Once input, the individual log *K* values were evaluated, together with all thermochemical data, using simultaneous multiple-least-squares regression.

The results of the thermochemical calculations are summarized in Table 4, where they are compared with thermochemical values tabulated by Helgeson *et al.* (1978) and Robie *et al.* (1978). For the sake of comparison, thermochemical data in Table 4 are cited at a pressure of 1 bar; *i.e.*, the ΔG values obtained in this study were recalculated to 1 bar. Results of three computer runs are compared. Experimental phase-equilibrium data were omitted for run A. Experimental data for reaction (1) were included for run B, and experimental data for both reactions (1) and (2) for run C. Note that the inclusion of phase-equilibrium data in the evaluation procedure does not significantly affect the thermodynamic values for the phases listed in Table 4. Moreover, the calculated thermochemical values are in reasonable agreement with the thermodynamic values reported by Robie *et al.* (1978) and Helgeson *et al.* (1978). The only significant discrepancy occurs in the free energy of talc; the calculated value falls between the values reported in the two compilations. As a further test of the calculated thermochemical values we may determine whether they can be used to calculate an equilibrium curve that passes through the experimental brackets. The results of this test are shown on a log $f(H_2O)$ *versus* 1/T diagram (Fig. 2). Note that the calculated curves for reactions (1) and (2) pass through all the experimentally determined brackets obtained during this study and by Johannes (1968), respectively.

In summary, the thermochemical correlation indicates that the experimental results of Johannes (1968) and those reported in this paper are internally consistent and consistent with the body of calorimetric data for chrysotile, forsterite, talc and brucite as well as for the reference elements and oxides (Table 2). Both sets of experimental data should be considered when compiling an internally consistent set of thermodynamic parameters for the minerals brucite, chrysotile, forsterite and talc. It must be emphasized that the thermochemical values were generated for the purpose of comparing the phase-equilibrium data for reactions (1) and (2) and testing these data for consistency with the body of calorimetric data for chrysotile, brucite, forsterite and talc. The calculated ther-

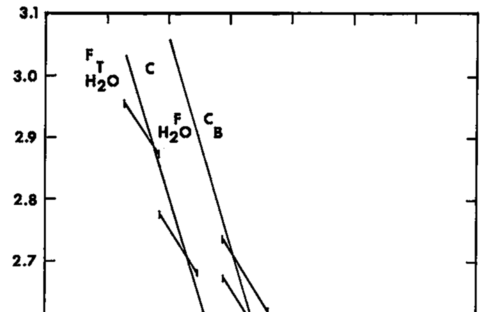

FIG. 2. Log f(H_2O) *versus* 1/T diagram for the reactions C + B = F + H_2O and C = F + T + H_2O. Solid lines through the brackets were calculated (Table 4, run C) using the experimental data of Johannes (1968), the experimental data in Table 1 and the thermochemical values in Tables 2 and 3. End points of each bracket correspond to the most distant part of the error bar for each experiment rather than its mean temperature.

mochemical values have not been tested against all other relevant phase-equilibrium data; until this is done, these values can only be considered provisional.

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