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The Stability of Talc

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Abstract

The stability of talc ($Mg_3Si_4O_{10}(OH)_2$) has been estimated using three separate lines of approach. The $\Delta G^\circ_f(25^\circ, 1, \text{talc})$ value obtained (−1320 kcal) seems to be consistent with observed natural occurrences of talc. Reassessment of the stability of chrysotile ($Mg_3Si_2O_5(OH)_4$), on the basis of this talc data, leads to a value of $\Delta G^\circ_f(25^\circ, 1, \text{chrys}) = -962$ kcal.

Introduction

The mineral talc ($Mg_3Si_4O_{10}(OH)_2$) has been found in a number of different types of geological environments. It occurs as an alteration product of serpentine (Hess, 1933; Chidester, 1968), it has been dredged from the ocean floor (Siever and Kastner, 1967), and it has been found in saline lake sediments (B. F. Jones, personal communication) and evaporites (Braitsch, 1962). Talc is a potential sink for magnesium and silica in the oceans and in saline lakes if, indeed, it actually precipitates in these environments and is not merely of detrital origin. In order to determine the stability field of talc at the earth's surface and to define the conditions under which talc might be expected to form, it is necessary to have accurate thermodynamic data. Values of the Gibbs energy of formation of talc have been reported by several investigators (Barany, 1963; Robie and Stout, 1963). Robie and Waldbaum (1968) list $\Delta G^\circ_f(25^\circ, 1, \text{talc})$* as -1324.386 ± 1.720 kcal/mol whereas Hostetler *et al.* (1971) determined $\Delta G^\circ_f(25^\circ, 1, \text{talc})$ to be −1319 kcal/mol for this mineral. A large uncertainty in the stability of talc results from these discrepancies in $\Delta G^\circ_f(25^\circ, 1, \text{talc})$ and makes environmental interpretations unreliable.

Problems arise in determining and assessing errors in experimentation. Errors in calorimetric studies are very difficult to assess except by repetition of experiments or by applying indirect evidence to test the validity of the thermodynamic properties derived from the experiments. An indirect test of thermodynamic values derived from experimentation is verification of their accuracy in predicting a mineral's stability in a given geological environment. Using the Gibbs energy data cited by Robie and Waldbaum, surface sea water and interstitial pore fluids from marine bottom muds are supersaturated with respect to talc. Accordingly, talc should be stable and perhaps forming in marine muds, but it is not a commonly observed solid in ocean sediments. The field observations, therefore, do not seem consistent with the above thermodynamic value for talc.

The entropy of talc tabulated in USGS Bulletin 1259 differs by more than 7 percent (298.15°K) from that predicted by summation of the entropies of its oxides after the volume correction is considered (Fyfe, Turner and Verhoogen, 1958). Generally the entropy estimate of a mineral by the above method is within 5 percent.

The verification of talc stability from hydrothermal studies is promising if the thermodynamic properties of the other phases involved are known precisely enough to test the talc value critically.

The compositional changes of the solution in which a solid is dissolving can be an extremely sensitive

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* Symbols: $\Delta G^\circ_f(T,P,\text{Sp})$ standard Gibbs energy of formation of a species Sp from the elements at temperature T(°C) and pressure P(bars); $\Delta H^\circ_f(T,P,\text{Sp})$, standard enthalpy of formation; $S^\circ(T,P,\text{Sp})$, standard entropy; $\Delta S^\circ_f(T,P,\text{Sp})$, standard entropy of formation; $C^\circ_P(T,P,\text{Sp})$, standard absolute isobaric heat capacity; ΔC°_P, standard heat capacity of formation from the elements; V°, volume in cm^3/mol at 25°C and 1 bar; $\hat{n}_i$, reaction coefficient of ith species in a reaction; f_{species}, fugacity of species; a_{species}, activity of species; [species], molality of species; $\Delta G^\circ_r(T,P,r,s)$, standard Gibbs energy of reaction r from source s at T and P; log $K_r(T,P,r,s)$, $\log_{10}$ equilibrium constant; $\Delta\log K_r(T,P,r)$ difference between two equilibrium constants for the same reaction. Standard refers to the species in an arbitrarily specified standard state. For gases and solids it is the pure substance at T of interest and 1 bar. For aqueous species it is the hypothetical ideal one molal solution at its T and P of interest.

method for deriving information about the composition of the dissolving solid(s) and the type of reaction (congruent or incongruent) occurring at any time during dissolution. Solubility studies, however, are also replete with difficulties. To determine the thermodynamic properties of any mineral by this method virtually necessitates using a pure solid phase which dissolves congruently. If such conditions are not achieved, the chemical evolution of the solution becomes complex and the validity of the thermodynamic properties obtained from analysis of the solutions rests on interpreting the history of the solution's composition.

Obtaining pure samples for dissolution (or calorimetric) studies is very difficult. Hydrothermally synthesized solids are dangerous starting materials, as seldom is there 100 percent conversion of the reactants to the product phase. The mixing of starting materials must be exact; otherwise one or more of the components will remain in excess. If there is less than 100 percent conversion or improper mixing of the starting materials, there will be more than one solid dissolving when the material is placed in solution.

Natural materials may be somewhat better, but obtaining pure end–member crystals is difficult. Chrysotile and talc often contain some structural Fe and/or Al which may complicate the dissolution reaction (Deer *et al.,* 1962). In addition to solid solution impurities, minute quantities of other phases may be included in or intergrown with the crystals. An excellent example is cited by Martinez and Comer (1964) who separated a fine amorphous material from the interstices of ore quality chrysotile fiber. Such accessory phases may complicate the chemistry of the solutions in which solids have dissolved.

Many low-temperature (25°C) experiments are almost impossible to reverse, in that it is difficult to precipitate sufficient amounts of solids (particularly silicates) for optical or X-ray identification. Dissolution experiments give at best the most stable thermodynamic values of the phase dissolved. If crystals do form and are very fine grained, the thermodynamic data may vary with each experiment depending on crystallinity and surface area effects.

With these considerations in mind, we have tried to evaluate the thermodynamic stability of talc. Our three separate lines of approach converge on a Gibbs energy value of −1320 ± 2 kcal/mol, which seems to be consistent with observed natural occurrences of talc.

Direct Solubility Measurements at 25°C

In 1966 a sample of synthetic talc prepared by George Skippen, then a graduate student at Johns Hopkins University, was obtained. This sample was divided into two 0.1 g portions. One was placed in a polyethylene bottle containing 50 ml of distilled water (sample A) and the other was put into a polyethylene bottle containing 50 ml of a 25 ppm $H_4SiO_{4(aq)}$ solution (sample B). Both were then placed on a shaker table. At the time these experiments were begun (June, 1967), it was thought that talc would equilibrate at a dissolved silica concentration intermediate between 0 and 25 ppm so that, in effect, equilibrium would be approached from both undersaturation and supersaturation. It was also suspected that equilibration would be slow; hence a long sampling interval was used. Table 1 lists silica release data which reveal that equilibration was essentially complete in less than three months at a silica value well above 25 ppm. The initial samples were analyzed for Mg^{++} by atomic absorption, for dissolved silica by the reduced silicomolybdate method (Mullin and Riley, 1955), and pH was measured using a glass electrode. The suspensions were kept on the shaker table for just under five years and aliquots were periodically removed for silica analysis. The silica concentrations remained constant over that period and the final aliquots were again analyzed for Mg^{++}, $H_4SiO_{4(aq)}$ and pH was measured (Table 1). X-ray diffraction data on the crystalline solids were obtained from smear mounts. The X-ray pattern was identical before and after the experiment (Table 2). The only noticeable effect was a marked increase in

TABLE 1. CATION-RELEASE DATA FOR TALC DISSOLUTION AT 25°C, 1 ATM *

Months	H_4SiO_4(ppm)	Mg^{++}(ppm)	pH
	SAMPLE A		
0	--	--	--
3	115(2)	13.7(1)	7.32(2)
11	113(2)	--	--
28	115(2)	--	--
53	114(2)	13.0(1)	7.35(2)
	SAMPLE B		
0	25.0(5)	--	--
3	121(2)	8.8(1)	7.40(2)
11	120(2)	--	--
28	123(2)	--	--
53	122(2)	8.8(1)	7.46(2)

* Numbers in parentheses refer to estimated standard deviations (esd) expressed in the least units cited. Thus 25.0(5) and 121(2) represent 25.0 (esd 0.5) and 121 (esd 2).

intensity and sharpening of the peaks after the experiment was completed, which probably reflects an increase in crystallinity of the solid as a result of aging and recrystallization. Assuming that the talc had equilibrated with the solution by the reaction

$$Mg_3Si_4O_{10}(OH)_2 + 6H^+ + 4H_2O = 3Mg^{++} + 4H_4SiO_4 \quad (1)$$

a Gibbs energy value can be calculated from the following:

$$\log K_r(25°, 1, \text{talc}) = 3 \log [Mg^{++}] + 4 \log [H_4SiO_4] + 6pH \quad (2)$$

$$\Delta G°_r(25°, 1, \text{talc}) = -1.364 \log K_r(25°, 1, \text{talc}) \quad (3)$$

$$\begin{aligned}\Delta G°_f(25°, 1, \text{talc}) &= 3\Delta G°_f(25°, 1, Mg^{++}) + 4\Delta G°_f(25°, 1, H_4SiO_4) \\ &\quad - 4\Delta G°_f(25°, 1, H_2O) - 6\Delta G°_f(25°, 1, H^+) \\ &\quad - \Delta G°_r(25°, 1, \text{talc}) \quad (4)\end{aligned}$$

A value for $\Delta G°_r(25°, 1, \text{talc})$ can be calculated from the experimental data and $\Delta G°_f(25°, 1, Mg^{++})$, $\Delta G°_f(25°, 1, H^+)$, and $\Delta G°_f(25°, 1, H_4SiO_4)$ given in Table 3. Substitution of these values into equation (4) permits calculation of $\Delta G°_f(25°, 1, \text{talc})$. Using the raw analytical data, the calculated values for the two runs are -1319.4 ± 1.5 kcal/mol and -1319.1 ± 1.5 kcal/mol. These values for $\Delta G°_f(25°, 1, \text{talc})$ are in good agreement with the value reported by Hostetler *et al.* (1971) but significantly less negative than that tabulated by Robie and Waldbaum (1968).

The activity of Mg^{++} deviates somewhat from the analytical concentration even at the low ionic strengths encountered in these dilute solutions, and the free energy values will be slightly more negative if a correction is made for Mg^{++} activity. Too little solution remained at the termination of the experiment to permit analysis for anions; however, the maximum gain in Gibbs energy due to activity coefficient corrections would only be on the order of one-tenth to several tenths of a kilocalorie, or less than the estimated error.

TABLE 2. THE d-SPACINGS OF SYNTHETIC TALC USED IN DISSOLUTION EXPERIMENT AT 25°C, 1 ATM

d(Å)	9.34	4.66	3.12	1.87	1.53
I	10	8	10	3	3
hkl	002	004	006	0·0·10	0·0·12

TABLE 3. GIBBS ENERGY OF FORMATION FOR SPECIES IN THE SYSTEM $MgO-SiO_2-H_2O$

Species	$\Delta G°_f(25°,1)\text{kcal mol}^{-1}$	Source
Mg^{++}(aq)	-108.900 ± 0.200	1
H_2O (aq)	-56.688 ± 0.020	1
H^+ (aq)	0	1
H_4SiO_4 (aq)	-312.5	2
Brucite	-199.460 ± 0.730	1
Chrysotile	-964.920	2
Talc	-1324.486 ± 1.720	1

* Sources of data: (1) Robie and Waldbaum (1968; (2) Hostetler, (1971)

Reinterpretation of chrysotile solubility data

Hostetler and Christ (1968) attempted to determine the Gibbs energy of formation of chrysotile from solubility studies on natural and synthetic chrysotile samples. They assumed in their calculations that chrysotile had dissolved congruently, but the Mg/Si ratios observed in their experiments suggest that this was not the case. A different interpretation of their data leads us to conclude that chrysotile actually dissolved incongruently to form talc and that the solution composition was really controlled by equilibrium with talc.

The data from experiment S–2 (natural chrysotile from New Idria) are plotted in $\log a_{Mg^{++}}/a_{H^+}{}^2$ vs $\log a_{H_4SiO_4}$ space in Figure 1a. The solution compositions are numbered sequentially starting with one. Solid lines represent mineral-solution stability boundaries drawn using the Gibbs energy of chrysotile cited by Hostetler and Christ (1968) and the Gibbs energy of talc from Robie and Waldbaum (1968). Dashed lines are metastable mineral–solution boundaries. Within mineral fields bounded by stable and metastable line segments, the solution is supersaturated with one or more of the minerals. The degree of supersaturation depends on the distance the phase lies from its equilibrium boundary with solution.

If the stability relations portrayed on this diagram are correct, the solution was already supersaturated with chrysotile at the time the first sample was taken (the solution composition lies above the metastable extention of the chrysotile–solution boundary in the talc field) and the degree of super–saturation increased as the experiment continued. This is not the behavior that would be expected of a phase dissolving congruently to saturation. In addition, the solution

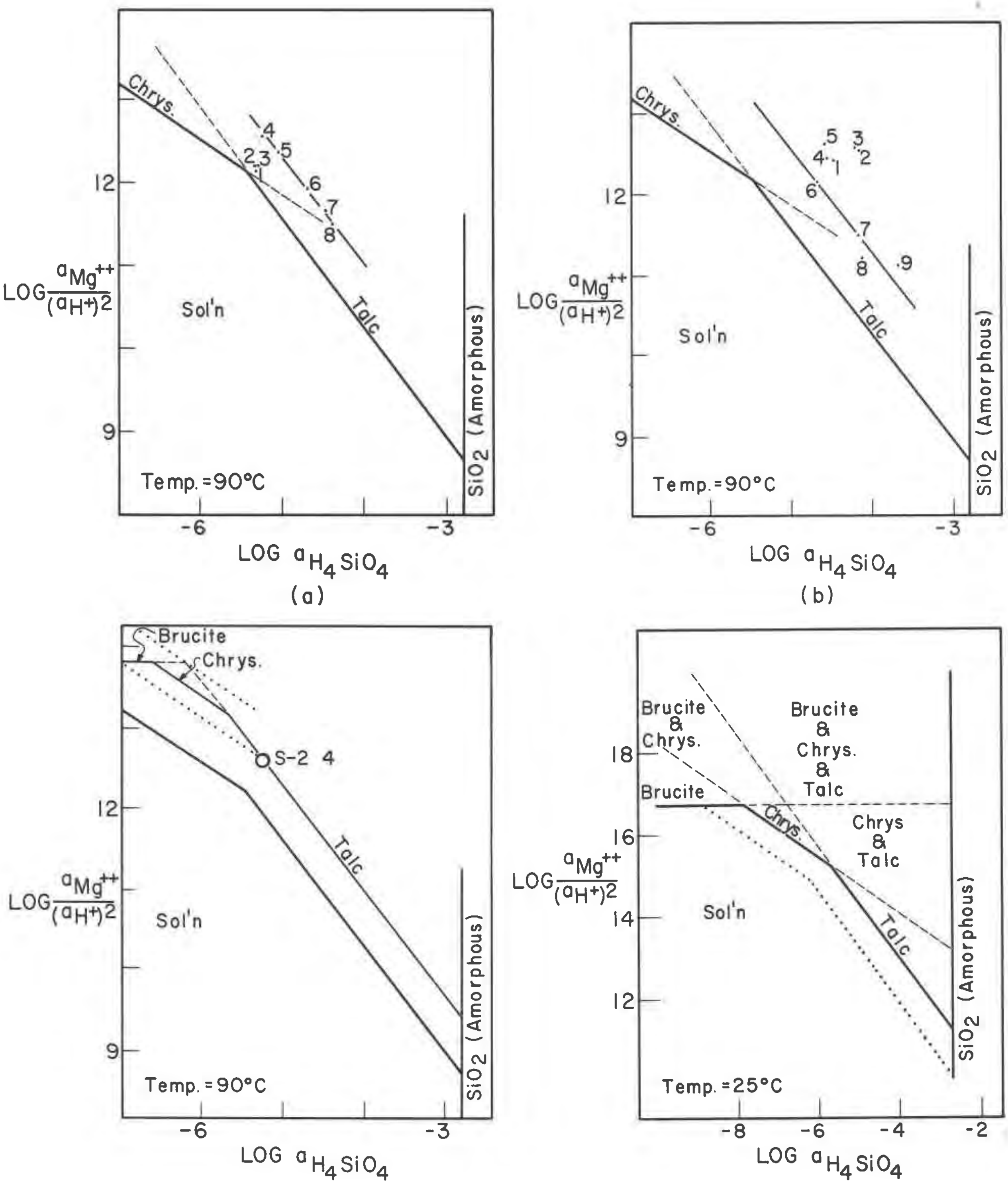

FIG. 1a. Plot of log $a_{Mg^{++}}/a_{H^+}{}^2$ vs. log $a_{H_4SiO_4}$ for the New Idria chrysotile (S-2) experiment at 90°C and 1 atm (from Hostetler and Christ, 1968).

b. Plot of log $a_{Mg^{++}}/a_{H^+}{}^2$ vs. log $a_{H_4SiO_4}$ for a synthetic chrysotile dissolution experiment at 90°C and 1 atm (from Hostetler and Christ, 1968).

c. Plot of log $a_{Mg^{++}}/a_{H^+}{}^2$ vs log $a_{H_4SiO_4}$ made to estimate log K_r(90°, 1, chrys).

d. Stability relations of some phases in the system MgO–SiO_2–H_2O at 25°C and 1 atm total pressure as a function of log $a_{Mg^{++}}/a_{H^+}{}^2$ vs. log $a_{H_4SiO_4}$. Dotted lines represent the stability field of talc and chrysotile calculated using data from Robie and Waldbaum (1968) and Hostetler and Christ (1968). Mineral fields bounded by the continuous and dashed lines are fields in which the solution is supersaturated with one or more of the minerals.

compositions plotted on the diagram indicate that the more stable phase under these conditions should be talc and not chrysotile. After approximately 50 hours (sample 4) the composition of the solution changed in the direction of higher silica activity and a lower $[Mg^{++}]/[H^+]^2$ ratio. Hostetler and Christ (1968) attribute this change to leakage of CO_2 into the system and accept sample 8 as representing the composition of a solution in equilibrium with chrysotile. We are forced to the conclusion that the solution very quickly supersaturated with chrysotile, the degree of supersaturation increased and then decreased as P_{CO_2} changed, until finally the system reached equilibrium with chrysotile (sample 8). This entire process must also have occurred metastably in the stability field of talc (Fig. 1a).

We believe this data may be better interpreted in the following mannner. Examination of Figure 1a shows that samples 4 to 8 plot along a straight line having a slope consistent with reaction of a solid phase containing magnesium and silicon in a ratio of 3:4. We suggest that chrysotile (Mg:Si = 3:2) dissolved incongruently to talc (Mg:Si = 3:4). During approximately the first fifty hours (to sample 4), talc rims on the original chrysotile fragments grew to a thickness sufficient to prevent direct contact between the solution and chrysotile. The solution composition was completely controlled by equilibrium with talc from then on (samples 4 to 8). The observed change in solution composition from S-2-4 to S-2-8 is consistent with CO_2 leaking into the system and reacting with a phase containing Mg:Si in a ratio of 3:4. If this interpretation is correct, talc equilibrium was approached from undersaturation in experiment S-2. Talc was the first phase to saturate and the straight line defined by samples 4 to 8 represents the talc solution boundary.

The experimental data from run S-1 (synthetic talc) show a similar behavior (Figure 1b). In this run, however, the solution was already supersaturated with talc at the time of the first sampling, suggesting the presence of magnesian phases more soluble than talc. After a time, the solution composition migrated in the direction of the talc boundary and the last samples define a line parallel to it.

We interpret this data in the following manner: The original starting materials were probably not completely converted to chrysotile and small amounts of one or more magnesium phases more soluble than chrysotile or talc were initially present in the synthetic chrysotile used in run S-1. These materials dissolved rapidly, supersaturating the solution with respect to talc. As talc began to form, the solution composition migrated back toward the talc saturation boundary. By the time sample 6 was taken, talc rims had isolated the remaining chrysotile from the solution and the more soluble magnesian phases were either completely dissolved or were also isolated from solution by talc rims. From this point on, the solution composition was completely controlled by equilibrium with talc. Changes in the solution composition are consistent with CO_2 reacting with a phase containing Mg and Si in a ratio of 3:4. In this run, talc equilibrium was approached from supersaturation.

If our interpretation of these experiments is correct, talc equilibrium has been approached from both supersaturation and undersaturation. The activity products from the runs are in excellent agreement and can be used to calculate a Gibbs energy of formation value for talc.

Log $K_{f\ talc}$ and Gibbs energy of formation

In run S-2 the talc solution curve was approached from undersaturation and samples S-2-4, S-2-5, S-2-6, S-2-7, and S-2-8 all appear to lie on the talc-solution equilibrium boundary, taking appropriate activities for the ions for each of these samples (Hostetler and Christ, 1968), an average log K_r (90°C, 1, talc) was

$$\log K_r(90°, 1, \text{talc}) = 17.01 \text{ (run S–2)} \qquad (5)$$

For run S-1, in which equilibrium was approached from supersaturation, an average log $K_r(90°, 1, \text{talc})$ was calculated in the same manner:

$$\log K_r(90°, 1, \text{talc}) = 16.73 \text{ (run S–1)} \qquad (6)$$

The average value for the two runs is:

$$\log K_r(90°, 1, \text{talc}) = 16.87 \pm 0.14 \qquad (7)$$

To estimate log $K_r(25°, 1, \text{talc})$ the distribution of the relative error in the entropy, enthalpy and heat capacity data for talc must be evaluated. It seems reasonable, from comparison of the entropy value for talc (62 cal K^{-1} mol^{-1}) tabulated in Robie and Waldbaum to that estimated by summation of its oxides (67 cal K^{-1} mol^{-1}), to suggest that the former entropy value is in error. This would introduce an error for the estimated value

$$\Delta G°_f(25°, 1, \text{talc}) = \Delta H°_f(25°, 1, \text{talc}) - 298\ \Delta S°_f(25°, 1, \text{talc}) \qquad (8)$$

and in the difference

$$\Delta G^\circ_f(90^\circ, 1, \text{talc}) - \Delta G^\circ_f(25^\circ, 1, \text{talc})$$
$$= -(90^\circ - 25^\circ)\,\Delta S^\circ_f(25^\circ, 1, \text{talc})$$
$$- 363 \int_{25^\circ}^{90^\circ} \Delta C^\circ_P \, d \ln T + \int_{25^\circ}^{90^\circ} \Delta C^\circ_P \, dT \qquad (9)$$

The entropy term in (8) is approximately five times the magnitude of the corresponding term in (9). Taking the difference between the two entropies of talc, a difference of Gibbs energy of 1490 cal results in equation (8) compared with 325 cal in (9). If the error exists only in the entropy of talc, the use of an incorrect entropy for talc will not significantly alter the magnitude of the change in Gibbs energy of talc over a 65° temperature interval while the absolute value of $\Delta G^\circ_f(25^\circ, 1, \text{talc})$ computed from (8) will be changed by approximately 1.5 kcal.

An error in the low-temperature (<25°C) heat capacity data for talc is unlikely (high-T not measured). A comparison of the C°_P estimated from the oxides with that measured at 25° is 78.58 versus 76.89 cal K^{-1} mol^{-1} (Robie and Stout, 1963), which is less than 2 percent difference. A discrepancy of this magnitude would contribute a negligible error in the estimation of the difference $\Delta G^\circ_f(90^\circ, 1, \text{talc}) - \Delta G^\circ_f(25^\circ, 1, \text{talc})$.

There is no means of computing $\Delta H^\circ_f(25^\circ, 1, \text{talc})$ as accurately as permitted by the techniques used for entropy and heat capacity estimates. Hence no thermochemical uncertainty can be assigned to it. However, if an error in the enthalpy does exist, it might also contribute substantially to the total error in the $\Delta G^\circ_f(25^\circ, 1, \text{talc})$.

It therefore seems likely that the majority of the error is contained in the $\Delta G^\circ_f(25^\circ, 1, \text{talc})$ value in Helgeson's tabulation (Helgeson, 1969) and that the error associated with his calculated Gibbs energy difference between 90° and 25°C is negligible in comparison. Assuming this is true, the $\Delta G^\circ_f(T, 1, \text{talc})$ and consequently $\log K_r(T, 1, \text{talc})$ tabulated by Helgeson at any temperature is wrong by a fixed amount. This is calculated by subtracting Helgeson's 1969 value from ours.

$$\Delta \log K_r(90^\circ, 1, \text{talc}) = \Delta \log K_r(25^\circ, 1, \text{talc}) \qquad (10)$$
$$= \log K_r(90^\circ, 1, \text{talc, this paper})$$
$$- \log K_r(90^\circ, 1, \text{talc, Helgeson})$$
$$= 2.21 \qquad (11)$$

which is used to calculate the $\log K_r(25^\circ, 1, \text{talc})$:

$$\log K_r(25^\circ, 1, \text{talc}) = \log K_r(25^\circ, 1, \text{talc, Helgeson})$$
$$+ \Delta \log K_r(90^\circ, 1, \text{talc})$$
$$= 21.22 \qquad (12)$$

For the reaction:

$$Mg_3Si_4O_{10}(OH)_2 + 6H + 4H_2O = 3Mg^{++} + 4H_4SiO_4 \qquad (13)$$

$$\log K_r(25^\circ, 1, \text{talc}) = 21.22 \qquad (14)$$

and

$$\Delta G^\circ_r(25^\circ, 1, \text{talc}) = -1.364 \log K_r(25^\circ, 1, \text{talc})$$
$$= -28.196 \text{ kcal/mol} \qquad (15)$$

Substituting values for the Gibbs energies of the other species in the equation (Table 3), the Gibbs energy of talc is:

$$\Delta G^\circ_f(25^\circ, 1, \text{talc}) = 3\,\Delta G^\circ_f(25^\circ, 1, Mg^{++})$$
$$+ 4\,\Delta G^\circ_f(25^\circ, 1, H_4SiO_4)$$
$$- 4\,\Delta G^\circ_f(25^\circ, 1, H_2O)$$
$$- 6\,\Delta G^\circ_f(25^\circ, 1, H^+)$$
$$- \Delta G^\circ_r(25^\circ, 1, \text{talc}) \qquad (16)$$

$$\Delta G^\circ_f(25^\circ, 1, \text{talc}) = -1321.38 \text{ kcal/mol} \qquad (17)$$

Stability of Chrysotile

The Gibbs energy of talc given by (17) permits reassessment of the limits of stability of chrysotile. On Figure 1c the brucite–solution and talc-solution curves were drawn for 90°C and one atmosphere total pressure. If chrysotile is stable under these conditions, the chrysotile–solution boundary must intersect with the brucite–solution curve at a greater value of log $a_{H_4SiO_4}$ than the talc–brucite intersection. The chrysotile solubility curve must also intersect the talc curve above the point labelled S–2–4 since talc formed at this point in Hostetler and Christ's experiment. The stoichiometry of the chrysotile dissolution reaction dictates the slope of the chrysotile–solution boundary on Figure 1c. Using this slope we have constructed a solubility curve for chrysotile and estimated error limits for the curve (Fig. 1c).

For the reaction:

$$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{++} + 2H_4SiO_4 + H_2O \qquad (18)$$

$\log K_r(90^\circ, 1, \text{chrys})$

$$= 27.50 \pm 0.5 \text{ (estimated from Fig. 3)} \qquad (19)$$

$$\log K_r(90^\circ, 1, \text{chrys}) = 25.60 \text{ (Helgeson, 1969)} \qquad (20)$$

The difference between these values at 90°C is 1.90 log units. If we again assume, as in the case of talc, that Helgeson's value for $\log K_r(90^\circ, 1, \text{chrys}) - \log K_r(25^\circ, 1, \text{chrys})$ is correct then Helgeson's 25°C value must be changed by an amount corresponding to the difference observed at 90°C:

$$\log K_r(25^\circ, 1, \text{chrys})$$
$$= 32.20 + 1.90 = 34.10 \pm 0.5 \qquad (21)$$

The Gibbs energy of the reaction is

$$\Delta G^\circ{}_r(25^\circ, 1, \text{chrys}) = -1.364 \log K_r(25^\circ, 1, \text{chrys})$$
$$= -46.51 \pm 0.68 \text{ kcal/mol} \qquad (22)$$

And the Gibbs energy of chrysotile at 25°C is:

$$\Delta G^\circ{}_f(25^\circ, 1, \text{chrys}) = 3\,\Delta G^\circ{}_f(25^\circ, 1, \text{Mg}^{++})$$
$$+ 2\,\Delta G^\circ{}_f(25^\circ, 1, \text{H}_4\text{SiO}_4) + \Delta G^\circ{}_f(25^\circ, 1, \text{H}_2\text{O})$$
$$- 6\,\Delta G_f(25^\circ, 1, \text{H}^+) - \Delta G^\circ{}_r(25^\circ, 1, \text{chrys}) \qquad (23)$$

Substituting values for the other species (Table 3)

$$\Delta G^\circ{}_f(25^\circ, 1, \text{chrys}) = -962.08 \pm 0.68 \text{ kcal/mol} \qquad (24)$$

which is approximately 3 kcal/mol higher than that calculated by Hostetler and Christ (1968).

Hydrothermal Talc Data

The retrieval of thermochemical data from chemical equilibria studied at high temperatures and pressures is another valuable technique for estimating the thermodynamic parameters of a mineral. Methods for doing this have been most recently proposed by Zen (1972), Fisher and Zen (1971) and Helgeson (1969, p. 741–792). The latter author's approach is used here for estimating thermodynamic data for talc.

The selection of reactions permitting retrieval of data on a certain phase is limited by the paucity of reactions that have been studied experimentally. Talc, however, has been involved in a number of experimental studies. Recently Skippen (1971) experimentally bracketed three reactions involving talc.

$$\text{Talc} + 3\text{ Calcite} + 2\text{ Quartz}$$
$$= 3\text{ Diopside} + 3\text{ CO}_2 + \text{H}_2\text{O} \qquad (25)$$

$$4\text{ Talc} + 5\text{ Dolomite}$$
$$= 5\text{ Diopside} + 6\text{ Fosterite} + 10\text{ CO}_2 + 4\text{H}_2\text{O} \qquad (26)$$

$$\text{Talc} = 3\text{ Enstatite} + \text{Quartz} + \text{H}_2\text{O} \qquad (27)$$

Thermodynamic data for the rest of the phases in the above reactions are well known with two exceptions, enstatite and diopside. MgSiO_3 may exist in several polymorphs, but data are only available for clinoenstatite. Experiments done at elevated temperatures and pressures involve orthoenstatite (Skippen, 1971; Williams, 1971). These studies suggest that enstatite should be approximately 1 kcal more stable than indicated by the tabulation of Robie and Waldbaum.

The enthalpy of formation of diopside tabulated in Robie and Waldbaum is an average value taken from Neuvonen (1952) and Kracek *et al.* (1953), who respectively measured the heat of solution of a natural and a synthetic diopside. The two values differ by 2.51 kcal. We chose to use the value of Neuvonen (1952) as it gave more consistent results in the retrieval of the enthalpy of formation of talc from reactions 25 and 26. Brown (1970) chose the same value for similar reasons.

The computer program "Kelleycob"* (Helgeson *et al.*, 1970) was used with the enthalpy, entropy, heat capacity, and volume data listed in Table 4 to calculate the apparent ΔG° reaction at the experimentally studied temperatures. This was compared with experimentally determined $\Delta G^\circ{}_r$. Since $\Delta H^\circ{}_f$ (298, 1, talc) had been set to zero for the Kelleycob calculation, the difference $\Delta G^\circ{}_r(T, P,$ experiment) $- \Delta G^\circ{}_r(T, P,$ Kelleycob) $= {}_{\hat{n}}\Delta H^\circ{}_f(25^\circ, 1,$ talc). Experimental data used are tabulated in Table 5.

The average enthalpy of formation of talc calculated from the three reactions cited above is -1409 ± 1 kcal/mol. This is 6 kcal less stable than the value tabulated by Robie and Waldbaum, yet it is within 1 kcal of the average enthalpy of talc calculated from the individual reactions. If the enthalpy of diopside from Robie and Waldbaum was used, there would be a difference of 3 kcal between reactions 25 and 26:

$$\Delta H^\circ{}_f(25^\circ, 1, \text{talc}) \text{ from Reaction 25}$$
$$= -1413.5 \text{ kcal/mol} \qquad (28)$$

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* "Kelleycob" calculates standard thermodynamics of reactions at high temperatures using the enthalpy and entropy value of reaction at 25°C and 1 bar and a heat capacity power function. High pressure values of standard thermodynamics of reaction are predicted from the volume change for the minerals. In these computations the heat capacity is assumed to be independent of pressure and the molar volumes independent of pressure and temperature.

TABLE 4. THERMOCHEMICAL DATA* FOR PHASES IN THE SYSTEM $CaO-MgO-SiO_2-H_2O-CO_2$

Phase	$\Delta H°_f(25°,1)$	(Ref)	S°(25°,1)	(Ref)	a	b x 10^3	c x 10^{-5}	(Ref)	V° (25°, 1)	(Ref)
Calcite	-288420.	1	22.15	1	24.98	5.24	-6.20	1	36.93	2
Quartz	-217650.	1	9.88	1	11.22	8.20	-2.70	1	22.69	2
Diopside	-766100.	3	34.20	1	52.87	7.84	-15.74	1	66.09	2
Dolomite	-557613.	2	37.09	2	37.65	--	--	1	64.34	2
Forsterite	-519000.	1	22.75	1	35.81	6.54	-8.52	1	43.79	2
CO_2	- 94050.	1	51.06	1	10.57	2.10	-2.06	1	--	
H_2O	- 57796.	1	45.10	1	7.30	2.46	--	1	--	
Talc	--		67.06	4	84.42	38.02	-15.24	4	136.25	2
Clino-Enstatite	-370140.	1	16.22	1	24.55	4.74	-6.28	1	31.47	2

Sources:
(1) Helgeson (1969)
(2) Robie and Waldbaum (1968)
(3) Neuvonen (1952)
(4) Oxide summation (data from Robie and Waldbaum, 1968)

* Values a, b, c represent constants in a heat capacity function of the form $a + bT + cT^{-2}$. Their cited values are from Helgeson (1969) except those for talc which are from an oxide summation using the data of Robie and Waldbaum (1968).

$\Delta H°_f$(25°, 1, talc) from Reaction 26

$$= -1410.5 \text{ kcal/mol} \qquad (29)$$

The use of clinoenstatite data in place of orthoenstatite data in Skippen's reactions leads to a $\Delta H°_f$(25°, 1, talc) consistent with that from reactions (25) and (26). If Skippen's and William's suggestion concerning orthoenstatite is correct, then the ΔH_f(25°, 1, talc) calculated from (27) would be approximately 3 kcal more negative. The discrepancy between Skippen's experimental reaction curves and those he calculated from thermochemical data tabulated in Robie and Waldbaum may be due to poor talc and tremolite values rather than the use of clinoenstatite for orthoenstatite. We prefer, therefore, −1409 kcal/mol to the value tabulated by Robie and Waldbaum.

TABLE 5 REVERSAL POINTS* FOR REACTIONS 25, 26 AND 27

Temp °C	Pressure (bars)	log f_{CO_2}	log f_{H_2O}	$\Delta H°_f$(25°,1, talc, cal)
		Reaction 25		
517 ± 27°	3000^N	3.56	2.77	-1409814
486 ± 8°	2000^N	3.20	2.52	-1409817
461 ± 19°	1000^N	2.82	2.22	-1410320
403 ± 25°	500^N	2.38	2.01	-1408696
				average -1409660
		Reaction 26		
580 ± 8°	2600^N	3.55	2.66	-1408818
561 ± 9°	2000^N	3.35	2.51	-1408816
533 ± 36°	2000^Q	2.77	2.81	-1410279
520 ± 15°	1000^N	2.95	2.20	-1407962
502 ± 38°	1000^Q	2.30	2.51	-1410867
491 ± 28°	500^N	2.59	1.94	-1408369
				average -1409185
		Reaction 27		
733 ± 7°	2000^N		3.15	-1407996
622 ± 31°	2000^Q		2.78	-1408203
646 ± 9°	2000^N		2.44	-1409337
				average -1408512

* Equilibrium points tabulated from Skippen (1971). $\Delta H°_f$, which is more completely writted as $\Delta H°$ (25°, 1, talc, cal), was calculated from the difference between the $G°_r$ determined from this data and that estimated using program "Kelleycob" with data of Table 5. Estimated standard deviations for temperatures are enclosed in parentheses.

N = NB, OH(GX, COH). Reaction buffered by nickel, bunsonite and graphite in a C-O-H atmosphere.

Q = QFM, OH(GX, COH). Reaction buffered by quartz, fayalite, magnetite and graphite in a C-O-H atmosphere.

The Gibbs energy of talc was calculated from:

$$\Delta G°_f(25°, 1, \text{talc}) = \Delta H°_f(25°, 1, \text{talc})$$

$$- 298\ \Delta S°_f(25°, 1, \text{talc}) \qquad (28)$$

$$= -1409000 - 298.15(-299.58) \qquad (29)$$

$$= -1319.7 \text{ kcal/mol} \qquad (30)$$

This value is in good agreement with those determined in the solubility studies reported here.

Conclusions

The experimental data cited in this study are in excellent agreement. These data and field evidence suggest that the Gibbs energy of formation of talc should be at least 3 to 5 kcal/mol less negative (−1320 ± 2 kcal) than the value tabulated by Robie and Waldbaum (1968).

Figure 1d depicts the stability of talc relative to brucite, chrysotile and amorphous silica. The continuous and the dashed talc and chrysotile boundaries are calculated from the Gibbs energies obtained in this paper. The dotted boundaries are calculated from the data of Robie and Waldbaum (1968) for talc and of Hostetler and Christ (1968) for chrysotile. Thermodynamic data for brucite and amorphous silica are from Robie and Waldbaum. Other data on chrysotile (Wildman *et al.*, 1971) agree well with our estimate and suggest that this mineral may be less stable than reported by Hostetler and Christ. Further work is needed on the stability of chrysotile.

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