

## Experimental determination of the pressure-temperature stability field and thermochemical properties of synthetic tremolite

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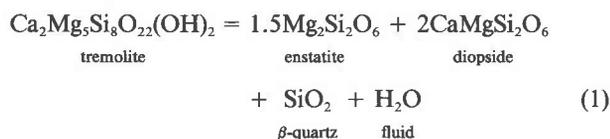
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### ABSTRACT

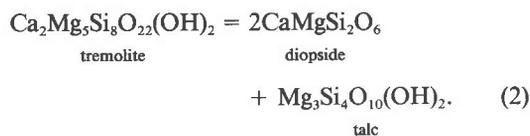
New experimental data for the breakdown of synthetic tremolite to the assemblage diopside + clinopyroxene + enstatitic orthopyroxene +  $\beta$ -quartz +  $H_2O$  in the pressure range of 1.5–7 kbar and to the assemblage diopside + talc in the range of 650–760 °C were combined with existing experimental data for these reactions and all pertinent experimental phase equilibria in order to obtain a refined value for the enthalpy of formation ( $\Delta H_{f,1 \text{ bar}, 298K}^0$ ) of tremolite. Using the least-squares regression procedure and data base of Holland and Powell (1990), the derived  $\Delta H_{f,1 \text{ bar}, 298K}^0$  for tremolite is  $-12302.90 \pm 7.05$  (1 $\sigma$ ) kJ/mol for fixed values of entropy, volume, heat capacity, expansivity, and compressibility for tremolite. This analysis was performed with the assumption that all phases were pure and had unit activity. This agrees with the value of  $-12300.47 \pm 14.81$  kJ/mol determined for natural stoichiometric tremolite by Welch and Pawley (in preparation). Assuming that Ca and Mg mix ideally on the M4 site in Mg-enriched, synthetic tremolite and that the compositions of the pyroxenes in equilibrium with synthetic tremolite are known, the  $\Delta H_{f,1 \text{ bar}, 298K}^0$  will be approximately 1 kJ/mol less negative or approximately  $-12302$  kJ/mol for stoichiometric tremolite. The  $dP/dT$  slope of the reaction tremolite = 2 diopside + talc is 8.8 bar/K. Extrapolation of this univariant boundary to low temperatures (200 °C) shows that tremolite is stable to at least 20 kbar and is not limited at low temperatures by this reaction at virtually any depth in the Earth's crust. The calculated decomposition temperature of tremolite at 1 bar is 448 °C, which is about 350 °C lower than the observed dehydration temperature of tremolite. It is suggested here that the dissolution of silica, rather than the loss of hydroxyls, may control the decomposition of tremolite in hydrothermal environments.

### INTRODUCTION

Tremolite is an important calcic amphibole whose pressure-temperature ( $P$ - $T$ ) stability and thermodynamic parameters must be well known for it to be used quantitatively in petrologic applications (e.g., Valley et al., 1983; Ghent, 1988). Our present knowledge of tremolite is based heavily on the pioneering work of Boyd (1959), who investigated the upper-thermal stability of synthetic tremolite according to the reaction



reported since this study. Gilbert and Troll (1974) investigated Reaction 1 at 10 kbar and above and found that the univariant boundary has a positive  $dP/dT$  slope up to 915 °C and 15.5 kbar [sic], corresponding to the  $\alpha$ - to  $\beta$ -quartz transition. Above this pressure, Reaction 1 involves  $\alpha$ -quartz and has a negative slope. Gilbert and Troll (1974) found the maximum pressure of tremolite stability to be approximately 26 kbar at 835 °C where it breaks down according to the reaction



over the pressure range of 0.4–2.0 kbar. Surprisingly little additional experimental work on Reaction 1 has been

The slope of Reaction 2 is approximately 23.3 bars/K according to Gilbert and Troll (1974, 1989 personal com-

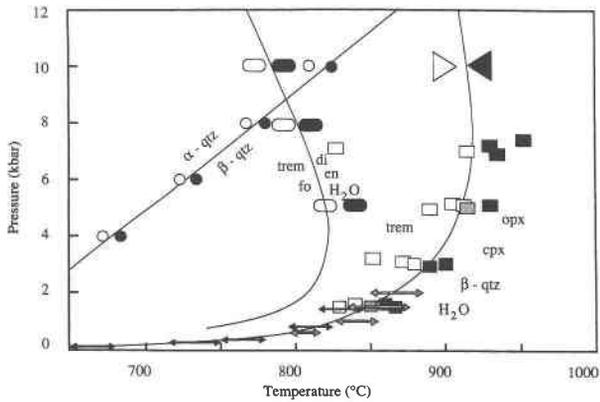


Fig. 1. Experimental data and calculated univariant curves for Reaction 1 ( $\text{tr} = 1.5 \text{ en} + 2 \text{ di} + \beta\text{-qtz} + \text{H}_2\text{O}$ ), Reaction 6 ( $\text{tr} + \text{fo} = 2.5 \text{ en} + 2 \text{ di} + \text{H}_2\text{O}$ ), and the  $\alpha$ - $\beta$  quartz transition. Symbols for reaction 1: boxes = this study; triangles = Gilbert and Troil (1974); light arrows = Boyd (1959); dark arrows = Yin and Greenwood (1983). Symbols for Reaction 6: ovals = Jenkins (1983). Symbols for  $\alpha$ - $\beta$  qtz reaction: circles = Yoder (1950). Open symbols indicate growth of the low-temperature assemblage, filled symbols indicate growth of the high-temperature assemblage, stippled boxes indicate no reaction, and the arrows indicate the maximum width of the reversal bracket. Abbreviations: cpx = clinopyroxene; di = diopside; en = enstatite; fo = forsterite; opx = orthopyroxene; qtz = quartz; trem = tremolite.

munication). Yin and Greenwood (1983) and Yin (1988, personal communication) investigated Reaction 1 in the range of 0.1–1.4 kbar and found the position of the univariant boundary to be in fairly close agreement with that of Boyd (1959). The experimental results for Reactions 1 and 2 obtained by these investigators are shown in Figures 1 and 2, respectively.

There are several aspects of the above experimental studies that require further attention. First, most thermodynamic data for tremolite are based heavily on the experimental data for Reaction 1 obtained over the limited pressure range of 0.1–2.0 kbar. Obtaining tight experimental reversals in the pressure range of 2–8 kbar would help immensely in defining the thermodynamic parameters for tremolite by expanding the pressure range of experimental data without exceeding the  $P$ - $T$  range where quartz becomes completely soluble in the ambient aqueous fluid (i.e., beyond the critical end-point pressure of 9.7 kbar at 1080 °C in the system  $\text{H}_2\text{O}$ - $\text{SiO}_2$ , Kennedy et al., 1962). Experiments performed above these  $P$ - $T$  conditions may suffer partial or complete loss of quartz via dissolution and a significantly lowered activity of  $\text{H}_2\text{O}$  in the ambient fluid. Secondly, the  $dP/dT$  slope and placement of Reaction 2 is controversial. Gilbert and Troil (1974) place the univariant curve approximately 3 kbar lower than is reported here. The study by Cao et al. (1986), who investigated this reaction indirectly in the system  $\text{H}_2\text{O}$ - $\text{CaO}$ - $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  and in the presence of Al-bearing phases, would place this curve approximately 16 kbar lower and with a steeper  $dP/dT$  slope (45 bars/K)

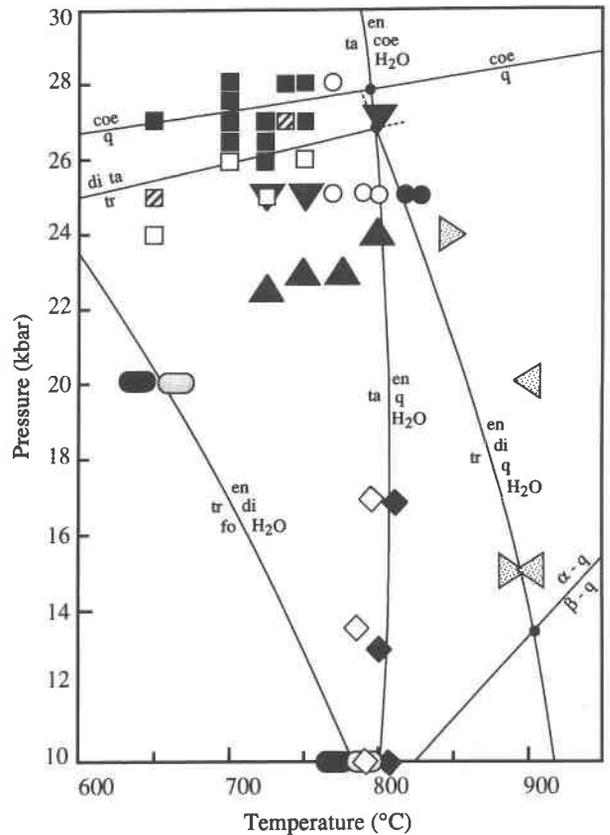


Fig. 2. Experimental data and calculated univariant curves for Reactions 2 ( $2 \text{ di} + \text{ta} = \text{tr}$ ), 3 ( $\text{tr} = 1.5 \text{ en} + 2 \text{ di} + \text{q} + \text{H}_2\text{O}$ ), 4 ( $\text{ta} = 1.5 \text{ en} + \text{q} + \text{H}_2\text{O}$ ), and 6 ( $\text{tr} + \text{fo} = 2.5 \text{ en} + 2 \text{ di} + \text{H}_2\text{O}$ ). Also shown is the calculated boundary for the quartz = coesite reaction ( $\text{q} = \text{coe}$ ). Symbols for Reaction 2: boxes = this study (open = tr growth, hachured = no reaction, filled = di + ta); dark stippled triangles = Gilbert and Troil (1974) (pointing up = tr growth, pointing down = di + ta growth). Symbols for Reaction 3: light stippled triangles = Gilbert and Troil (1974) (pointing right = tr growth, pointing left = pyroxene growth). Symbols for Reaction 4: circles = this study; diamonds = Chernosky et al. (1985) (open = ta growth, filled = en + q growth). Symbols for Reaction 6: ovals = Jenkins (1983) (filled = tr + fo growth, shaded = en + di growth). Abbreviations: coe = coesite; q = quartz ( $\alpha$ -quartz, unless otherwise shown); ta = talc; tr = tremolite; others as in Figure 1.

than is reported here. The implication of this study is that the presence of other elements, such as Al, may have an extreme effect on the lower-thermal or upper-pressure stability limits of tremolitic amphibole and that the position of Reaction 2 in the Al-free system should be well documented to correctly determine the effect of such elements.

The purpose of this paper is to report new experimental data for Reactions 1 and 2, to review all extant experimental data for these reactions in order to provide a comprehensive view of the upper-thermal and upper-pressure stability limits of tremolite, and to derive a value for the

TABLE 1. Phases used for experiments on Reactions 1, 2, and 4 in the text

Phase (code no.)	Composition	Synthesis conditions			t (h)	Starting mixtures				
		T (°C)	P (kbar)	Form		Rn 1		Rn 2		Rn 4 TEQ
						TREM 13	17	TR 1	2	
Orthopyroxene (OPX 6-1)	(Mg <sub>0.99</sub> Ca <sub>0.01</sub> )MgSi <sub>2</sub> O <sub>6</sub>	930	6.3	oxides	54	X	X	O	O	O
Enstatite	MgSiO <sub>3</sub>	1000	15.0	oxides	4	O	O	O	O	X
Clinopyroxene (CPX 4-1)	(Ca <sub>0.98</sub> Mg <sub>1.02</sub> )MgSi <sub>2</sub> O <sub>6</sub>	925	5.9	oxides	95	X	X	O	O	O
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	1250	1 atm	glass	48	O	O	O	X	O
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	1250	18.0	glass	3	O	O	X	O	O
Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	700	17.5	oxides	26	O	O	O	X	O
Talc	MgSi <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	750	12.0	oxides	16	O	O	X	O	X
Quartz	SiO <sub>2</sub>	790	2.0	oxide	16	X	X	O	O	O
Quartz	SiO <sub>2</sub>	—	—	natural	—	O	O	O	O	X
Tremolite (TREM 1-21)	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	740	2.0	oxides	188	X	X	O	O	O
Tremolite	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	806	2.0	crystals	214					
Tremolite	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	800	13.0	gel	24	O	O	X	O	O
Tremolite	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	730	22.0	crystals	72					
Tremolite (TREM 1-3)	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	750	15.0	oxides	44	O	O	O	X	O
Tremolite	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	750	18.0	crystals	61					

Note: Abbreviations: Rn = reaction; O = phase absent, X = phase present in mixture. Column headings TREM 13,17; TR 1,2; and TEQ refer to the prefixes for the experiment numbers in Tables 2-4.

enthalpy of formation of tremolite that is consistent with these data.

## EXPERIMENTAL METHODS

### Apparatus

Experiments performed below 8 kbar were conducted at SUNY-Binghamton in internally heated gas vessels using Ar as the pressure medium. Pressures were monitored throughout each experiment with both a bourdon-tube gauge and a factory-calibrated manganin cell. The cited uncertainties in pressure measurement include both the accuracy ( $\pm 50$  bars) and any fluctuation in pressure during the experiment. Temperatures were measured by two Inconel-sheathed, chromel-alumel thermocouples that were calibrated against the freezing point of Sn (231.9 °C) and NaCl (800.5 °C). The tips of the thermocouples were positioned at either end of the capsules and the entire sample and thermocouple arrangement packed with ceramic wool in a cylindrical copper cup to minimize thermal gradients. The cited temperature uncertainties include both the accuracy of the thermocouple couples ( $\pm 2$  °C) as well as any thermal gradient across the sample.

Experiments above 8 kbar were performed in piston-cylinder presses using 3/4-inch (1.905 cm) diameter NaCl pressure media at the University of Chicago. Considerable effort has been devoted toward calibrating the sample pressure in this pressure medium. Detailed discussions of the calibration results can be found, for example, in Holland (1980), Jenkins (1981), and Jenkins et al. (1985). In brief, the procedure followed for generating pressures involves pressurizing the NaCl assemblage at room temperature to several kilobars below the desired pressure and then using the well-calibrated thermal expansion of the pressure medium to obtain the final pressure upon heating. This procedure does not strictly con-

form to either the hot or cold piston-out criteria described by Johannes et al. (1971) but has been shown to give results on the albite = jadeite + quartz reaction, as well as several other reactions that require virtually no additional friction correction. Pressure uncertainties, incorporating accuracy as well as precision, vary from approximately 200–400 bars depending on the pressure range and diameter of the piston-cylinder assemblage used (Jenkins et al., 1985). For the pressure range of this study (20–30 kbar), uncertainties are estimated to be  $\pm 200$  bars. Temperatures were measured with chromel-alumel thermocouples, with the tip situated on top of the radially mounted sample capsule, and are believed to be accurate to  $\pm 5$  °C.

### Starting materials and procedures

The phases and starting mixtures used for investigating Reactions 1 and 2 are listed in Table 1. All of the synthetic phases were made hydrothermally in Au or Pt capsules except for diopside, which was made at 1 atm by annealing glass of the composition CaMgSi<sub>2</sub>O<sub>6</sub> at approximately 1250 °C. All of the tremolite samples were made in a two-step procedure, involving one intermediate grinding and retreatment. As discussed by Jenkins (1987), it is believed that all of these synthetic tremolite samples have approximately 10 mol% Mg substituted for Ca in the M4 site and that the compositions indicated in Table 1 are for the starting mixtures, not the actual phase compositions.

Starting mixtures for Reaction 1 and for the TR-1 series of experiments for Reaction 2 consisted of reactants and products mixed in stoichiometric proportions. The starting mixture for the TR-2 series of experiments consisted of a 3:1 ratio of talc + diopside to tremolite in order to make the intensities of the diopside 220 and 221

TABLE 2. Experimental results for Reaction 1 in the text

Experiment no. (TREM-)	Pressure (kbar)	Temperature (°C)	Time (h)	Results*
17-1	1.50(5)	830(3)	215	tr growth (m)
13-16	1.58(5)	840(3)	217	tr growth (m)
17-6	1.52(5)	851(3)	331	no reaction
17-9	1.53(5)	860(3)	81	pyroxene growth (s)
17-4	1.50(5)	868(3)	112	pyroxene growth (vs)
13-1	3.25(8)	852(4)	96	tr growth (vs)
13-3	3.07(5)	874(3)	55	tr growth (s)
13-5	3.02(6)	880(3)	316	tr growth (m)
13-4	2.87(5)	888(2)	162	pyroxene growth (m)
13-2	3.00(5)	901(2)	136	pyroxene growth (vs)
13-6	4.92(6)	891(2)	188	tr growth (vs)
13-8	5.02(5)	905(3)	69	tr growth (s)
13-9	4.97(5)	914(3)	145	tr growth (s)
13-10	4.98(5)	919(5)	144	no reaction
13-7	5.05(10)	930(5)	53	pyroxene growth (vs)
17-2	7.08(13)	828(3)	52	tr growth (vs)
13-15	7.05(15)	916(3)	92	tr growth (vs)
17-3	7.19(17)	929(4)	52	pyroxene growth (m)
13-13	6.85(18)	933(4)	76	pyroxene growth (vs)
13-12	7.4(6)	950(4)	69	pyroxene growth (vs)

Note: Results arranged in order of increasing pressure. Uncertainty in last digit shown in parentheses. Abbreviation: tr = tremolite.

\* Extent of reaction indicated in parentheses by the symbols m = moderate, s = strong, and vs = very strong, corresponding to a change of 20–50%, 50–80%, and greater than 80%, respectively, in the relative peak heights of the X-ray diffractometer patterns.

reflections about the same as the tremolite 240 and 151 reflections on an X-ray diffractometer pattern. This was done in an attempt to enhance the reaction signal deduced from the X-ray pattern.

Each experimental sample was prepared by sealing a portion of the starting mixture in a Pt capsule with 15–30 wt% H<sub>2</sub>O. At the conclusion of the experiment, the capsule was checked for leakage by examining the seams for any signs of rupture and by checking for any weight loss.

### Analytical methods

All experimental products were analyzed with a Norlco X-ray diffractometer using Ni-filtered Cu radiation. The reaction direction for Reaction 1 could be readily determined from the relative peak heights of the phases on the X-ray diffractometer pattern. In particular, the 310, 151, and 240 reflections of tremolite, 220 and 221 reflections of diopside, and the 610 reflection of enstatite were found to be sensitive indicators of the extent of reaction. A minimum of 20% change in the relative peak heights was considered necessary to indicate a significant amount of reaction. Reaction 2 could not be analyzed so readily in this manner. As a consequence of the much lower temperatures and smaller energetics (i.e.,  $\Delta S$  and  $\Delta H$ ), the extent of reaction for Reaction 2 was too small to discern via X-ray criteria within a few kilobars of the univariant boundary. Greater sensitivity was achieved by examining the infrared (IR) spectra of the experimental products and monitoring the variation in the peak-height ratio of the talc 665 cm<sup>-1</sup> to tremolite 755 cm<sup>-1</sup> vibrations. A detailed

TABLE 3. Experimental results for Reaction 2 in the text

Experiment no. (TR-)	Pressure (kbar)	Temperature (°C)	Time (d)	Results*
1-13	24.0	650	3	tr growth (m)
1-15	25.0	650	3	no reaction (XRD only)**
1-16	27.0	650	3	ta + di growth (m, XRD only)**
1-5	26.0	700	1	tr growth (m, XRD only)**
1-12	26.5	700	3	ta + di growth (s)
1-7	27.0	700	3	ta + di growth (m, XRD only)**
1-14	27.5	700	3	ta + di growth (s, XRD only)**
1-6	28.0	700	1	ta + di growth (s)
2-22	25.0	725	2	tr growth (w)
2-24	26.0	725	3	ta + di growth (w)
2-26	26.0	725	3	ta + di growth (m)
2-28	26.5	725	3	ta + di growth (vs)
2-25	27.0	725	3	ta + di growth (vs)
1-10	27.0	740	3	no reaction
1-11	28.0	740	2	ta + di growth (s)
2-21	26.0	750	4	tr growth (s)
2-19	27.0	750	1	ta + di growth (m)
2-20	28.0	750	1	ta + di growth (s, XRD only)**
1-9	27.0	760	2	tr growth (s), minor enstatite nucleated

Note: Results are arranged in order of increasing temperature. Uncertainty in pressure and temperature are 0.2 kbar and 5 °C, respectively. Abbreviations: di = diopside; ta = talc; tr = tremolite.

\* Extent of reaction indicated in parentheses by the symbols w = weak, m = moderate, s = strong, and vs = very strong, corresponding to a change of 10–30%, 30–50%, 50–80%, and >80%, respectively, in the band intensities of the infrared (IR) spectrum. Note that as little as 10% relative change in band heights is considered significant owing to the greater sensitivity of IR spectroscopy.

\*\* Results based only on X-ray diffraction data, no IR spectrum obtained. Extent of reaction estimate as in Table 4.

description of this analytical method and a comparison of the sensitivity of the IR vs. X-ray diffractometer method is given in Jenkins and Clare (1990).

### EXPERIMENTAL RESULTS

The experimental results for Reaction 1 are listed in Table 2 and are shown by the solid and open squares in Figure 1. For comparison, the lower-pressure data of Boyd (1959) and of Yin and Greenwood (1983) are shown by light and dark double-headed arrows, respectively, while the higher-pressure data of Gilbert and Troll (1974) are shown by triangles. There is very good agreement between all of the experimental reversals even though they were obtained by four different studies in four different laboratories. The univariant curves drawn on Figure 1 have been calculated from thermodynamic data derived in this study as discussed below.

Experimental results for Reaction 2 are listed in Table 3 and are shown by the solid and open squares in Figure 2. The experimental results for Reaction 2 from Gilbert and Troll (1974) are shown by the triangles pointing up and down. Notice that Gilbert and Troll (1974) found talc and diopside growth to occur approximately 3 kbar lower than was observed in this study. Several of the experimental samples from the study of Gilbert and Troll (1974) were kindly made available to the first author for examination. Analysis of one of these lower-pressure talc

**TABLE 4.** Experimental results on Reaction 4 in the text

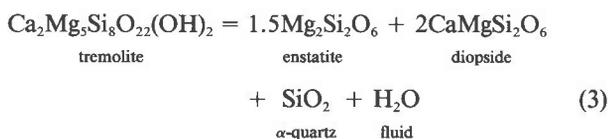
Experiment no. (TEQ-)	Pressure (kbar)	Temperature (°C)	Time (h)	Results*
3	28.0	770	22	ta growth (s)
6	25.0	770	72	ta growth (vs)
7	25.0	790	22	ta growth (s)
11	25.0	800	5.0	ta growth (vs)
12	25.0	820	5.0	en + q growth (m)
13	25.0	830	6.5	en + q growth (vs)

Note: Results arranged in order of increasing temperature. Uncertainty in pressure and temperature are 0.2 kbar and 5 °C, respectively. Abbreviations: en = enstatite, q =  $\alpha$ -quartz, ta = talc.

\* Extent of reaction indicated in parentheses based on a qualitative assessment of the changes in the relative peak heights of the X-ray diffraction patterns; m = moderate, s = strong, and vs = very strong.

+ diopside growth experiments (750 °C, 25 kbar) by IR spectroscopy as well as X-ray diffractometry confirmed the growth of talc and diopside and indicated that a genuine discrepancy, i.e., one that is not an artifact of the analytical technique, exists between this study and that of Gilbert and Troll (1974). The origin of this discrepancy is not obvious. It probably stems from the different piston-cylinder pressure media used by the two studies: 3/4-inch diameter NaCl assemblage used in this study vs. a 1/2-inch diameter talc + BN + pyrophyllite assemblage used by Gilbert and Troll (1974). The latter assemblage, however, normally tends to over- rather than underestimate the true sample pressure (Johannes et al., 1971) and should lead to higher observed pressures. The presence of "positive anvil effects" (Johannes et al., 1971) may exist for an assemblage that involves pyrophyllite parts directly surrounding the sample yielding sample pressures that are apparently higher than the nominal (gauge) pressure. Other factors such as experiment duration and sample preparation appear to be comparable. Until the source of this discrepancy is resolved, we prefer the data that were obtained in this study with the NaCl pressure media, which has been studied extensively in terms of its pressure calibration (e.g., Johannes et al., 1971; Holland, 1980).

Experimental results for the reaction



which was studied by Gilbert and Troll (1974) are shown in Figure 2 by the triangles pointing left and right. The filled and open circles in Figure 2 refer to the reaction



which was studied here. The phases used for studying Reaction 4 are listed in Table 1 and the experimental results are listed in Table 4.

Reaction 3 was also investigated in this study (by T.J.B.H.) but the results were inconclusive because quartz could not be identified among the products. These experiments were performed with starting mixtures consisting of equal proportions of tremolite and the anhydrous break-down products with excess H<sub>2</sub>O (20–40 wt%). It is surmised that quartz was dissolved into the vapor phase because of the relatively high ratio of H<sub>2</sub>O to quartz and because of the high pressures of these experiments (above 15 kbar). The experiments performed by Gilbert and Troll (1974) involved starting mixtures which were either predominantly tremolite with a trace of the break-down products or predominantly the breakdown products with a trace of tremolite. In this approach there is sufficient quartz to ensure its presence during the growth of tremolite but probably not enough to ensure its presence during the breakdown of tremolite. Therefore, the tremolite growth experiments of Gilbert and Troll (1974) at 10, 15, and 24 kbar are considered more reliable than the breakdown experiments. The calculated curve for Reaction 3 is in excellent agreement with these data below 24 kbar.

Reaction 4 was investigated primarily to provide additional experimental control on the location of the invariant point arising from the intersection of Reactions 1 and 2. The data define a fairly tight bracket for the location of this univariant reaction between 800 and 820 °C at 25 kbar.

### THERMODYNAMIC ANALYSIS

A thermodynamic analysis of the experimental data discussed above has been performed with the twofold objective of (1) discerning whether or not all of the extant data for a given univariant reaction are consistent with each other based on existing entropy, volume, heat capacity, and  $f_{\text{H}_2\text{O}}$  data and (2) using Reactions 1–3 to refine a preferred value for the enthalpy of formation ( $\Delta H_{f,1 \text{ bar}, 298\text{K}}^0$ ) of tremolite.

The fundamental thermodynamic expression which serves as the basis for our analysis is given in Equation 5 below:

$$\begin{aligned} \Delta G_{P,T} &= \Delta H_{P_0,T_0}^0 - T\Delta S_{P_0,T_0}^0 \\ &+ \int_{T_0}^T \Delta C_P^0 dT - T \int_{T_0}^T \frac{\Delta C_P^0}{T} dT \\ &+ P[\Delta V_{P_0,T_0}^{\text{solids}} + \Delta(\alpha V)(T - T_0) - \Delta(\beta V)P/2] \\ &+ RT \ln K_a + RT \ln f_{P,T}^{\text{H}_2\text{O}} \end{aligned} \quad (5)$$

where  $\Delta G_{P,T}$  is the Gibbs free energy of the reaction at  $P$  and  $T$ ;  $\Delta H_{P_0,T_0}^0$ ,  $\Delta S_{P_0,T_0}^0$ , and  $\Delta C_P^0$  are the change in the enthalpy, entropy, and heat capacity, respectively, of the reaction at the reference pressure ( $P_0$ ) and temperature ( $T_0$ );  $\Delta V_{P_0,T_0}^{\text{solids}}$  is the volume change of the solids for the reaction;  $\alpha$  and  $\beta$  are the thermal expansivity and isobaric compressibility, respectively, of the solid phases;  $f$  is the

TABLE 5. Thermochemical values at 298 K and 1 bar used in this study

Phase	$\Delta H_f^0$ (kJ/mol)	$\sigma(\Delta H_f)$ (kJ/mol)	$S$ (J/mol K)	$V$ (J/bar)	$C_p$				$\alpha V$ $\times 10^{-5}$	$\beta V$ $\times 10^{-3}$
					$a$	$b$ $\times 10^{-5}$	$c$	$d$		
Tremolite	-12302.90	7.05	550.00	27.270	1.2144	2.6528	-12362.0	-7.3885	84.5	36.00
Enstatite	-3089.38	2.08	132.50	6.262	0.3562	-0.2990	-596.9	-3.1853	18.0	4.60
Forsterite	-2171.87	1.62	94.10	4.366	0.2349	0.1069	-542.9	-1.9064	16.0	3.20
Diopside	-3200.15	1.90	142.70	6.619	0.3145	0.0041	-2745.9	-2.0201	22.0	5.50
Talc	-5894.90	3.70	260.80	13.625	0.5343	3.7416	-8805.2	-2.1532	37.0	26.00
$\alpha$ -Quartz	-910.80	0.74	41.50	2.269	0.0979	-0.3350	-636.2	-0.7740	8.0	5.92
$\beta$ -Quartz	-909.07	0.74	43.54	2.367	0.0979	-0.3350	-636.2	-0.7740	0.0	2.60
Coesite	-908.17	0.74	39.00	2.064	0.1087	-0.4387	0.0	-1.0725	2.2	2.00
H <sub>2</sub> O (steam)	-241.81	0.03	188.80	—	0.0401	0.8656	487.5	-0.2512	—	—

Note: The heat capacity coefficients apply to the experiment (kJ/K):  $C_p = a + bT + cT^{-2} + d/\sqrt{T}$ ;  $\alpha V$  in kJ/kbar K;  $\beta V$  in kJ/kbar<sup>2</sup>.

fugacity of H<sub>2</sub>O at the  $P$  and  $T$  of interest; and  $K_a$  is the equilibrium constant for the reaction. The standard state is that of unit activity for the solids at the  $P$  and  $T$  of interest and of unit fugacity for H<sub>2</sub>O at 1 bar and the  $T$  of interest. At equilibrium  $\Delta G_{P,T}$  is zero by definition. It is a basic simplifying assumption that all of the thermodynamic values except for  $\Delta H_{f,P_0,T_0}^0$  are known and have no uncertainty (or at least have much less uncertainty than enthalpy data). The major advantage of this assumption is that one can determine the uncertainties of, and correlations between, any derived values of  $\Delta H_{f,P_0,T_0}^0$  for the phases involved. The reader is referred to the discussions of Powell and Holland (1985) and Holland and Powell (1990) for further justification for this assumption.

Internal consistency among a set of experimental data can be shown in the following manner. Knowing values for  $S$ ,  $C_p$ ,  $V$ ,  $f_{H_2O}$ , and  $K_a$ , one can solve Equation 5 explicitly for values of  $\Delta H_{f,P_0,T_0}^0$  by assuming  $\Delta G_{P,T}$  is zero at the extreme  $P$  and  $T$  range of each pair of experiments that bracket the univariant boundary. Each experiment bracketing the univariant boundary yields a corresponding maximum and minimum value for  $\Delta H_{f,P_0,T_0}^0$ , i.e., a set of bracketing enthalpy values. Internal consistency for a set of experimental data is demonstrated if at least one value of  $\Delta H_{f,P_0,T_0}^0$  lies between all of the maximum and minimum values obtained from the experimental brackets.

The enthalpy of formation for tremolite was initially derived by the least-squares regression technique of Powell and Holland (1985) and Holland and Powell (1990) using the new experimental data presented here and the entire mineral data base (123 minerals) of Holland and Powell (1990). It soon became apparent that only the enthalpies of tremolite and talc were significantly changed; the enthalpies of all other phases were changed only slightly (generally less than 0.05 kJ/mol). Rather than revise the entire data base of Holland and Powell (1990) with new enthalpy values that are well within the existing  $1\sigma$  range of uncertainty, we have performed a least-squares regression only for the enthalpies of formation of tremolite and talc and have fixed the enthalpies of all other

phases to those values given in Holland and Powell (1990). Further details of the least-squares refinement procedure are given below.

Values or expressions for  $S$ ,  $C_p$ ,  $V$ ,  $\alpha V$ , and  $\beta V$  for all of the phases were taken from Holland and Powell (1990) and are given in Table 5. For pressures above 0.3 kbar, the  $f_{H_2O}$  data were calculated from the equation of Holland and Powell (1990), which represents the variation of  $RT \ln f$  as function of  $P$  and  $T$  over the range of 0.1–40 kbar and 300–1200 °C. This equation is based on the  $f_{H_2O}$  data of Burnham et al. (1969) below 10 kbar and that of Delany and Helgeson (1978) and Halbach and Chatterjee (1982) above 10 kbar. The equation is formulated on the premise that the Gibbs free energy of formation of H<sub>2</sub>O (=  $RT \ln f$ ) varies as a relatively simple monotonic function of pressure and temperature, especially above 10 kbar (Delany and Helgeson, 1978). This equation is well suited for the purposes of thermochemical data extraction because it is designed to cover the  $P$ - $T$  range over which most experimental phase equilibria involving hydrous phases are obtained and covers certain pressure ranges that other equations of state do not, e.g., Equation 15 of Delany and Helgeson (1978) is best above 10 kbar, the equation of Haar et al. (1984, Appendix A) does not go above 10 kbar, and Equation 14 of Saxena and Fei (1987) is not recommended below 2 kbar. For pressures below 0.3 kbar, the equation of Holland and Powell (1990) was found to be insufficiently accurate (especially in the vicinity of 0.2 kbar) and a Berthelot equation of state in virial form was used instead:

$$RT \ln f = RT \ln P + \left( A + \frac{B}{T^2} \right) P$$

where parameter  $A = 2.564$  and  $B = -5.0966 \times 10^6$  (units: J, bar, K). For the range of 1–300 bar and 300–1200 °C this equation fits the available data for H<sub>2</sub>O (see references in Haar et al., 1984) with an average absolute deviation of 110 J, except in the immediate vicinity of the critical point.

The value of  $K_a$  will be treated in two ways as discussed below.

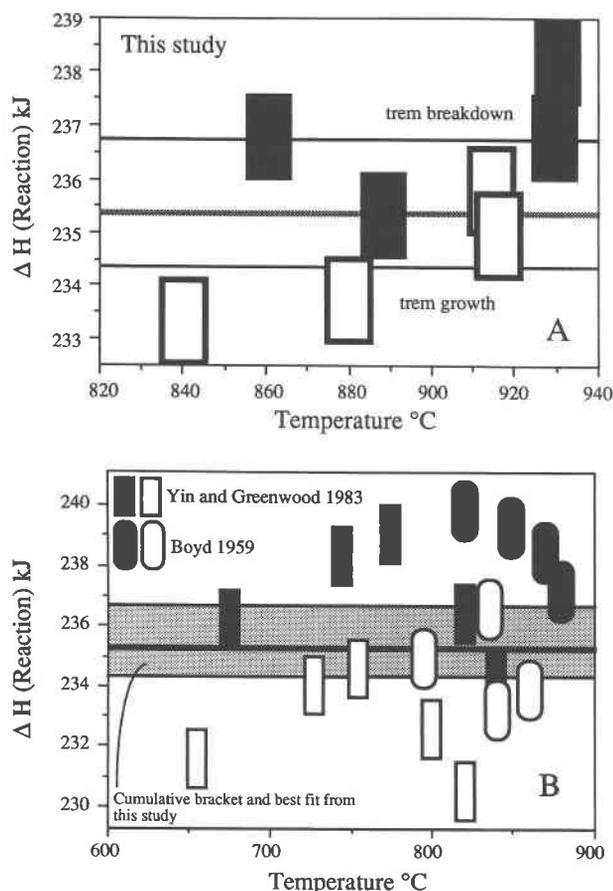


Fig. 3. (A) Internal consistency analysis of the data from this study for Reaction 1 (per two moles of tremolite), showing  $\Delta H_{1 \text{ bar}, 298\text{K}}^0$  of reaction derived from the bracketing experiments for tremolite growth (open symbols) and tremolite breakdown (filled symbols) as a function of temperature. Thin lines: consistent region or overall enthalpy bracket used in the regression as defined by Holland and Powell (1990). Stippled line: least squares solution for the enthalpy of reaction. (B) Internal consistency analysis of the data from Boyd (1959) and from Yin and Greenwood (1983). Shaded area: consistent region or cumulative bracket from A. Bold line: least squares solution for the enthalpy of reaction, same as in A.

#### Assumption of pure phases

Although there is solid solution occurring in tremolite, diopside, and enstatite and probably dissolution of at least quartz into the ambient  $\text{H}_2\text{O}$ , our initial thermodynamic treatment will be made under the assumption that each phase is pure and that  $K_a$  is unity. This assumption stems from the lack of a well verified activity-composition relationship for the solution of Mg into tremolite (Jenkins, 1987) and from the largely unknown amount of dissolution of quartz into the ambient fluid along the univariant curves of Reactions 1 and 3. It is also true, to a first approximation, that the reduction in the activities of the

components on both sides of the reaction will be similar in magnitude and tend to keep the value of  $K_a$  near 1.

Figure 3A is a plot of the derived values of  $\Delta H_{1 \text{ bar}, 298\text{K}}^0$  of reaction as a function of temperature for Reaction 1 (per two moles of tremolite) for the four experimental reversals reported in this study. The solid squares represent the bracketing experiments for the breakdown of tremolite while the open squares are those for the growth of tremolite. There is a narrow range of feasible values between 234.40 and 236.75 kJ which can satisfy (pass between) all of the bracketing experiments if one takes into consideration the uncertainties in pressure and temperature associated with each experiment.

In order to derive an enthalpy of formation for tremolite that is internally consistent with a large number of other phases, it is necessary to relax the extremely tight constraints placed on the feasible range of enthalpy values by the experimental data as exemplified by the experiments shown in Figure 3A. Powell and Holland (1985, p. 334) discuss the reason and method for defining a minimum width for the feasible or consistent region of  $\Delta H_{P_0, T_0}^0$  of reaction. The method used here and in Holland and Powell (1990) is slightly different. The experimental uncertainty in  $P$  and  $T$  associated with the ends of each experimental bracket gives rise to a corresponding uncertainty in the derived enthalpy of reaction, referred to here as  $uH$  (see Appendix). A consistent region, or overall bracket ( $\Delta$ ), is sought which satisfies all of the data and has a width of at least  $3(uH)$ . This is equivalent to saying that the narrowest a bracket can be is three times the experimental uncertainty on its ends. The factor of 3 is larger than the factor of 2 used by Powell and Holland (1985) but still obeys the criterion established by Demarest and Haselton (1981) that the quantity  $(uH)/(0.5\Delta) = 1.5$  ( $=d/s$  of Demarest and Haselton, 1981) be less than 2 for a Gaussian probability curve for the overall enthalpy of reaction bracket. If this interval is less than  $3(uH)$  then the consistent region is widened as follows. (1) The median of the low enthalpy bracket ends and the median of the high enthalpy bracket ends are determined. (2) These two values are averaged and set equal to the midpoint of the consistent region ( $= C$ ). (3) The location of the consistent region is then centered on this average value  $C$  and has a width given by  $C + 1.5(uH)$  and  $C - 1.5(uH)$ . For weighting purposes, the standard deviation of  $\Delta H$  is taken as  $1/4$  the width of the consistent region, that is to say,  $\sigma_{\Delta H} = 0.75(uH)$ . The upper and lower horizontal lines in Figure 3A are the consistent region or overall bracket ( $= \Delta$ ) for the experiments performed in this study. The thicker middle line is the  $\Delta H_{P_0, T_0}^0$  of reaction obtained from the least-squares regression of the entire experimental data set (see below).

Figure 3B is a plot of the data from Boyd (1959) and from Yin and Greenwood (1983), where the solid symbols correspond to tremolite breakdown and the open symbols to tremolite growth. The consistent region from Figure 3A is reproduced here as the shaded band ("Brack-

et from this study") to show that there is fairly good agreement in the derived enthalpies of reaction between this study and those of Boyd (1959) and of Yin and Greenwood (1983).

An internal consistency analysis of the data for Reaction 2 from this study is shown in Figure 4. Figure 4 shows the values of  $\Delta H_{f, \text{bar}, 298\text{K}}^0$  of reaction for the bracketing experiments demonstrating talc + diopside growth (open squares) and tremolite growth (closed squares). There is no range of enthalpy values that will satisfy all of the experiments. If the highest temperature experiment is rejected because of the possible complications from the nucleation of enstatite, then a narrow consistency range exists between  $-7.65$  and  $-7.77$  kJ. The width of this consistent region does not quite obey the  $3(uH)$  criterion and was widened further to  $-7.83$  to  $-7.55$  kJ (thin horizontal lines on Fig. 4).

As mentioned above, a least-squares regression was performed according to the procedure of Holland and Powell (1985) but allowing only the enthalpies of formation of tremolite and talc to vary. The enthalpies of all other phases were fixed at those values given by Holland and Powell (1990). The enthalpies of formation of tremolite and talc were refined using the phase equilibria described here together with all reactions in the data base of Holland and Powell (1990) that involve tremolite and talc. The experimental phase equilibria, low and high enthalpy of reaction values, widened enthalpy ranges ( $H: x \leftrightarrow y$ ), and the resultant least-squares-determined enthalpy of reaction [calc( $H$ )] for these equilibria are listed in Appendix Table 1. The derived values of  $\Delta H_{f, \text{bar}, 298\text{K}}^0$  for tremolite and talc can be found in the first column of Table 5 and their associated uncertainties ( $1\sigma$ ) in the second column. Also given in Table 5 are the  $\Delta H_{f, \text{bar}, 298\text{K}}^0$ ,  $S$ ,  $V$ ,  $C_p$ ,  $V\alpha$ , and  $V\beta$  terms for all of the phases considered in Figures 1 and 2. The value obtained for tremolite is  $-12302.90 \pm 7.05$  kJ/mol, which is in excellent agreement with the value reported by Berman (1988) ( $-12305.578$  kJ/mol) but considerably more positive than the values reported by Helgeson et al. (1978) ( $-12319.696$  kJ/mol) and Robie et al. (1978) ( $-12355.080 \pm 17.3$  kJ/mol).

### Solid solutions

It is important to consider how solid solution in tremolite and the coexisting phases might affect the derived  $\Delta H_{f, P_0, T_0}^0$  of the component  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  (= trem). At present there is no experimental information on the compositions of orthopyroxene (opx) and clinopyroxene (cpx) in equilibrium with tremolitic amphibole and quartz (Reaction 1) or on the composition of cpx in equilibrium with talc and tremolite (Reaction 2) in the system  $\text{H}_2\text{O}$ - $\text{CaO}$ - $\text{MgO}$ - $\text{SiO}_2$ . For the purposes of this analysis, therefore, it is assumed that the compositions of opx and cpx in equilibrium with tremolitic amphibole and quartz are the same as those of coexisting opx and cpx in the absence of these phases and that the composition of cpx in equi-

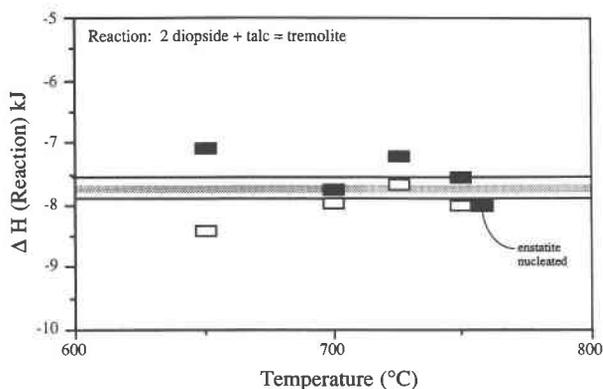


Fig. 4. Internal consistency analysis of the data from this study for Reaction 2. Open squares = di + ta growth; Filled squares = tr growth. Lines as in Figure 3A.

librium with talc and tremolite is pure diopside. Both of these assumptions are supported by the lack of any shifts in X-ray peak positions, appearance of extraneous phases, or unaccounted for changes in the proportions of phases that would be expected to accompany an extensive re-equilibration of the pyroxenes used in the starting mixtures. As argued by Jenkins (1987), it is assumed that the synthetic tremolite used in all of these reactions is not strictly that of tremolite, but is that of an Mg-enriched tremolite with the composition  $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2$ . Furthermore, the composition of synthetic tremolite is assumed to be constant over the pressure and temperature range considered in this study.

The compositions of coexisting opx and cpx over the temperature range of interest (600–900 °C) are essentially constant (Lindsley et al., 1981) and are listed in Table 1. The activity expressions for the components  $\text{Mg}_2\text{Si}_2\text{O}_6$  and  $\text{CaMgSi}_2\text{O}_6$  in opx and cpx, respectively, used in this analysis were those of Lindsley et al. (1981), who modeled the nonideal mixing in opx with a one-parameter Margules expression and in cpx with a two-parameter Margules expression. A simple ideal activity model for tremolite was used where the activity of trem is given by the expression  $a_{\text{trem}}^{\text{ampb}} = (X_{\text{Ca}}^{\text{M4}})^2$ . For the synthetic tremolite used here, the activity of trem is  $(0.9)^2 = 0.81$ .

Using the above activity-composition relationships, the calculated values of  $K_x$  do not deviate more than approximately 5% from 1.0 at even the highest temperatures encountered for tremolite stability. Considering the uncertainties in phase compositions and activity-compositions, it was deemed unwarranted to perform a least-squares regression of the full data set; however, an internal consistency analysis of the experiments for Reactions 1 and 2 was performed. The results of this analysis suggest that the bracketing values of  $\Delta H_{f, P_0, T_0}^0$  are shifted approximately 0.61 kJ lower for Reaction 1 (per 1 mol of tremolite) and approximately 1.73 kJ lower for Reaction 2. Although these shifts do not change the status of in-

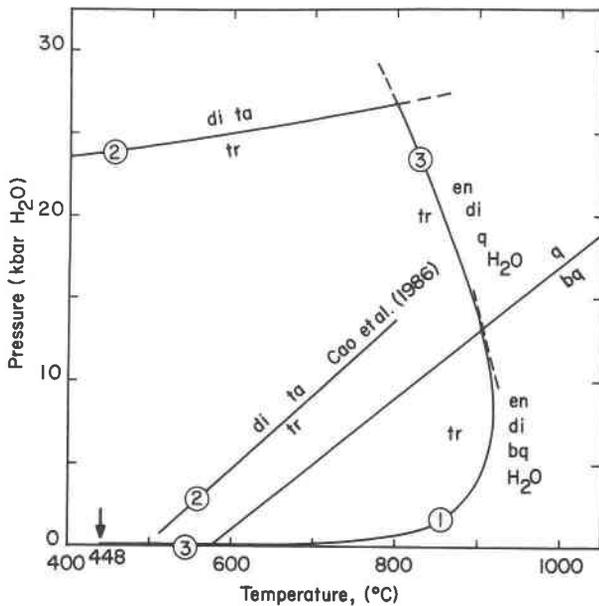


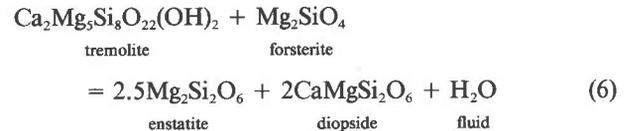
Fig. 5. Calculated locations of Reactions 1, 2, and 3 that delimit the upper-thermal and upper-pressure stability of synthetic tremolite in the system  $\text{H}_2\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2$ . Also shown is the univariant boundary for the reaction  $\alpha$ -quartz =  $\beta$ -quartz ( $q = \text{bq}$ ). The boundary for Reaction 2 from Cao et al. (1986) is shown for comparison. Abbreviations as in Figures 1 and 2. Arrow indicates the thermal stability of tremolite at 1 bar calculated according to Reaction 3.

ternal consistency within a given set of experiments, they do affect the derived value of  $\Delta H_{f,1 \text{ bar}, 298 \text{ K}}^0$  for tremolite. It is suggested here that provision for the solid solution effects in tremolite and pyroxene, with our current knowledge of the compositions and activity-composition relations in these solid phases, results in an increase of approximately 1 kJ/mol, or a value of  $-12302$  kJ/mol, in the  $\Delta H_{f,1 \text{ bar}, 298 \text{ K}}^0$  of tremolite. This compares very well with the value of  $-12300.47 \pm 14.8$  kJ/mol derived from the experimental study of natural, on-composition, tremolite by Welch and Pawley (in preparation).

#### TREMOLITE PHASE EQUILIBRIA

The univariant boundaries for Reactions 1–4 have been calculated using the thermochemical data listed in Table 5, the  $f_{\text{H}_2\text{O}}$  equations of Holland and Powell (1990) and the Berthelot equation given above, and the computer program Thermocalc (Holland and Powell, 1990). These curves are shown in Figures 1 and 2. There is, in general, excellent agreement between the calculated univariant boundaries and the experimental brackets for essentially all reactions except Reaction 2 (2 diopside + talc = tremolite), where it is simply not possible to satisfy the reversals obtained both in this study and in studies of Gilbert and Troll (1974) with one univariant curve. As discussed in the Experimental Results section, we have favored the experimental results obtained in this study because they were obtained with a pressure medium (NaCl) that is be-

lieved to be more hydrostatic than the pressure medium used by Gilbert and Troll (1974). It might be pointed out that the calculated curve for Reaction 3 is in excellent agreement with the 15 kbar reversal of Gilbert and Troll (1974), which suggests that there is better agreement concerning the measurement of temperature than of pressure between this study and that of Gilbert and Troll (1974). The univariant boundary for the  $\alpha$ - $\beta$  quartz transition, as calculated from the data of Holland and Powell (1990) based on the review of Mirwald and Massone (1980), is also shown. The calculated boundary for the reaction



is shown in Figures 1 and 2 along with the experimental data of Jenkins (1983) for this reaction (open and closed ovals). This reaction demonstrates that the thermodynamic data derived here are consistent with reactions limiting the stability of tremolite in quartz-free as well as quartz-bearing assemblages.

The univariant curves delimiting the stability field of synthetic tremolite in the system  $\text{H}_2\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2$  have been combined into one diagram in Figure 5. It can be seen in Figure 5 that tremolite by itself has a wide  $P$ - $T$  range of stability, having a maximum thermal stability of 918 °C at 7.5 kbar and a maximum pressure stability of 26.8 kbar at 798 °C. The slope of Reaction 2, as mentioned in the Introduction, is of considerable interest because the lower-thermal stability of tremolite may be dictated by this reaction. The  $dP/dT$  slope observed in this study is approximately 8.8 bar/K. This is much less than the 45 bar/K slope observed by Cao et al. (1986) who indicated that tremolitic amphibole has a minimum temperature of stability of approximately 500 °C (Fig. 5). These authors recognized that the reaction boundary shown by Gilbert et al. (1982) and thermodynamic calculations using the data of Robie et al. (1978) or Helgeson et al. (1978) indicated that Reaction 2 occurs at much higher pressures and with a shallower slope. Cao et al. (1986) conducted their experiments in an Al-bearing system and suggested that this may explain the difference in the location of this boundary; however, there is not enough information on the compositions of the experimental product phases in the Cao et al. (1986) study to allow a more detailed analysis of the effect of Al. At least in the system  $\text{H}_2\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2$ , tremolite should be stable up to pressures of 21 kbar even at the lowest grades of metamorphism (200 °C) and should not transform to a talc + diopside assemblage, by Reaction 2, at typical crustal metamorphic conditions.

The 1-bar stability of tremolite was calculated using the newly refined thermodynamic data obtained in this study by assuming an ambient  $f_{\text{H}_2\text{O}}$  of 1 bar and by assuming that it decomposes at this pressure according to

Reaction 3. The calculated decomposition temperature is 448 °C. This is nearly 350 °C lower than the dehydroxylation (and presumably decomposition) temperature for natural tremolite in the presence of an H<sub>2</sub>O-free environment (N) reported by Freeman (1966). Two possible explanations are proposed here for the large difference between the calculated and observed 1-bar decomposition temperature. First, it is possible that tremolite dehydrates at very low pressures (i.e., near 1 bar) to a single Mg-rich clinopyroxene and quartz and that this process occurs at a much higher temperature than Reaction 3. This decomposition mechanism has been proposed by Freeman and Taylor (1960, cited by Ghose, 1981) and has its counterpart in the dehydration of grunerite to clinoferrrosilite and silica (Ghose and Weidner, 1971). Second, the experimentally observed higher decomposition temperature may result from a simple overstepping of the theoretical temperature because of sluggish kinetics, especially when seeds of the breakdown products are not present. Unfortunately the magnitude of this overstepping (350 °C) is far greater than one would predict. A mixture of forsterite + tremolite, for example, will decompose (unseeded) to enstatite and diopside with only approximately 50 °C overstep in temperature at 12–15 kbar in a hydrothermal environment (Jenkins, 1980). Similar overstep temperatures have been observed for the breakdown of layered silicates in hydrothermal experiments performed in the range of 2–7 kbar (Ridley and Thompson, 1986). Based on the observation of Jenkins (1987) that the incongruent dissolution of tremolite is largely controlled by silica solubility in the ambient fluid of hydrothermal experiments, it is proposed here that the greatly enhanced breakdown of tremolite with only a few tens of bars of H<sub>2</sub>O pressure is influenced more by the dissolution of silica than by the loss of H<sub>2</sub>O from the tremolite structure. The enhanced solubility of quartz with increasing H<sub>2</sub>O pressures in the range of 200–1000 bars has recently been studied by Ragnarsdottir and Walther (1983). A careful crystallochemical study of the 1 bar decomposition of tremolite is needed before one can choose between these two explanations.

### SUMMARY

New experimental data for Reactions 1, 2, and 4 were combined with existing experimental data for these reactions, Reaction 3, and all of the experimental phase equilibria data pertinent to tremolite phase equilibria in order to obtain a refined value for the enthalpy of formation ( $\Delta H_{f,1 \text{ bar}, 298\text{K}}^0$ ) of tremolite. Based on the least-squares regression procedure and data base of Holland and Powell (1990), the derived  $\Delta H_{f,1 \text{ bar}, 298\text{K}}^0$  for tremolite is  $-12302.90 \pm 7.05$  kJ/mol for the values of entropy and volume for tremolite given in Table 5. This analysis was performed with the assumption that all phases were pure and had unit activity. Assuming that Ca and Mg mix ideally on the M4 site in synthetic tremolite and that the compositions of the pyroxene coexisting with synthetic tremolite are known, then this value will be approximately 1 kJ/mol more positive, or approximately

$-12302$  kJ/mol for stoichiometric tremolite. This is in excellent agreement with the  $\Delta H_{f,1 \text{ bar}, 298\text{K}}^0$  of  $-12300.47 \pm 14.81$  kJ/mol determined for on-composition natural tremolite by Welch and Pawley (in preparation). The calculated univariant boundaries for Reactions 1–3 indicate an upper-thermal stability for tremolite of 918 °C at 7.5 kbar and an upper-pressure stability of 26.8 kbar at 798 °C. The  $dP/dT$  slope of Reaction 2 that is consistent with both the experimental and thermochemical data in the system H<sub>2</sub>O–CaO–MgO–SiO<sub>2</sub> is approximately 8.8 bar/K (approximately constant over the temperature range of 200–800 °C), much less than the 45 bar/K slope predicted by Cao et al. (1986) in the system H<sub>2</sub>O–CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>. In view of this, the lower-temperature stability of tremolite does not appear to be limited by Reaction 2 at pressures within the Earth's crust. The calculated decomposition temperature of tremolite at 1 bar is 448 °C, which is approximately 350 °C lower than the observed dehydration temperature of tremolite. It is suggested that the dissolution of silica, rather than the loss of H<sub>2</sub>O, from tremolite may be the rate-limiting step for tremolite decomposition in hydrothermal environments.

### ACKNOWLEDGMENTS

Financial support for this study was provided by National Science Foundation grants EAR-8107110 to Robert C. Newton at the University of Chicago and EAR-8803437 to D.M.J. Financial support was also provided by an NSF Summer Research Fellowship to A.K.C. while at the University of Chicago. The authors are indebted to M. Charles Gilbert and Hui-An Yin for their assistance in supplying experimental samples, data, and details of experimental procedure that would not otherwise be readily available. The careful manuscript reviews by J.V. Chernosky and R.G. Berman are greatly appreciated. Special thanks are given to Anne Darling and Dave Tuttle for assistance in manuscript preparation.

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MANUSCRIPT RECEIVED MARCH 12, 1990

MANUSCRIPT ACCEPTED JANUARY 14, 1991

APPENDIX TABLE 1. Data pertinent to the enthalpies of formation of tremolite and talc

Reaction and source	In K	X (CO <sub>2</sub> )	P (kbar)	T (°C)	H (low)	H (high)	miss	calc	2sd	Summary	
1. 2tr = 3en + 4di + 2bq + 2H <sub>2</sub> O (Yin and Greenwood, 1983)	0	0	0.1	655	675	231.57	236.20		671	2	H: (232.94 ↔ 235.96)
	0	0	0.25	725	745	234.00	238.24		731	2	calc(H) = 235.29 (sd 0.35) within bracket uH = 1.01, ds = -0.4
	0	0	0.3	755	775	234.75	239.01		758	2	
	0	0	0.8	800	820	232.58	236.32		815	3	
	0	0	1.4	820	840	230.50	233.96	8	848	3	
(Boyd, 1959)	0	0	0.6	795	820	234.95	239.85		797	3	H: (235.33 ↔ 238.03)
	0	0	1.0	835	850	236.60	239.35	-7	828	3	calc(H) = 235.29 (sd 0.35) within bracket
	0	0	1.5	840	870	233.28	238.48		852	3	uH = 0.90, ds = 0.4
	0	0	2.0	860	880	233.94	237.28		868	3	H: (234.40 ↔ 236.75)
(This study)	0	0	1.5	840	860	233.28	236.74		852	3	calc(H) = 235.29 (sd 0.35) within bracket
	0	0	3.0	880		233.76			890	3	uH = 0.78, ds = -0.3
	0	0	2.9		888		235.29		888	3	
	0	0	5.0	914	930	235.77	238.16	-3	911	3	
	0	0	7.1	916	929	234.97	236.82		918	3	
2. 2di + ta = tr (This study)	0	—	27.0	24.0	650	-8.41	-7.05		25.43	0.38	H: (-7.83 ↔ -7.55)
	0	—	26.5	26.0	700	-7.99	-7.76	-0.14	25.86	0.38	calc(H) = -7.70 (sd 0.11)
	0	—	26.0	25.0	725	-7.66	-7.20	0.08	26.08	0.38	within bracket
	0	—	27.0	26.0	750	-8.02	-7.56		26.31	0.38	uH = 0.09, ds = -0.5
4. 2ta = 3en + 2bq + 2H <sub>2</sub> O (Skippen, 1971; Chernosky, 1976; Chernosky et al., 1985)	0	0	0.5	656	672	217.04	220.21		670	2	
	0	0	1.0	700	721	219.35	223.19		703	2	
	0	0	2.0	725	735	218.11	219.79	1	736	2	H: (217.82 ↔ 220.49) calc(H) = 219.90 (sd 0.32) within bracket uH = 0.89, ds = 0.2
4. 2ta = 3en + 2q + 2H <sub>2</sub> O (Chernosky et al., 1985)	0	0	10.0	790	800	214.67	216.04	3	803	3	H: (214.21 ↔ 216.16)
	0	0	13.0		800		215.51	7	807	3	calc(H) = 216.44 (sd 0.32)
	0	0	13.6	785		213.50			807	3	too high but OK
	0	0	17.0	795		214.83			808	3	uH = 0.65, ds = 0.5
4. 2ta = 3en + 2q + 2H <sub>2</sub> O (This study)	0	0	25.0	800	820	216.48	218.88		800	3	H: (216.48 ↔ 218.88)
	0	0	28.0	770		213.54			795	4	calc(H) = 216.44 (sd 0.32) uH = 0.60, ds = 2.0
6. 2tr + 2fo = 5en + di + 2H <sub>2</sub> O (Jenkins, 1983)	0	0	5.0	820	840	218.64	221.54	-2	818	3	H: (217.43 ↔ 219.58)
	0	0	8.0	790	810	216.91	219.61		801	4	calc(H) = 218.41 (sd 0.46)
	0	0	10.0	770	790	216.84	219.45		782	4	within bracket
	0	0	20.0	640	660	217.59	219.91		647	4	uH = 0.72, ds = 0.6

Note: Results from the least-squares analysis of experimental data pertinent to the enthalpies of formation of tremolite and talc. Reaction numbers correspond to those given in the text.

Abbreviations: In K = equilibrium constant used for the reaction under consideration; X(CO<sub>2</sub>) = the mole fraction of CO<sub>2</sub> for the reaction under consideration; P and T = the pressures (kbar) and temperatures (°C) of each particular experimental bracket unadjusted for experimental uncertainties; H(low) and H(high) = enthalpy brackets used in the least squares regression; miss = misfit of the calculated to observed temperature (K) or pressure (kbar) range of a bracket; calc = calculated pressure or temperature and its associated uncertainty (2 sd) based on the least-squares regression; H: (x ↔ y) = expanded enthalpy bracket; calc(H) = enthalpy of reaction and its associated uncertainty (sd) from the least-squares regression; uH = enthalpy uncertainty due to pressure and temperature measurement uncertainty at the extremes of the brackets; ds = a bracket width parameter as defined in Holland and Powell (1985). All enthalpies are in kJ.