Tremolite: New enthalpy and entropy data from a phase equilibrium study of the reaction tremolite = 2 diopside + 1.5 orthoenstatite + β-quartz + H$_2$O

Mark D. Welch,* **Alison R. Pawley****

Department of Geology and Geophysics, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW, United Kingdom

Abstract

New enthalpy and entropy data have been obtained for a natural end-member tremolite from phase equilibrium experiments on the high-temperature dehydration reaction tremolite = 2 diopside + 1.5 orthoenstatite + β-quartz + H$_2$O. Six reversed experimental brackets were obtained at 0.25 kbar (996–1033 K), 0.6 kbar (1038–1058 K), 1 kbar (1075–1104 K), 1.5 kbar (1101–1125 K), 2 kbar (1115–1128 K), and 8 kbar (1179–1209 K), from which the enthalpy of formation and the third-law entropy of tremolite have been calculated using the internally consistent thermodynamic dataset Thermocalc of Holland and Powell (1990). The values obtained are ΔH_f^o(Tr) = −12299.48 ± 14.84 kJ/mol and S^o(Tr) = 0.5525 ± 0.0100 kJ/mol·K, which are in excellent agreement with the values given in Thermocalc and agree well with the values of Berman et al. (1985). We use the new thermodynamic data to calculate revised limits of tremolite stability in the system CaO-MgO-SiO$_2$-H$_2$O (CMSH). We also discuss the apparent major discrepancy between values for ΔH_f^o(Tr) obtained from solution calorimetry (Kiseleva and Ogorodova, 1984) and the phase equilibrium values. The difference between enthalpies for end-member tremolite determined from phase equilibrium and calorimetric studies (36 kJ) is comparable to that observed for talc (Kiseleva and Ogorodova, 1984), perhaps suggesting anomalous dissolution behavior of the talc-like elements of tremolite.

Introduction

Tremolitic amphiboles are important constituents of hydrated basic and ultrabasic rocks and siliceous marbles in the greenschist and albite-amphibolite facies. These amphiboles are the first to grow in these rocks, and as such they are substrates for a range of continuous reactions (most importantly coupled exchange reactions); these reactions can lead to zoned amphiboles of use in elucidating the pressure-temperature-time evolution of metamorphic rocks (cf. Holland and Richardson, 1979). The procurement of well constrained thermodynamic data for end-member tremolite Ca$_2$Mg$_5$Si$_8$O$_{22}$(OH)$_2$ is therefore an important objective. However, despite the dozen or so experimental studies of tremolite stability that have been made over the last 30 years, good agreement on experimentally derived thermodynamic data is lacking. Some sources of discrepancy are discussed below.

Boyd (1959) made the first experimental study of tremolite stability in the synthetic system CaO-MgO-SiO$_2$-H$_2$O (CMSH) at H$_2$O pressures up to 2 kbar. He found that amphibole was stable at ~800 °C/0.6 kbar and ~870 °C/2 kbar. A number of later studies of tremolite equilib-

ria have been made in the systems CMSH and CMSH-CO$_2$ under geologically relevant conditions. These are summarized in Table 1, from which it is evident that most of the amphiboles studied do not approach ideal tremolite composition closely. The results of these studies have been used as sources for deriving thermodynamic data for tremolite (Table 1). Not surprisingly, given the chemical diversity of the amphiboles used, there is poor agreement between thermodynamic datasets. Furthermore, the microstructural states of these amphiboles were not determined. Maresch and Czank (1988) have shown that the intensity shifts in X-ray diffraction patterns used to infer reaction direction in reversal experiments can also arise from the preferential elimination of chain-multiplicity faults (Czank and Liebau, 1980) in polysomatically disordered reactant amphibole, leading to the spurious location of amphibole equilibria in pressure-temperature space (see also Graham et al., 1989, p. 70).

The experiments on synthetic tremolite deserve further comment. End-member tremolite is notoriously difficult to synthesize: assemblages such as diopside + talc + amphibole ± quartz, amphibole + diopside + enstatite, and amphibole + diopside + quartz are common synthesis products. Complete yields of amphibole from tremolite syntheses have never been achieved, and yet end-member tremolite, although very rare, does occur in nature—the one used in this study is one example, that of Kiseleva and Ogorodova (1984) is another. Jenkins (1987) ad-

---

TABLE 1. Tremolite starting materials used in experimental studies of tremolite stability and thermochemistry

Authors	Reaction/technique	Tremolite composition	Ca/Mg	Data set	Notes
Weeks (1956)	Hf calorimetry	$(Ca_{1.73}Mn_{0.04})(Mg_{5.09}Fe_{0.01})(Si_{8.06}-Al_{0.08})O_{22.10}(OH)_{2.06}$	0.34	R	Skarn termolite, Balmat, New York
Boyd (1959)	Tr = Di + En + Qz + H_2O	Synthetic tremolite (oxide mix, glass)	<0.40	H, HP	
Robie & Stout (1963)	Low-T calorimetry (Cp)	$(Na_{0.11}K_{0.02})(Ca_{1.90}Mg_{0.10})(Mg_{5.04}-Fe_{0.01})(Si_{7.89}Al_{0.08})O_{22}(OH)_{1.94}$	0.37	see Table 3	Falls Village, New York
Metz (1967, 1976)	Tr + Dol = Fo + Cc + CO_2 + H_2O	$Na_{0.11}(Ca_{1.73}Mg_{0.27})(Mg_{4.96}Al_{0.14})-(Si_{7.93}Al_{0.07})O_{22}(OH)_{1.56}$	0.33	HP, BBG	Natural tremolite, Campo Lungo
Hoschek (1973)	Phl + Cc + Qz = Tr + Ksp + CO_2 + H_2O	Synthetic tremolite (gel)	<0.40	HP, BBG	
Hewitt (1975)	Phl + Cc + Qz = Tr + Ksp + CO_2 + H_2O	$Na_{0.08}(Ca_{1.94}Mg_{0.05})(Mg_{4.98}Fe_{0.02})-(Si_{7.84}Al_{0.10})O_{22}(OH)_{2.14}F_{0.06}$	0.385	HP	Gouverneur, New York
		$(Na,K)_{0.55}(Ca_{1.73}Mg_{0.24})(Mg_{4.76}-Fe_{0.05}Al_{0.18})(Si_{7.85}Al_{0.12})O_{22}-(OH)_{0.8}F_{0.66}$	0.346		
		Synthetic tremolite (oxide mix)	<0.40		
Slaughther et al. (1975) and Eggert & Kerrick (1981)	Tr + Cc = Dol + Di + CO_2 + H_2O			BBG, HP	St. Gotthard, Switzerland
	Dol + Qz + H_2O = Tr + Cc + CO_2	$Ca_{2.16}(Mg_{4.94}Fe_{0.03})$			
	Tc + Cc + Qz = Tr + CO_2 + H_2O	$(Si_{7.92}Al_{0.01})O_{22}(OH)_{2.0}F_{0.03}$	0.437		
	Dol + Tc + Qz = Tr + CO_2 Tr + Cc + Qz = Di + CO_2 + H_2O				
Jenkins (1983)	Tr + Fo = Di + En + H_2O	Synthetic tremolite (gel, glass, oxide mix)	<0.40	BBG, HP	≤90% synthetic amphibole yield
Yin & Greenwood (1983)	Tr = Di + En + Qz + H_2O	Synthetic tremolite (gel, oxide mix)	<0.40	BBG	
Skippen & McKinstry (1985)	Tr + Fo = Di + En + H_2O	$Ca_{2.16}(Mg_{4.94}Fe_{0.03})(Si_{7.92}Al_{0.01})-O_{22}(OH)_{2.0}F_{0.03}$	0.437		St. Gotthard, Switzerland
Kiseleva & Ogorodova (1984)	high-T lead borate calorimetry	$Ca_{2.01}Mg_{4.98}Si_{8.02}O_{22}(OH)_{1.95}$	0.404		Marble, Karelia
Welch (1987)	Tr = Di + En + Qz + H_2O	$Na_{0.01}Ca_{2.00}(Mg_{4.98}Fe_{0.02})Si_{8.00}-O_{22}(OH)_{2.0}$	0.400		Locality unknown. HRTEM (structurally ordered) IR, Raman

Note: From Graham et al. (1989). Abbreviations: Tr = tremolite, Di = diopside, En = enstatite, Qz = quartz, Dol = dolomite, Cc = calcite, Fo = forsterite, Phl = phlogopite, Ksp = potassium feldspar, Tc = talc, R = Robie et al. (1978), H = Helgeson et al. (1978), HP = Holland and Powell (1985), BBG = Berman et al. (1985).

dressed the problem of tremolite synthesis and presented a cogent case for incongruent dissolution of tremolite (specifically the SiO_2 component) in supercritical H_2O as a major control on experimental products. With increasing initial H_2O contents, the incongruent dissolution process leads to the following sequence of assemblages in which the fluids are SiO_2 undersaturated:

$$Tr + H_2O = Tr_{ss} + Di + En + fluid \quad (1)$$
$$Tr + H_2O = Di + En + fluid \quad (2)$$
$$Tr + H_2O = Di + Fo + En + fluid \quad (3)$$
$$Tr + H_2O = Di + Fo + fluid. \quad (4)$$
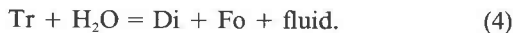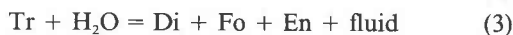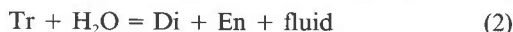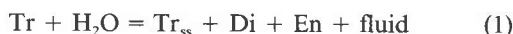
Reaction 1 (see Appendix 1 for abbreviations) involves a change in amphibole chemistry from tremolite to a tremolite-magnesiocummingtonite (Tr-Mc) amphibole (Jenkins, 1987). Hence, changes in modal proportions and amphibole chemistry can occur. The quartz solubility data of Anderson and Burnham (1965) imply that assemblages 3 and 4 are restricted to bulk compositions with very high H_2O/Tr ratios (i.e., >90 wt% H_2O) at $P < 10$ kbar and $T < 900$ °C. Jenkins (1987) attempted to synthesize Tr-Mc amphiboles at 5 mol% intervals from tremolite to $Tr_{75}Mc_{25}$ at 6 kbar and 13 kbar (750–852 °C) and found

that the stable amphibole was limited to within a few mole percent of $Tr_{90}Mc_{10}$; Tr_{100} gave Tr-Mc amphibole + clinopyroxene. He also demonstrated from dissolution and regrowth experiments that the yield of amphibole could be increased by adding enough quartz to give a SiO_2-saturated fluid. Following from this, Jenkins attempted to synthesize tremolite at 6 kbar/850 °C (well inside the nominal stability field calculated from thermodynamic data sets) and obtained Tr-Mc amphibole + clinopyroxene + quartz, a high-temperature assemblage frequently encountered in previous studies. This result strongly suggested that end-member tremolite is unstable under these conditions and starts to break down at a lower temperature by continuous reaction: Tr = Tr_{ss} + Cpx + Qz + fluid. The end-member natural tremolite samples are then inferred to be stable at temperatures significantly below the univariant dehydration of the limiting Mg-saturated Tr-Mc amphiboles: Tr_{ss} = Cpx + Opx + Qz + fluid. Amphibole composition is inferred to change continuously along the univariant dehydration boundary (cf. Graham et al., 1989, their Fig. 9). An important corollary of the incongruent dissolution phenomenon is that tremolite phase equilibria in SiO_2-saturated systems may be thermodynamically incompatible with those deter-

mined in SiO_2-undersaturated (e.g., forsterite-bearing) systems.

A further complication with tremolite syntheses is the rapid growth of diopside ($\pm$ talc) in the first hour or so of an experiment (Welch, 1987). When gels are used, this problem may be even worse because of the presence of diopside crystallites produced during firing of the gel at 850–900 °C. Similar crystallization behavior has been observed in some other calcic amphiboles such as edenite, magnesio-hornblende, and richterite. In some cases (e.g., richterite), diopside can be reacted out by crushing and re-reacting, suggesting that the diopside in synthesis products is being preserved by an amphibole armor and thereby isolated from the reacting gel or oxide mix.

This study was undertaken to derive well-constrained enthalpy and entropy data for end-member tremolite from phase-equilibrium experiments on the reaction Tr = 2Di + 1.5En + β-Qz + H_2O using a natural end-member tremolite sample and, if possible, to clarify the nature of the breakdown.

EXPERIMENTAL METHODS

Starting materials

Diopside and orthorhombic enstatite were synthesized hydrothermally from stoichiometric gels at 4 kbar/900 °C and 2 kbar/900 °C, respectively. Pure natural α-quartz that had been acid washed was used. The specimen of tremolite came from the University of Edinburgh collection, but its locality is unknown. A chemical analysis (the average of 31 microprobe analyses for the cations and also F and H_2O analyses determined by other methods) is given in Table 2, from which it can be seen that the specimen has the ideal tremolite composition and is F free. High-resolution transmission electron microscopy revealed that the amphibole is exceptionally free of polysomatic (chain-width) and polytypic (stacking) faults and mineral inclusions. As such, this tremolite sample is the most suitable specimen for thermodynamic analysis of any tremolite yet studied (see Table 1).

Cleavage fragments of tremolite were removed from the hand specimen (a tremolite-calcite-quartz rock) using a razor blade; then they were crushed and left to stand overnight in 30 vol% ethanoic acid to remove any carbonate residues adhering to crystals. Examination by optical microscopy and powder X-ray diffraction showed that calcite was absent, the sample being amphibole with very minor amounts of quartz. Two complimentary starting mixes were prepared: 85%Tr : 15%Di-En-Qz and 15%Tr : 85%Di-En-Qz, the diopside, enstatite, and quartz being mixed in tremolite proportions (4:3:2). All phases were crushed and sieved to <15 μm. Approximately 0.02 g of mix was loaded into a Pt capsule (already welded at one end) along with 4–10 wt% distilled H_2O, and the capsule was welded shut. Each experiment was conducted with pairs of mixes. At the conditions of our cold-seal experiments (0.25–2.0 kbar/700–930 °C), the data of Anderson and Burnham (1965) indicate that the hydrous

TABLE 2. Average microprobe analysis of natural tremolite (n = 31)

Oxide	Wt%	2σ (sample)	Atoms (O = 24)
SiO_2	58.61	(0.52)	7.95
TiO_2	0.02	(0.01)	0.00
Al_2O_3	0.03	(0.02)	0.01
Cr_2O_3	0.01	(0.01)	0.00
FeO*	0.43	(0.02)	0.05
MnO	0.03	(0.01)	0.00
MgO	25.01	(0.30)	5.06
CaO	13.65	(0.18)	1.98
Na_2O	0.02	(0.01)	0.00
K_2O	0.02	(0.01)	0.00
F**	0.05	(0.00)	0.00
H_2O†	2.19	(0.22)	1.98
Σ	100.07 (±0.95)‡	(1.30)	17.03

* Fe_2O_3 was not detected in wet-chemical analysis (M.J. Saunders, analyst).

** Wet-chemical analysis (M.J. Saunders, analyst).

† H_2O content determined by H extraction method (see Holdaway et al., 1986).

‡ This error is the total of analytical uncertainties (Σ 2σ).

fluids have SiO_2 molalities of ~0.1 mol SiO_2/kg H_2O, which corresponds to <0.01 mol% SiO_2 in the fluid. With regard to our experiments at 8 kbar/900–940 °C, we have interpolated a SiO_2 molality of ~1.7 at 900 °C from the data of Anderson and Burnham (1965, their Fig. 4), corresponding to ~3 mol% SiO_2 in the fluid. Therefore, we consider the fluids in all our experiments to be essentially pure H_2O, while acknowledging that high quartz solubility (and by implication incongruent dissolution) is likely to exert an important control on tremolite stability at higher pressures and temperatures (>10 kbar/>800 °C).

Apparatus

Experiments at 700–930 °C and 0.25–2.0 kbar were performed using vertical cold-seal vessels (Nimonic 105), and those at 8 kbar used an internally heated gas vessel (Holloway, 1971). Ar was used as the pressure medium. Temperature and pressure were recorded at least once a day.

Temperatures of the experiments were measured using an external Pt/Pt13Rh thermocouple and are accurate to ±3 °C (Ford, 1972). Experimental temperatures in experiments were extremely stable: diurnal and long-term variations (2σ) were ±2 °C. The temperature profiles of the furnaces used in this study were measured at 1 atm and 600, 800, and 900 °C using an internal axial Pt/Pt13Rh thermocouple The isothermal hot-spot zone (3–5 cm long) of each furnace was located and the furnace positioned relative to the vessel so that the charge zone (2 cm long) coincided with the hot spot. Vessel-furnace pairs were kept the same throughout the study. The internally heated pressure vessel was calibrated for temperature at 8 kbar using NaCl melting (detection of latent heat) and is accurate to ± 5 °C. In all experiments, samples were heated isobarically to temperature. Samples were
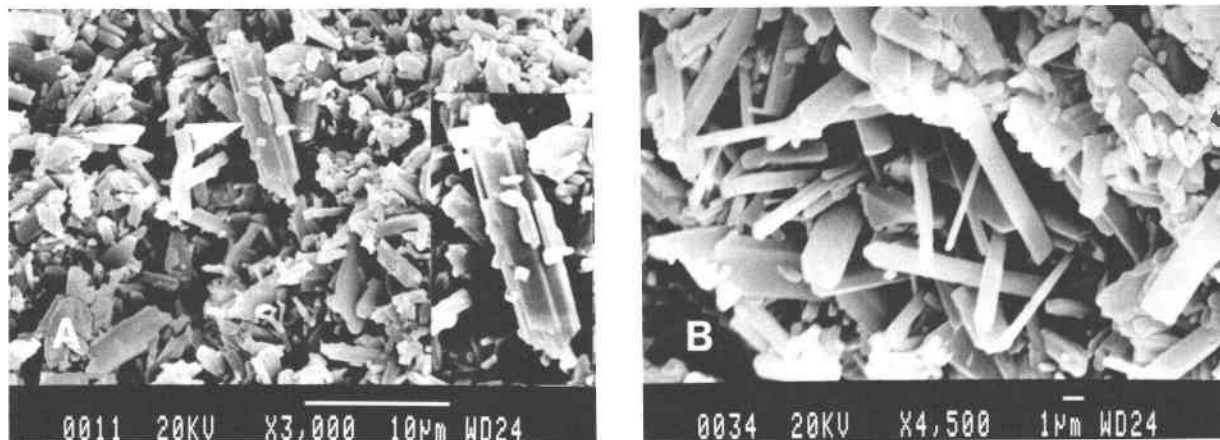
Fig. 1. Scanning electron micrographs of experimental products. (A) Tremolite growth (TD29: 0.6 kbar, 765 °C) in which most tremolite grains have retained their original prismatic faces and sharp outlines. Fretted terminations with protrusions can be seen on the large tremolite grain (arrowed and inset). (B) Typical product in which dehydration has occurred (TD13: 1 kbar, 831 °C). The view is mostly of pyroxene blades with well developed sharp faces; some small equant quartz grains can be also seen.

quenched in a jet of compressed air. All quenches were isobaric.

Pressures of the experiments were measured by a Heise gauge and are accurate to ±30 bars (±10 guaranteed accuracy, ±20 hysteresis), although they could be read to within 5 bars. Cold-seal pressure vessels were closed off from the gauge. As a check on the extent to which the gauge + line volume buffered pressure drops, dummy experiments were performed at 0.5–2 kbar and 650–900 °C in which the pressure vessel was either (1) open continuously to the gauge or (2) shut off from the gauge. By using segments of hollow filler rod it was possible to achieve pressure drops that were very close to those observed upon opening a vessel to the gauge. Pressure drops could thus be standardized so that they corresponded to the true vessel pressures, i.e., gauge + line volume = vessel volume.

The internally heated gas vessel was calibrated for pressure (Manganin gauge) using the freezing point of mercury at 298 K, and our quoted pressures are accurate to ±20 bars. Pressure was recorded by a Manganin gauge open continuously to the vessel.

Experimental product examination

Products were examined using the petrological microscope, powder X-ray diffraction (Ni-filtered $CuK\alpha_1$ radiation), scanning electron microscopy (SEM), and in some cases the electron microprobe. Reaction direction was inferred from changes in the intensities of certain strong diagnostic X-ray reflections. A change in intensity of at least 25% relative to starting material diffractograms was taken as evidence of reaction. Multiple repeated smears were made to check for any orientational biases, but the intensities of all reflections were reproducible to within 10% relative. Microprobe analysis was performed using a Camebax microprobe equipped with a backscattered

electron imaging facility; element standards were wollastonite and periclase; a current of 20 nA and accelerating potential of 20 kV were used. A number of products (including all those within and defining the experimental brackets) were examined by SEM to see if reaction textures could be recognized and correlated with the X-ray results. SEM could also show the presence of impurities below the detection limit of XRD (<5%) and indicate whether dissolution had occurred (Jenkins, 1987). An analytical facility was used that enabled phases to be identified and distinguished readily. Some representative electron micrographs are shown in Figure 1. Figure 1A is from an experiment at 0.6 kbar/765 °C (TD29) in which tremolite grew (X-rays). This view is dominated by tremolite grains that have retained their original prismatic faces and sharp outlines. The relatively large grain (arrowed and inset) shows clear ledges and irregular sharp protruding terminations, the latter giving a "fretted" appearance. This texture is the same as that interpreted by Jenkins (1987, his Fig. 3b) to indicate tremolite growth. The fretted habit is typical of experiments in which tremolite grew. Other tremolite grains commonly show distinct en-echelon growth ledges. In all cases the SEM observations are consistent with the X-ray results. Evidently, the 25% XRD criterion is good enough to give unequivocal microtextures. We did not observe tremolite with smooth rounded edges, such as are characteristic of partially dissolved and recrystallized cleavage fragments (see Jenkins, 1987, his Fig. 3a), nor did we observe any impurities in grain mounts (RI oils) or SEM samples.

THERMODYNAMIC ANALYSIS

We now give details of our thermodynamic treatment of the phase equilibrium data. For internal consistency we have chosen a single thermodynamic dataset Thermocalc (Holland and Powell, 1990). This dataset was

TABLE 3. Experimental results for the reaction Tr = 2Di + 1.5En + β-Qz + H₂O

Experiment	P (kbar)*	T (°C)	Duration (h)	85Tr**	85Prod**	Direction†
TD1	0.241	700	606	Tr‡	Tr	H
TD2	0.245	713	606	Tr	Tr + Pr	H
TD3§	0.244	723	557	Tr	Tr + Pr	H
TD7	0.237	735	746	Tr + Pr	Tr + Pr	N
TD4	0.240	740	556	Tr + Pr	Tr + Pr	N
TD8	0.222	748	746	Tr + Pr	Tr + Pr	N
TD5§	0.225	760	556	Tr + Pr	Pr + ?Tr	D
TD6	0.231	780	555	Pr	Pr	D
TD28	0.616	758	475	Tr	Tr + ?Pr	H
TD29§	0.609	765	474	Tr	Tr + Pr	H
TD34	0.598	778	668	Tr + Pr	Tr + Pr	N
TD30§	0.604	785	474	Tr + Pr	Pr + ?Tr	D
TD31	0.611	800	439	Tr + Pr	Pr	D
TD32	0.627	820	440	Pr	Pr	D
TD33	0.596	839	437	Pr	Pr	D
TD9	0.998	780	500	Tr	Tr	H
TD10	1.014	802	501	Tr	Tr + ?Pr	H
TD11§	1.000	812	503	Tr	Tr + Pr	H
TD15	1.007	818	690	Tr + Pr	Tr + Pr	N
TD12	0.989	824	503	Tr + Pr	Tr + Pr	N
TD13§	0.996	831	505	Pr + ?Tr	Pr	D
TD14	1.010	850	506	Pr	Pr	D
TD22§	1.487	828	413	Tr	Tr	H
TD23	1.472	834	389	Tr + ?Pr	Tr + Pr	H
TD24	1.476	843	389	Tr + Pr	Tr + Pr	N
TD27	1.419	845	629	Tr + Pr	Tr + Pr	N
TD25§	1.477	852	388	Pr	Pr	D
TD26	1.473	880	386	Pr	Pr	D
TD16	1.974	820	454	Tr	Tr	H
TD17	1.986	835	455	Tr	Tr	H
TD18§	1.990	842	433	Tr	Tr + ?Pr	H
TD19§	1.982	855	433	Tr + Pr	Pr + ?Tr	D
TD20	1.985	880	430	Pr	Pr	D
TD21	1.956	901	428	Pr	Pr	D
TD35§	8.020–8.060	911	120	Tr	Tr	H
TD36§	7.960–7.990	931	143	Pr	Pr	D

* The given pressures are the mean for each experiment (see text).
** Starting materials (mineral mixes).
† Interpretation of reaction direction: H = hydration (tremolite growth), D = dehydration, N = no reaction.
‡ Experimental products: Tr = tremolite, Pr = dehydration products.
§ Experiment defining a bracket limit.

chosen over that of Berman et al. (1985) because it enables the derivation of uncertainties of enthalpies to be extracted.

Six reversed experimental brackets were obtained for the reaction Tr = 2Di + 1.5En + β-Qz + H₂O. Data for all experiments are given in Table 3. Experiments lasted 120–746 h. These six brackets were used to derive enthalpy and entropy data for tremolite as follows. At each point along the univariant reaction boundary, the following equilibrium relation holds:

$$\Delta G_r = 0 = \Delta H_r^0 - T\Delta S_r^0 + \int_{298}^T \Delta C_P \, dT$$

$$- T \int_{298}^T \Delta C_P/T \, dT + \int_{1\,bar}^P \Delta V_s \, dP$$

$$+ nRT \ln f_{H_2O} + RT \ln K_s. \quad (5)$$

When expansivities and compressibilities are available and $P \gg 1$ bar, then Equation 5 can be expanded thus:

$$0 = \Delta H_r^0 - T\Delta S_r^0 + \int_{298}^T \Delta C_P \, dT - T \int_{298}^T \Delta C_P/T \, dT$$

$$+ P\Delta V_s^0 + P\Delta(\alpha V)_s(T\text{-}298) - \frac{P^2\Delta(\beta V)}{2}$$

$$+ nRT \ln f_{H_2O} + RT \ln K_s. \quad (6)$$

Rearranging Equation 5 gives another having a more obvious linear form:

$$T\Delta S_r^0 - \Delta H_r^0 = \int_{298}^T \Delta C_P \, dT - T \int_{298}^T \Delta C_P/T \, dT$$

$$+ \int_{1\,bar}^P \Delta V \, dP + nRT \ln f_{H_2O}$$

$$+ RT \ln K_s. \quad (7)$$

The right hand side of Equation 7 is combined into a single term here referred to as G'. Note that this is not the same as the G' of Jenkins (1983, 1984). By plotting
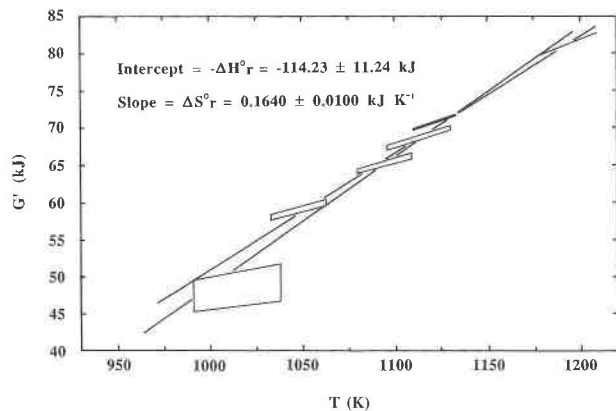
Fig. 2. Plot of G' against absolute temperature. Lines of maximum and minimum slope through all quadrilaterals define the minimum-maximum uncertainties on ΔH_r^0 and ΔS_r^0. See text.

G' against absolute temperature, values for $-\Delta H_r^0$ and ΔS_r^0 are obtained as the intercept and slope, respectively.

Water fugacities were taken from Thermocalc and are correct to within ± 0.1 kJ. This uncertainty amounts to < 1 °C in the location of the tremolite dehydration reaction. The uncertainty on our 8 kbar data arising from the Thermocalc fit is $< \pm 0.1$ kJ. With regard to the equilibrium-constant term, K_s, electron microprobe data for amphiboles and pyroxenes from the highest- and lowest-temperature experimental brackets indicate that, within analytical error, these have end-member compositions. Hence, $K_s = 1$ in all our calculations.

The Thermocalc data used in our calculations are given in Table 4. Values for f_{H_2O} and G' are given with the pressures and temperatures of the six experimental brackets (expanded by uncertainties in pressure of ± 0.02–0.03 kbar and temperature of $\pm$ 5°C) in Table 5. A plot of G' against absolute temperature is shown in Figure 2. The limits of the bracket data give rise to six quadrilaterals. Lines of maximum and minimum slope passing through all quadrilaterals define an envelope within which the univariant curve must lie. Maximal uncertainties ($>2\sigma$) are derived from the two limiting slopes: $\Delta H_r^0 = 114.23 \pm 11.24$ kJ, $\Delta S_r^0 = 0.16400 \pm 0.0100$ kJ/K. The correlation coefficient relating ΔH_r^0 and ΔS_r^0 is 0.985. These data were used to calculate the position of the tremolite dehydration reaction: Figure 3 shows the position defined by the above uncertainties, along with our experimental brackets (expanded by experimental uncertainties). With respect to a mean line (not shown in Fig. 3), the reaction is located to within $\pm$ 10 °C by the experimental data. Enthalpy and entropy data for tremolite were calculated from ΔH_r^0 and ΔS_r^0 as follows:

$$\Delta H_f^0(Tr) = \sum(\Delta H_f^0(2Di, 1.5En, \beta\text{-}Qz, H_2O)) - \Delta H_r^0$$

$$= -12299.48 \pm 14.84 \text{ kJ/mol} \qquad (8)$$

$$S^0(Tr) = \sum S^0(2Di, 1.5En, \beta\text{-}Qz, H_2O) - \Delta S_r^0$$

$$= 0.5525 \pm 0.0010 \text{ kJ/mol·K}. \qquad (9)$$
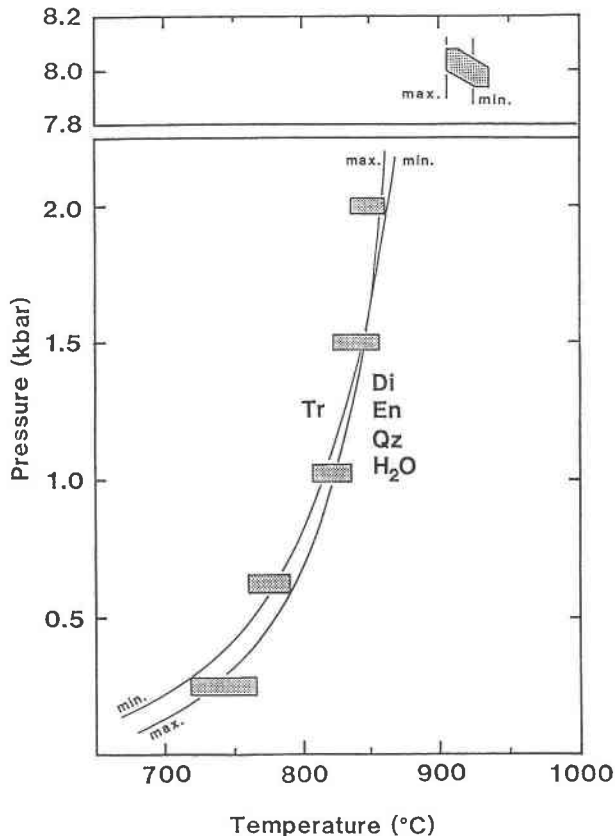
Fig. 3. Experimental brackets for the reaction Tr = 2Di + 1.5En + β-Qz + H_2O. Also shown is the minimum-maximum envelope calculated from the minimum-maximum slope data of the G' against T plot.

The uncertainty on $\Delta H_f^0(Tr)$ is 2σ of the mean and is calculated from the uncertainties on the enthalpies of formation of diopside, orthoenstatite, β-quartz, and H_2O given in Table 4 and the uncertainty on ΔH_r^0 above. As Thermocalc does not give uncertainties on third-law entropies, the uncertainty on $S^0(Tr)$ is taken as the uncertainty on ΔS_r^0 above. These new phase equilibrium data for tremolite are discussed in the next section.

COMPARISONS WITH PUBLISHED THERMODYNAMIC DATA

A compilation of enthalpy and entropy data for tremolite, including our new values, is given in Table 6. There is excellent agreement between our phase equilibrium values and those of Thermocalc, and good agreement with the data of Berman et al. (1985). The value for $\Delta H_f^0(Tr)$ of Robie et al. (1978), obtained by integrating the C_P data of Robie and Stout (1963), is clearly discrepant. The calorimetrically derived value for $\Delta H_f^0(Tr)$ obtained by Kiseleva and Ogorodova (1984) deserves some discussion as there is a major difference between our value for $\Delta H_f^0(Tr)$ and theirs for a natural tremolite that is chemically identical to ours in terms of cation proportions but of unknown F content. To facilitate a direct, internally

TABLE 4. Thermodynamic data used in calculating tremolite equilibria

Phase	ΔH_f^0	$\sigma\Delta H_f^0$	S^0 ($\times10^{-3}$)	V^0	a	b ($\times10^{-5}$)	c	d	αV ($\times10^{-5}$)	βV ($\times10^{-3}$)
Tremolite	−12299.48*	7.42	552.50*	27.245*	1.2144	2.6528	−12363.0	−7.3885	84.5	36.0
Diopside	−3200.15	1.90	142.70	6.619	0.3145	0.0041	−2745.9	−2.0201	22.0	5.5
Orthoenstatite	−3089.38	2.08	132.50	6.262	0.3562	−0.2990	596.9	−3.1853	18.0	4.6
α-quartz	−910.80	0.74	41.50	2.269	0.0979	−0.3350	−636.2	−0.7740	8.0	5.9
β-quartz	−909.07	0.74	43.54	2.367	0.0979	−0.3350	−636.2	−0.7740	0.0	2.6
Forsterite	−2171.87	1.62	94.10	4.366	0.2349	0.1069	542.9	−1.9064	16.0	3.2
Talc	−5895.23	3.70	260.80	13.625	0.5343	3.7416	−8805.2	−2.1532	39.0	23.0
H_2O	−241.81	0.03	188.80	0.000	0.0401	0.8656	487.5	−0.2512	0.0	0.0

Note: Units are in kJ, K, and kbar. Numbers in parentheses are those by which the values in the column below must be multiplied.
* This study.

consistent comparison between the two studies, we have recalculated their ΔH_f^0(Tr) using their $\Delta H_{solution,973K}$ (Tr) = 388.65 kJ/mol and a calorimetric cycle based upon the reaction tremolite = 2 diopside + 2 periclase + 4 β-quartz + brucite. Although various other reactions could have been chosen, this one results in the smallest error on the derived $\Delta H_{solution}$(Tr). Solution calorimetric data for diopside (Weill et al., 1980), periclase (Davies and Navrotsky, 1981), β-quartz (Akaogi and Navrotsky, 1984), and brucite (Clemens et al., 1987) were used with the heat capacities from Thermocalc to calculate ΔH_f^0(Tr) as follows:

$$\Delta H_f^0(\text{Tr}) = \sum\Delta H_f(2\text{Di}, 2\text{Per}, 4\beta\text{-Qz}, \text{Bru})$$
$$+ \Delta H_{\text{solution,976K}}(\text{Tr}) + \int_{298}^{976}\Delta C_p\,dT. \quad (10)$$

From this we obtain a value for ΔH_f^0(Tr) of −12336.63 ± 13.94 kJ/mol. When uncertainties are considered, there is a minimum difference of 8.37 kJ. Interestingly, an anal-

ogous calculation for talc using a value $\Delta H_{solution,973K}$ (Tc) = 207.57 ± 3.49 kJ/mol taken from Kiseleva and Ogorodova (1984) gives ΔH_f^0(Tc) = −5923.57 ± 10.50 kJ/mol compared with a value of −5895.23 ± 7.40 kJ/mol derived from phase equilibria experiments (Thermocalc). The difference is comparable to that observed for tremolite. The crystal-chemical similarities between tremolite and talc (e.g., Thompson, 1981) suggest a genuine, possibly anomalous, calorimetric effect associated with dissolution of the talc-like elements of the tremolite structure in lead-borate flux. However, we should also point out that as Kiseleva and Ogorodova did not analyze for F, their value for $\Delta H_{solution}$ (Tr) may result from a significantly higher F content than ours. In fact, their value is slightly more endothermic than that obtained for synthetic end-member fluortremolite by Graham and Navrotsky (1986).

CALCULATION OF THE LIMITS OF TREMOLITE STABILITY IN CMSH

Our values for the enthalpy and entropy of tremolite derived from phase equilibrium experiments have been used to calculate revised limits of tremolite stability in the CMSH system to 30 kbar. These are shown in Figure 4. In the absence of any published uncertainties on the third-law entropies of diopside, orthoenstatite, forsterite, quartz, and H_2O and the lack of a systematic rationale for combining uncertainties in enthalpy and entropy, we

TABLE 5. Values of G' and f_{H_2O} for the experimental brackets

P (kbar)	T (°C)	f_{H_2O} (kbar)	G' (kJ)
0.202	718	0.151	45.34
0.286	718	0.261	49.66*
0.194	765	0.133	46.85
0.276	765	0.245	51.71
0.569	760	0.532	57.61
0.649	760	0.594	58.34
0.560	790	0.534	59.58**
0.648	790	0.596	60.48
0.949	807	0.838	63.82
1.051	807	0.912	64.34
0.939	836	0.847	65.93
1.053	836	0.935	66.57
1.426	823	1.204	67.10
1.548	823	1.296	67.49
1.423	857	1.236	69.80
1.531	857	1.321	70.18
1.940	837	1.623	69.67
2.040	837	1.705	69.89
1.917	860	1.639	71.53*
2.047	860	1.749	71.83
8.000	906	11.067	79.77
8.080	906	11.270	79.77**
7.940	936	11.102	82.65
8.010	936	11.284	82.65

* Value lying on the line of minimum slope in G' plot.
** Value lying on the line of maximum slope in G' plot.

TABLE 6. Compilation of enthalpy and entropy data for tremolite

Source	ΔH_f^0 (kJ/mol)	S^0 (kJ/mol·K)
Robie et al. (1978)	−12355.08 (17.32)*	0.54890** (0.0013)
Helgeson et al. (1978)	−12319.70	0.54890** (0.0013)
Berman et al. (1985)	−12311.30	0.55115
Holland and Powell (1990)	−12302.50 (14.12)	0.55000
Kiseleva and	−12347.53 (10.88)‡	—
Ogorodova (1984)†	−12336.63 (13.94)§	—
This study	−12300.47 (14.84)	0.55250 (0.0100)

* Uncertainties in brackets are 2σ.
** From Robie and Stout (1963); calorimetrically determined value.
† High temperature solution calorimetry. Their sample was a natural end-member tremolite (possible F) from a Karelian marble.
‡ Value given by Kiseleva and Ogorodova.
§ Value calculated using internally consistent data from Thermocalc and the heats of solution for diopside, periclase, brucite, and β-quartz specified in the text.
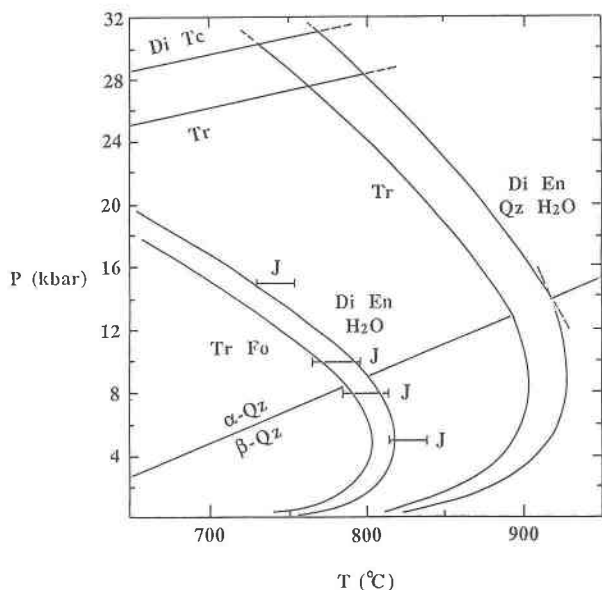
Fig. 4. Stability relations of tremolite in the CMSH system calculated from the thermodynamic data for the natural stoichiometric tremolite of this study. J = Jenkins (1983) for the reaction Tr + Fo = 2Di + 2.5En + H_2O, using synthetic tremolite. See text for discussion.

have chosen to use the method of calculating correlated uncertainties advocated by Powell and Holland (1985), in which only uncertainties in enthalpies are considered. The correlation matrices used were taken from Table 3a of Holland and Powell (1985).

Tr = 2Di + 1.5En + Qz + H_2O

The minimum-maximum derivation of the median reaction curve from the G' vs. T plot implies that at 853 °C the uncertainty in its location is zero. Clearly, this is unrealistic, and so we have calculated the uncertainty on the reaction in the same way as we have for Tr = 2Di + Tc and Tr + Fo = 2Di + 2.5En + H_2O, using only the uncertainties on the enthalpies of formation given in Thermocalc and our uncertainty on ΔH_f^0(Tr) ($\sigma = \pm 7.4$ kJ). This reaction is located to ± 6–12 °C and reaches a thermal maximum of 925 °C at about 8 kbar.

Tr + Fo = 2Di + 2.5En + H_2O
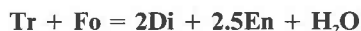
The location of this reaction calculated from our data is in good agreement with the experimental determination of Jenkins (1983) for synthetic "tremolite" (Tr-Mc amphibole?). We obtain an uncertainty in the position of this reaction of ± 10–13 °C over the pressure range 1–16 kbar. The position of the reaction is shown as an envelope in Figure 4.

Tr = 2Di + Tc

This is a "biopyribole" reaction (see Thompson 1981, his Table 3) in which amphibole disproportionates into pyroxene and sheet silicate. Our phase equilibrium data

for tremolite give the following thermodynamic quantities: $\Delta H_r^0 = 4.0 \pm 0.7$ kJ; $\Delta S_r^0 = -0.0063 \pm 0.0010$ kJ/K; $\Delta V_s^0 = -0.382$ kJ/kbar. Hence, there will be very small free-energy differentials at experimental temperatures to drive this reaction: ΔG_r^0 is only about 6.5 kJ. The limits set upon the location of this reaction by the uncertainty in the enthalpy of reaction are shown in Figure 4 and amount to ± 1.5 kbar. Combining this with our envelope for the SiO_2-saturated tremolite dehydration reaction gives the location of the invariant point as 27–31 kbar/730–800 °C. In passing we note that our $\pm 2\sigma$ envelope passes through the brackets defined by some recent experiments on this reaction by Jenkins et al. (unpublished data) using synthetic tremolite (T. Holland, personal communication).

CONCLUSION

We have presented new enthalpy and entropy data for a natural end-member tremolite determined from phase equilibrium experiments. The data are in excellent agreement with those of Thermocalc and agree well with those of Berman et al. (1985). The uncertainty on ΔH_f^0(Tr) ($2\sigma = \pm 14.84$ kJ) is comparable to that of Thermocalc (± 14.12 kJ) and is necessarily quite large because tremolite is a "non-anchor phase" (terminology of Holland and Powell, 1990) in the dataset and therefore incorporates uncertainties on substituent phases. Calculations made using the phase equilibrium values give plausible positions for some important tremolite equilibria in CMSH. The calculated position of the reaction Tr + Fo = 2Di + 2.5En + H_2O agrees well with the experimental data of Jenkins (1983). However, at $P > 10$ kbar and $T > 800$ °C it is likely that incongruent dissolution of tremolite will occur, stabilising Tr-Mc amphiboles and thereby displacing the univariant dehydration reaction $Tr_{ss} = Di + En + H_2O$ to temperatures above the end-member reaction. In this respect the calculated curve for end-member tremolite serves as a reference datum.

REFERENCES CITED

Akaogi, M., and Navrotsky, A. (1984) The quartz-coesite-stishovite transformations and calculation of phase diagrams. Physics of the Earth and Planetary Interiors, 36, 124–134.
Anderson, G.M., and Burnham, C.W. (1965) The solubility of quartz in supercritical water. American Journal of Science, 263, 499–511.
Berman, R.G., Brown, T.H., and Greenwood, H.J. (1985) An internally consistent thermodynamic database for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. Technical Record TR377. Scientific Document Distribution Office Atomic Energy Authority of Canada Ltd., Research Company, Chalk River, Ontario.

Boyd, F.R. (1959) Hydrothermal investigations of the amphiboles. In P.H. Abelson, Ed., Researches in geochemistry, p. 377–396. Wiley, New York.

Clemens, J.D., Circone, S., Navrotsky, A., McMillan, P.F., and Wall, V.J. (1987) Phlogopite: High-temperature solution calorimetry, thermodynamic properties, Al-Si and stacking disorder, and phase equilibria. Geochimica et Cosmochimica Acta, 51, 2569–2578.

Czank, M., and Liebau, F. (1980) Periodicity faults in chain silicates: A new type of planar lattice fault observed with high-resolution electron microscopy. Physics and Chemistry of Minerals, 6, 85–93.

Davies, P.K., and Navrotsky, A. (1981) Thermodynamics of solid solution formation in NiO-MgO and NiO-ZnO. Journal of Solid State Chemistry, 38, 264–276.

Eggert, R.G., and Kerrick, D.M. (1981) Metamorphic equilibria in the siliceous dolomite system: 6 kbar experimental data and geologic implications. Geochimica et Cosmochimica Acta, 45, 1039–1049.

Ford, C.E. (1972) Temperature distribution in "Tuttle" hydrothermal pressure vessels. Progress in experimental petrology. Natural Environmental Research Council Publication Series D, 2, 87–88.

Graham, C.M., and Navrotsky, A. (1986) Thermochemistry of the tremolite-edenite amphiboles using fluorine analogues, and applications to amphibole-plagioclase-quartz equilibria. Contributions to Mineralogy and Petrology, 93, 18–32.

Graham, C.M., Maresch, W.V., Welch, M.D., and Pawley, A.R. (1989) Experimental studies on amphiboles: A review with thermodynamic perspectives. European Journal of Mineralogy, 1, 63–83.

Helgeson, H.C., Delaney, J.M., Nesbitt, H.W., and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of minerals. American Journal of Science, 278A, 1–229.

Hewitt, D.A. (1975) Stability of the assemblage phlogopite-calcite-quartz. American Mineralogist 60, 391–397.

Holdaway, M.J., Dutrow, B.L., Borthwick, J., Shore, P., Harmon, R.S., and Hinton, R.W. (1986) H content of staurolite as determined by H extraction line and ion microprobe. American Mineralogist, 71, 1135–1141.

Holland, T.J.B., and Powell, R. (1985) An internally consistent thermodynamic dataset with uncertainties and correlations: 2. Data and results. Journal of Metamorphic Geology, 3, 232–370.

——— (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2. Journal of Metamorphic Geology, 8, 89–124.

Holland, T.J.B., and Richardson, S.W. (1979) Amphibole zonation in metabasites as a guide to the evolution of metamorphic conditions. Contributions to Mineralogy and Petrology, 70, 143–148.

Holloway, J.R. (1971) Internally-heated gas vessels. In G.C. Ulmer, Ed., Research techniques for high pressures and high temperatures. Springer-Verlag, New York.

Hoschek, G. (1973) Die reaktion Phlogopit + Calcit + Quarz = Tremolit + Alkalifeldspat + H_2O + CO_2. Contributions to Mineralogy and Petrology, 39, 231–237.

Jenkins, D.M. (1983) Stability and composition relations of calcic amphiboles in ultramafic rocks. Contributions to Mineralogy and Petrology, 83, 375–384.

——— (1984) Upper-pressure stability of synthetic margarite plus quartz. Contributions to Mineralogy and Petrology, 88, 332–339.

——— (1987) Synthesis and characterization of tremolite in the system H_2O-CaO-MgO-SiO_2. American Mineralogist, 72, 707–715.

Kiseleva, I.A., and Ogorodova, L.P. (1984) High-temperature solution calorimetry for determining the enthalpies of formation for hydroxyl-containing minerals such as talc and tremolite. Geochemistry International, 12, 36–46.

Maresch, W.V., and Czank, M. (1988) Crystal chemistry, growth kinetics and phase relationships of structurally disordered [Mn^{2+}, Mg] amphiboles Fortschritte der Mineralogie, 66, 69–121.

Metz, P. (1967) Experimentelle Bildung von Forsterit und Calcit aus Tremolit und Dolomit. Geochimica et Cosmochimica Acta, 31, 1517–1532.

——— (1976) Experimental investigation of the metamorphism of siliceous dolomites III—equilibrium data for the reaction: 1 Tremolite + 11 Dolomite = 8 Forsterite + 13 Calcite + 9 CO_2 + 11 H_2O for the total pressure of 3000 and 5000 bars. Contributions to Mineralogy and Petrology, 58, 137–148.

Powell, R., and Holland, T.J.B. (1985) An internally-consistent thermodynamic dataset with uncertainties and correlations: 1. Methods and a worked example. Journal of Metamorphic Geology, 3, 327–342.

Robie, R.A., and Stout, J.W. (1963) Heat capacity from 12–305 K, and entropy of talc and tremolite. Journal of Physical Chemistry, 67, 2252–2256.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and one atmosphere pressure and at higher temperatures. U.S. Geological Survey Bulletin 1259, 456.

Skippen, G., and McKinstry, B.W. (1985) Synthetic and natural tremolite in equilibrium with forsterite, enstatite, diopside and fluid. Contributions to Mineralogy and Petrology, 89, 256–262.

Slaughter, J., Kerrick, D.M., and Wall, V.J. (1975) Experimental and thermodynamic study of equilibria in the system CaO-MgO-SiO_2-H_2O-CO_2. American Journal of Science, 275, 143–165.

Thompson, J.B. (1981) An introduction to the mineralogy and petrology of the biopyriboles. In Mineralogical Society of America Reviews in Mineralogy, 9A, 141–188.

Weeks, W.F. (1956) Heats of formation of metamorphic minerals in the system CaO-MgO-SiO_2-H_2O and their petrological significance. Journal of Geology, 64, 456–472.

Weill, D.F., Hon, R., and Navrotsky, A. (1980) The igneous system $CaMgSi_2O_6 \cdot CaAl_2Si_2O_8NaAlSi_3O_8$: Variations on a classic theme by Bowen. In R.B. Hargreaves, Ed., Physics of magmatic processes, p. 49–92. Princeton University Press, Princeton, New Jersey.

Welch, M.D. (1987) Experimental studies of amphiboles in the system Na_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-SiF_4 and its subsystems, p. 101–136. Unpublished Ph.D. thesis, University of Edinburgh, Edinburgh, United Kingdom.

Yin, H.A., and Greenwood, H.J. (1983) Displacement of equilibria of OH-tremolite and F-tremolite solid solution. I Determination of the equilibrium P-T curve of OH-tremolite. Eos, 64, 347.

APPENDIX 1.

Glossary of thermodynamic terms used in this paper

P	Total pressure (kbar)
T	Temperature (°C, K)
V_s^0	Volume of a solid phase (kJ/kbar)
R	Universal gas constant (0.008314 kJ/K)
ΔH_f^0	Molar enthalpy of formation of a phase from the elements at 298.15 K and 1 bar (kJ/mol)
S^0	Molar third-law entropy of a phase at 298.15 K and 1 bar (kJ/mol·K)
ΔH_r^0	Enthalpy of reaction at 298.15 K and 1 bar (kJ)
ΔS_r^0	Entropy of reaction at 298.15 K and 1 bar (kJ/K)
C_P	Molar heat capacity of a phase at constant P (kJ/mol·K), formulated as a polynomial in temperature: $C_P = a + bT + cT^{-2} + dT^{1/2}$
αV	Product of volume and isobaric expansivity for a solid phase (kJ/K·kbar)
βV	Product of volume and isothermal compressibility for a solid phase (kJ/kbar)

List of formulae and abbreviations used in this paper

tremolite (Tr)	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Magnesiocummingtonite (Mc)	$Mg_7Si_8O_{22}(OH)_2$
Diopside (Di)	$CaMgSi_2O_6$
Orthoenstatite (En)	$Mg_2Si_2O_6$
Quartz (α, β) (Qz)	SiO_2
Forsterite (Fo)	Mg_2SiO_4
Talc (Tc)	$Mg_3Si_4O_{10}(OH)_2$