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# Thermodynamic properties of tremolite: A correction and some comments

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## ABSTRACT

Microprobe analysis of tremolite from "St. Gotthard," Switzerland, shows that it is close to end-member in composition (Ca = 1.97 apfu), and not hypercalcic (Ca = 2.16 apfu), as a previous wet-chemical analysis suggested. The latter formula, and a corresponding thermodynamic activity (0.67), were used in the experimental database for the extraction of an optimal set of thermodynamic properties for tremolite (Chernosky et al. 1998). We derive a revised enthalpy of formation of tremolite (–12307.9 kJ/mol) based on bracketing experiments for the breakdown reactions of tremolite and tremolite + forsterite, and the assumption of time-averaged effective equilibrium compositions of phases in the experimental charges. Mg-cummingtonite substitution in tremolite is accommodated during free-energy minimization calculations by allowing the stoichiometry of the standard-state reaction to vary with the changing bulk composition of the amphibole. The breakdown temperature of tremolite is lowered with increasing cummingtonite component. Our procedure also allows continuous variation in the equilibrium compositions and activities of pyroxene and amphibole phase-components with *P* and *T*.

## INTRODUCTION

We provide a microprobe analysis of tremolite from "St. Gotthard," Switzerland, a sample that has figured prominently in experimental phase-equilibrium studies of tremolite equilibria. Our analysis indicates a formula content for Ca of 1.97 atoms per formula unit (apfu), which is considerably different from the value of 2.16 apfu derived from a previous wet-chemical analysis (Slaughter et al. 1975), a number that is improbable for an otherwise pure tremolite. The wet-chemical analysis has been cited in many studies of tremolite phase equilibria, including a recent attempt to derive the thermodynamic properties of standard-state tremolite (Chernosky et al. 1998). In light of this problem, we provide a revised assessment of the thermodynamic properties of end-member tremolite.

To retrieve the properties of tremolite from high-*TP* bracketing experiments on tremolite equilibria, impurities in the tremolites used, including the Mg-cummingtonite component (Mg replacing Ca), have in the past been corrected for by using activities based on ideal on-site mixing models. Such corrections to the standard-state reaction free-energy probably suffice for equilibrium shifts caused by minor impurities such as F, Fe, Na, and Al in the starting tremolite. Here, we use a free-energy minimization approach employing "subMELTS" (Asimov and Ghiorso 1998), a subsolidus version of MELTS (Ghiorso and Sack 1995). The free-energy minimization technique accommodates the Mg-cummingtonite substitution by adjusting the standard-state Gibbs free-energy of reaction to correspond to the bulk composition of the reacting tremolite, hence to a varying reaction stoichiometry. A simple activity correction for added Mg, for example, $a_{\text{trem}} = (X_{\text{Ca}}^{\text{M4}})^2$, leaves the standard-state reaction stoichiometry unchanged and, on its own, increases the stability limit of tremolite. In our approach, the stability limit of tremolite decreases as Mg is introduced. This result is intuitively sensible because the breakdown temperature of Mg-cummingtonite (Ghiorso et al. 1995; Evans and Ghiorso 1995) is on the order of 100 °C lower than that of tremolite (~800 cf. 900 °C). Free-energy minimization also accommodates the *P*- and *T*-dependent variation in the activity coefficients of the participating phase-components, which in some cases depart significantly from unity as a consequence of wide miscibility gaps.

## ST. GOTTHARD TREMOLITE

A sample of tremolite from "St. Gotthard" has been used repeatedly in phase-equilibrium experiments (Slaughter et al. 1975; Eggert and Kerrick 1981; Skippen and McKinstry 1985; Chernosky and Berman 1988; Chernosky et al. 1998) designed to constrain the phase relations and thermodynamic properties of the amphibole end-member tremolite (Holland and Powell 1990; Gottschalk 1997; Chernosky et al. 1998). The same material was also used in high-temperature calorimetry (Krupka et al. 1985), but (fortunately) these authors did not correct the high-*T* heat capacity of tremolite for deviations from the ideal chemical composition. This sample appears never to have been analyzed with the electron microprobe. Instead, the results of a wet-chemical and emission spectrographic analysis conducted at Pennsylvania State University (Slaughter et al. 1975) have been cited, in these and other papers. This analysis showed that the tremolite was suitably poor in Ti, Al, Mn, Na, K, and F

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for use as starting material in experiments on the stability of end-member tremolite. However, relative to ideal tremolite, the derived formula: $Ca_{2.16}(Mg_{4.92}Fe_{0.03})(Si_{7.93}Al_{0.01})O_{22}(OH_{1.97}F_{0.03})$ shows excess Ca and deficient occupancies of the amphibole C (M1+M2+M3) and T sites. Although Ca on the A-site of calcic amphibole has been reported in synthetic fluor-edenite (Boschmann et al. 1994), synthetic fluor-pargasite (Oberti et al. 1995), and natural cannilloite (Hawthorne et al. 1996), in the present case only vacancies provide the charge balance for Ca on A. On crystal-chemical grounds the analysis is therefore suspect. For thermodynamic modeling of tremolite, amphibole compositions with more than 2 atoms of Ca pfu have required use of an activity model (e.g., Skippen and Carmichael 1977; Chernosky et al. 1998) containing the multiplier (3-Ca-Na-K). In the case of the St. Gotthard tremolite with the suspect analysis, this model leads to an activity of tremolite of 0.67 (Chernosky et al. 1998).

Microprobe analyses in the literature of tremolite from the dolomitic marbles of the "St. Gotthard" area, more specifically from Alpe Campolungo and Alpe Cadonighino, Ticino, Switzerland, do not show Ca apfu in excess of 2.0 (Mercolli 1980; Walther 1983). Furthermore, the cell dimensions of St. Gotthard tremolite, as measured by Krupka et al. (1985), are virtually identical to those of the Edinburgh University tremolite CG-1 (Welch and Pawley 1991; Yang and Evans 1996), which is very close to end-member in composition, with Ca apfu = 1.97–1.98 (Tables 1 and 2). The crystallographic comparison thus provides another reason to regard the original analysis of the St. Gotthard sample as suspect. In fact, a near-perfect tremolite formula can be derived from the original analysis if CaO alone is adjusted downward. However, in a powdered sample of the St. Gotthard tremolite provided by D. M. Kerrick to J. V. Chernosky and then to us, we find with the microprobe no evidence for calcite impurities, either as inclusions or separate grains.

After separating out the fines, we were able to prepare a polished mount of the St. Gotthard tremolite and locate 10 crystals large enough for successful microprobe analysis. The average of nine low-Al crystals is given in Table 2. The tenth crystal contained 0.5–0.6 wt% $Al_2O_3$. In our opinion, the average low-Al composition probably best represents the bulk composition of tremolite induced to react to pyroxene in the experiments, more aluminous compositions likely remaining unreacted. To see how frequent in the population were the more-aluminous grains, we analyzed for Al, Fe, Mg, and Ca in another 50 crystals; 13 of these had analysis totals low by up to 5% due to overlap on the epoxy mounting medium and these analyses were corrected upward. In Figure 1 it can be seen that few crystals have $Al_2O_3$ in excess of 0.2 wt%, and there is no correlation with FeO. The overall average (n = 60) for $Al_2O_3$ is 0.10 wt%, which is too small to have a detectable effect on reversal brackets; the potential stabilization provided by the substitution of Al for Mg, Na for □, and F for OH is on the order of 0.5 kJ (perhaps less because F is at the detection limit), which would provide only a 7 °C upward shift in the breakdown equilibrium. Our analysis shows that the St. Gotthard tremolite contains 1.5% cummingtonite component (Cm) in solid solution. Its composition is indistinguishable from the Edinburgh tremolite CG-1 (Table 2), leading us to speculate that the two samples might be from the same locality. The original analysis of the St. Gotthard tremolite is seriously in error only for CaO, but we are reluctant to argue for analytical error. If all oxide values are corrected for between 1.5 and 3% calcite impurity, they would be a good match for our microprobe analysis. Most important is the closeness of the sample to end-member tremolite, like tremolite CG-1, which after all makes it ideal for use in equilibrium and calorimetric experiments in the system CMSH.

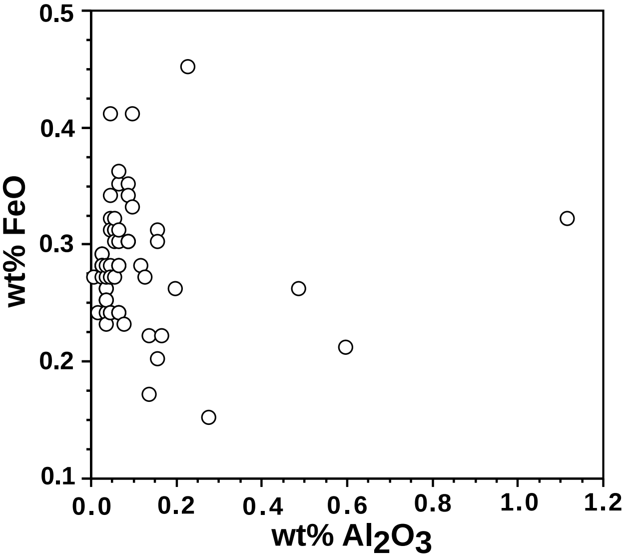

**FIGURE 1.** FeO vs. $Al_2O_3$ in 52 grains of St. Gotthard tremolite.

**TABLE 1.** Cell dimensions of tremolite used in phase-equilibrium experiments

| | *a* | *b* | *c* | β | *V* |
|---|---|---|---|---|---|
| St. Gotthard (1) | 9.838(1) | 18.049(2) | 5.2775(8) | 104.752(12) | 906.2 |
| St. Gotthard (2)* | 9.885 | 18.049 | 5.256 | 105.85 | 902.1 |
| CG-1 (3) | 9.8356(12) | 18.055(22) | 5.2785(6) | 104.782(9) | 906.4(2) |
| CG-1 (4) | 9.8385(4) | 18.0554(8) | 5.2778(4) | 104.751(5) | 906.6(1) |

*Note:* (1) Krupka et al. (1985), (2) Skippen and McKinstry (1985), (3) Yang and Evans (1996), single-crystal refinement, (4) Yang and Evans (1996), Rietveld powder method.
*The cell dimensions of Skippen and McKinstry for the St. Gotthard tremolite appear to be in error.

**TABLE 2.** Chemical compositions of tremolite used in phase-equilibrium experiments

| | St. Gotthard | | CG-1 |
|---|---|---|---|
| | (1) | (2) | (3) |
| $SiO_2$ | 58.2 | 59.06 (43)† | 59.19 |
| $TiO_2$ | <0.02 | 0.01 (01) | 0.01 |
| $Al_2O_3$ | 0.07 | 0.07 (03) | 0.04 |
| FeO | 0.27 | 0.29 (06) | 0.25 |
| MgO | 24.2 | 24.55 (31) | 24.74 |
| MnO | 0.02 | 0.02 (02) | 0.02 |
| CaO | 14.8 | 13.59 (09) | 13.63 |
| $Na_2O$ | <0.05 | 0.03 (01) | 0.05 |
| $K_2O$ | <0.05 | 0.01 (01) | 0.01 |
| $H_2O$* | 2.19 | 2.20 | 2.19 |
| F | 0.07 | 0.03 (02) | 0.06 |
| less O = F | 0.03 | 0.01 | 0.03 |
| Total | 99.8 | 99.84 | 100.16 |
| **Proportions of cations based on 23 oxygen atoms** | | | |
| Si | 7.93 | 8.004 | 7.997 |
| Ti | 0.00 | 0.001 | 0.001 |
| Al | 0.011 | 0.011 | 0.006 |
| Fe | 0.031 | 0.033 | 0.028 |
| Mg | 4.92 | 4.960 | 4.983 |
| Mn | 0.002 | 0.002 | 0.002 |
| Ca | 2.16 | 1.973 | 1.973 |
| Na | 0.01 | 0.008 | 0.013 |
| K | 0.00 | 0.002 | 0.002 |
| Sum | 15.064 | 14.994 | 15.005 |
| F | 0.03 | 0.013 | 0.025 |
| OH | 1.97 | 1.987 | 1.975 |

*Note:* (1) Slaughter et al. (1975), assuming zero $Fe_2O_3$ according to formula given, (2) new analysis, nine crystals, this work, (3) Yang and Evans (1996, Table 1).
* Calculated % $H_2O$.
† Standard deviation.

**TABLE 3.** Thermodynamic properties of end-member tremolite

$\Delta H^0_f$: –12307.9 kJ $S^0$: 549.5 J/K $V^0$: 27.312 J/bar
Reference state: 298 K and 1 bar
$C^0_P = 1229.36 - 64.019 \times 10^2\ T^{-1/2} - 320.899 \times 10^5\ T^{-2} + 420.881 \times 10^7\ T^{-3}$ (J/K), Berman (1988)

Volume: $V_{P,T}/V_{1,298} = 1 - 1.4763 \times 10^{-6} (P-1) + 8.9462 \times 10^{-12} (P-1)^2 + 24.374 \times 10^{-6} (T-298) + 98.338 \times 10^{-0} (T-298)^2$

## THERMODYNAMIC PROPERTIES OF TREMOLITE

If an activity much closer to unity is used for the St. Gotthard tremolite, then this will be reflected in the thermodynamic parameters extracted from experiments that used it as starting material, producing notably a more negative enthalpy of formation. However, for reasons discussed below, our analysis does not explicitly use the compositions of the amphibole and pyroxene starting materials. Also, because they are plentiful, we consider only bracketing experiments with bulk compositions that closely approximate the pure system CMSH. This paper is a commentary on problems that concern tremolite; it is not meant to supplant attempts to extract optimized, internally consistent data for tremolite from the *entire* data set of mineral phase equilibria (e.g., Gottschalk 1997; Holland and Powell 1998; Chernosky et al. 1998).

For molar volume we adopt the value of 27.312 J/bar recommended by Yang and Evans (1996). This is a small upward extrapolation to end-member tremolite from CG-1 tremolite; natural and synthetic tremolites tend to contain Mg-cummingtonite in solid solution, and the standard-state volume cannot be modeled on them without correction. For entropy we adopt a value of 549.5 J/K, which reflects the agreement that already exists, namely, a calorimetric value of 548.90 ± 1.3 J/K (Robie and Hemingway 1995), and values based on internally consistent evaluations of equilibrium experiments: 550 J/K (Holland and Powell 1998), 549.209 ± 0.539 J/K (Gottschalk 1997), and 549.86 J/K (Chernosky et al. 1998). Our heat capacity is after Krupka et al. (1985), as in Berman (1988). Compressibility is from Comodi et al. (1991), and expansivity from Sueno et al. (1973), as in Berman (1988). These data are listed in Table 3. The enthalpy of formation of tremolite remains as the parameter to be constrained by experimental phase-equilibrium experiments at high *T* and *P*.

The extensive body of available experimental data comprises tremolite breakdown reactions 1 and 2 at high *T* and reaction 3 at high *P*, and eight mixed-volatile $CO_2$-$H_2O$ reactions (Chernosky et al. 1998, Table 1) at temperatures below 650 °C, such as reaction 4. We consider only those experiments that used as starting material synthetic tremolite or one of the relatively pure natural tremolites St. Gotthard and CG-1.

$$\text{Tr} = 2\ \text{Di} + 3\ \text{En} + \text{Qtz} + H_2O \qquad (1)$$

$$\text{Tr} + \text{Fo} = 2\ \text{Di} + 5\ \text{En} + H_2O \qquad (2)$$

$$\text{Tr} = 2\ \text{Di} + \text{Tlc} \qquad (3)$$

$$\text{Tr} + 3\ \text{Cc} + 2\ \text{Qtz} = 5\ \text{Di} + H_2O + 3\ CO_2 \qquad (4)$$

Forty-six half-brackets have been determined for reaction 1 in experiments using synthetic tremolite (Boyd 1959; Gilbert and Troll 1974; Yin and Greenwood 1983; Jenkins et al. 1991) and natural tremolite CG-1 (Welch and Pawley 1991). High-resolution transmission electron microscopy showed that CG-1 is exceptionally free of chain-width errors and stacking faults, but this is not true of the synthetic tremolites (Ahn et al. 1991). Nevertheless, the half-brackets for reaction 1 are in overall good mutual agreement and tightly constrain the univariant curve (Fig. 2). We used subMELTS to determine an enthalpy of formation of tremolite that, with thermodynamic data for the other end-members from Berman (1988), produces a *PT*-curve with a minimal number of inconsistencies with half-brackets. SubMELTS includes the thermodynamic properties of quadrilateral pyroxenes (Sack and Ghiorso 1994) and our current model for the properties along the join tremolite–Mg-cummingtonite, based on a composition- ($X_{Fe}$, $X_{Mg}$, and $X_{Ca}$) and temperature-dependent ordering model and field constraints on solvus widths and tieline orientations for the entire amphibole quadrilateral (Ghiorso and Evans, in preparation).

We believe that the best approach in the fitting is to assume that the effective compositions of minerals in the phase-equilibrium experiments are those corresponding to equilibrium along the respective univariant curves, not those of the starting materials. This assumption differs from Chernosky et al. (1998), who allowed for the metastable growth of tremolite in experiments where the starting pyroxenes were end-member rather than equilibrium solvus compositions. We justify our assumption with the following observations.

Reaction 1 takes place in the laboratory at high *P* and *T* via dissolution and growth mechanisms, with as many as five independent reactions proceeding at different rates (Bozhilov

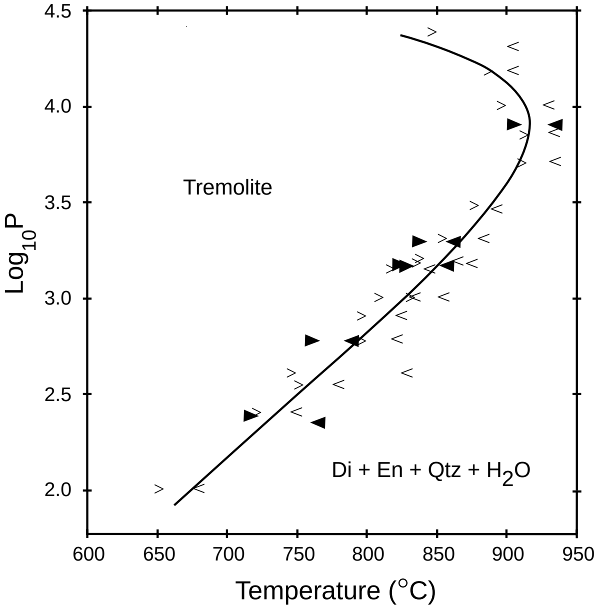

**FIGURE 2.** Reaction 1': critical experimental brackets and curve calculated with subMELTS. Open symbols, synthetic tremolite, from Boyd (1959), Gilbert and Troll (1974), Yin and Greenwood (1983), and Jenkins et al. (1991). Filled symbols, natural Edinburgh tremolite CG-1, from Welch and Pawley (1991).

1997). This observation suggests that the concentrations of species dissolved in the $H_2O$ fluid likely vary with time, and perhaps also with location in the charge. A consistent dependence of fluid composition on the solid-solution compositions of starting materials may never hold at all. Chernosky et al. (1998) argued that equilibrium solvus pyroxene compositions were unlikely to form early so as to control tremolite stability in all the experiments, that is, tremolite growth is faster than growth of new stable pyroxene compositions. This assumption (Chernosky et al. 1998) was supported because without it there were contradictions with several sets of 500–650 °C mixed-volatile experiments (Eggert and Kerrick 1981; Chernosky and Berman 1988) in which the St. Gotthard tremolite was used. With our revised composition for this tremolite, these contradictions are lessened or eliminated. Metastable growth of tremolite from pyroxenes of end-member composition implies that certain concentrations of Ca, Mg, and Si in the fluid should prevail throughout the experiment. These concentrations differ from those assumed to attend the reverse reaction, the dissolution of tremolite and growth of new (solvus) pyroxenes. We question whether this duality is likely in experiments that are identical in set-up except for small temperature differences.

Even when prepared very carefully and under kinetically favorable conditions, synthetic tremolite is variable in composition as well as crystal quality (Zimmerman et al. 1996; Bozhilov 1997). It is probably not justified to assume that the fraction of this tremolite that breaks down at high temperature in an equilibrium experiment is an average of the compositions and structural states of the starting tremolite; it will be biased toward those compositions and structural states that are less stable. However, the lack of serious disagreement in results for reaction 1 between runs with synthetic tremolite (average composition of ~$Tr_{90}Cm_{10}$, Jenkins et al. 1991) and natural tremolite CG-1 (~$Tr_{99}Cm_1$, with minor Fe, and F at the detection limit, Table 2) argues for a minor role for compositional and structural differences in the starting material. Certainly, the composition of *product* tremolite formed from synthetic pyroxenes, quartz, and $H_2O$ is likely to be independent of the composition of the *reactant* tremolite used (whether $Cm_{10}$ or $Cm_1$).

The compositions of product minerals have never been determined unambiguously in any of the phase-equilibrium experiments on tremolite because grain sizes are too small. Welch and Pawley (1991) claimed that electron microprobe analyses of tremolite and pyroxenes in run products showed, within analytical error, that they were end-member in composition, but it is not clear if new as opposed to starting material was analyzed. We favor the idea that many of the grain margins of growing and dissolving crystals at the end of each experiment might well reflect equilibrium compositions. We shall therefore extract the enthalpy of tremolite from the high-temperature reactions 1 and 2 under this assumption.

Equilibrium pyroxene and amphibole compositions can be determined using subMELTS. For reaction 1 at 5 kbar and 910 °C they are, in mol%: $Tr_{92}Cm_8$, $Di_{91}En_9$, $En_{97.5}Di_{2.5}$ (Fig. 3). Our tremolite contains less Cm than that calculated by Will and Powell (1992) because we find a strong dependence on Fe/Mg of the amphibole solvus width close to the Mg-end of the amphibole quadrilateral. Reaction 1 is more accurately expressed as:

$$(1-x)\ Tr + x\ Cm = 2\ (1-x)\ Di + (3 + 4x)\ En + Qtz + H_2O \qquad (1')$$

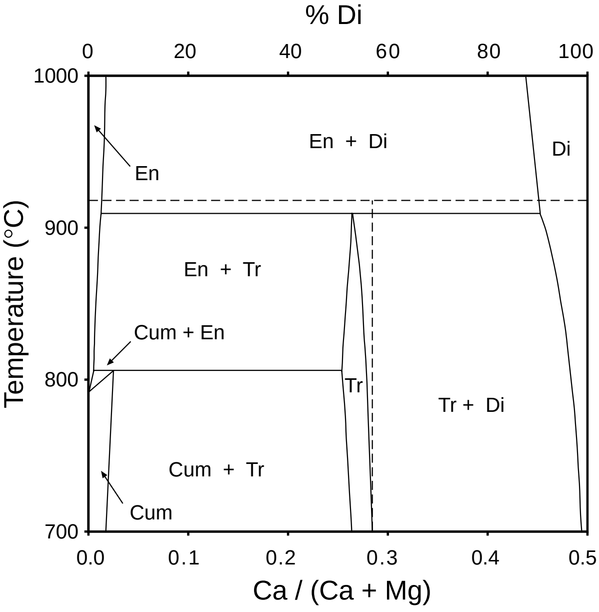

**FIGURE 3.** Calculated *T-X* projection at 5 kbar for equilibria among tremolite, diopside, enstatite, Mg-cummingtonite, quartz, and $H_2O$. Dashed lines: phase boundaries for standard-state compositions. Below 770 °C, Mg-cummingtonite is metastable with respect to talc.

Reaction 1' shows that increase in the amount (x) of Mg-cummingtonite (Cm) in solution in the tremolite greatly increases the stoichiometric amount of enstatite. The Di and En are contained in clinopyroxene and orthopyroxene as diopside and clinoenstatite, and orthodiopside and enstatite components, respectively. The standard-state Gibbs energy of reaction 1' is: (1–x) $\Delta G^0_{(1)}$ + x $\Delta G^0_{(5)}$ where reaction 5 is:

$$\mathrm{Cm = 7\ En + Qtz + H_2O} \qquad (5)$$

At 5 kbar the computed stable equilibrium curve for 1' is 9 °C lower than reaction curve 1 for phases in their standard states (Fig. 3). This downward shift represents the combined effect of the chemical potentials of all six pyroxene and amphibole phase-components, and the change in $\Delta G^0$ from reaction 1 to reaction 1'. Assuming an experimental temperature uncertainty of ±10 °C, our fit through the half-brackets (Fig. 2) misses three of them; but only one half-bracket is violated (24 kbar, Gilbert and Troll 1974) if the uncertainty is extended to ±13 °C. Our curve, plotted as log $P$ vs. $T$ to aid visualization, corresponds to a heat of formation of tremolite at 298 K and 1 bar of –12307.9 kJ/mol (Table 3). Violations of half-brackets increase by two or more if we displace our curve by 10 °C upward or downward. This suggests a fit uncertainty in $\Delta H_f$ of tremolite of less than 0.8 kJ/mol. The use by Jenkins et al. (1991) of approximately solvus pyroxene compositions ($\mathrm{Di_{95}}$ and $\mathrm{En_{99}}$) appears to have had no detectable effect on the results when compared with the other studies that used end-member pyroxene compositions.

When the enthalpy of tremolite derived from reaction 1' is applied to the calculation of reaction 2, also with subMELTS, we have reason to expect good agreement with the experimental brackets; activity-induced shifts from standard-state equilibrium for reactions 1' and 2 are similar, and the thermodynamics of the coupling reaction 2–1: Fo + Qtz = 2 En are very well known. Indeed, our curve for reaction 2 fits the experiments by Jenkins (1983) using synthetic tremolite and solvus pyroxene compositions ($\mathrm{Di_{90}}$ and $\mathrm{En_{97}}$) very well (Fig. 4). This agreement argues against bias in the experimental results arising from differences in incongruent solution of the tremolite in silica-saturated and silica-undersaturated systems (Jenkins 1987; Graham et al. 1989).

However, growth of tremolite in runs conducted in three laboratories (Skippen and McKinstry 1985; Chernosky et al. 1998), using the St. Gotthard tremolite as starting material, is reported at least 30 °C above our curve (Fig. 4). This is in curious contrast with the agreement found in the case of reaction 1' between runs with synthetic and pure natural tremolite CG-1, which is virtually identical in composition to the St. Gotthard tremolite. The previous explanation for this difference (Chernosky et al. 1998) was based on a composition and corresponding activity (0.67) now known to be in error. The conditions of growth of *product* tremolite should be expected to be independent of the properties of the starting tremolite, and yet they are apparently not the same in the two types of experiment. Ahn et al. (1991) suggested that the crystal quality of seed tremolite could influence the quality of tremolite that grows on it; but we did not see this effect in reaction 1. Furthermore, the SEM photographs of Chernosky et al. (1998, Fig. 4) suggest independent nucleation and growth of tremolite in reaction 2.

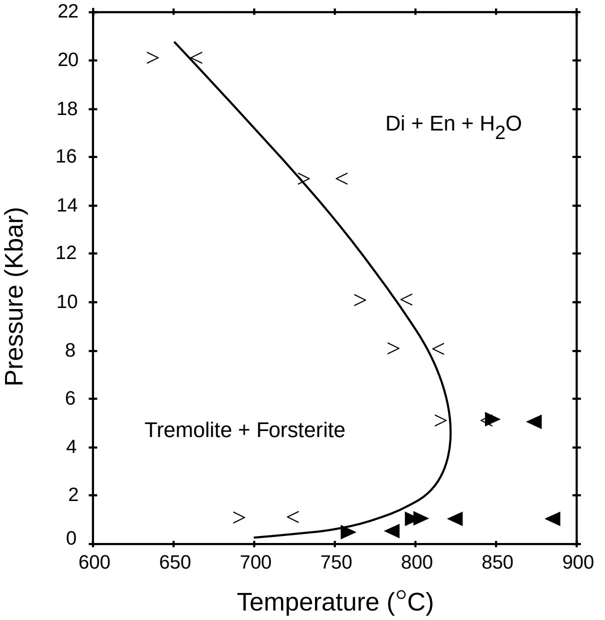

**FIGURE 4.** Reaction 2: critical experimental brackets and curve calculated with subMELTS. Open symbols, synthetic tremolite, from Jenkins (1983) and Skippen and McKinstry (1985). Filled symbols, natural St. Gotthard tremolite, 1 kbar from Skippen and McKinstry (1985) and 0.5 to 5 kbar from Chernosky et al. (1998).

A remote possibility is that pure tremolite (no Cm) grew metastably from end-member pyroxene reactants, essentially the standard-state reaction. From everything we know about synthetic tremolite (Jenkins 1987; Graham et al. 1989; Zimmerman et al. 1996; Bozhilov 1997), this does not happen. We should not be surprised to find that the St. Gotthard tremolite is more stable than synthetic tremolite. Depending on the care exercised during preparation, synthetic OH-tremolite is likely to possess additional free energy owing to its fine grain size and the presence of chain-width errors and dislocations (e.g., Ahn et al. 1991; Maresch et al. 1994). Some of the earlier experiments using synthetic tremolite appear to have suffered from these problems, for example, the one kilobar experiments (Fig. 4) of Skippen and McKinstry (1985) on reaction 2. However, the agreement in the case of reaction 1' between runs using synthetic and nearly pure natural tremolite suggests that the synthetic tremolite was not detectably destabilized by structural defects. We can only suggest at this time that the source of the discrepancy (Fig. 4) may lie in the techniques used in different laboratories. Not obvious to the casual reader is the difficulty in determining reaction direction at temperatures close to equilibrium in this sluggish system. Much experience of the investigator is required to use relative changes in peak heights in powder XRD patterns, the conventional technique, and to interpret SEM images of run products.

The low reaction-volume equilibrium 3 is a potential critical test of the correctness of the thermodynamic properties adopted for tremolite, diopside, and talc. Several half-brackets for reaction 3 using synthetic tremolite, diopside and talc were obtained by Jenkins et al. (1991). Unfortunately, the test is undermined by uncertainty in the volume data, particularly in the compressibility of talc (e.g., Bose and Ganguly 1995, Fig. 2). In Figure 5 we show for illustration calculated curves using two of the many expressions for the compressibility of talc in the literature (Pawley et al. 1995; Chernosky et al. 1998).

Further constraints on the thermodynamic properties of tremolite are possible if we consider experimental brackets obtained for reactions in $CO_2$-$H_2O$ fluid. These have mostly involved either synthetic tremolite or the St. Gotthard tremolite, together with synthetic calcite, dolomite, diopside, forsterite, talc, and quartz (Slaughter et al. 1975; Eggert and Kerrick 1981; Metz 1983; Puhan and Metz 1987; Chernosky and Berman 1988; Chernosky et al. 1998). As a class, these experiments require measurement not only of $P$ and $T$ but also the operative or final $X_{CO_2}$. Accurate data for $CO_2$ and $CO_2$-$H_2O$ mixtures are needed. Furthermore, the reaction entropies per mol tremolite of all the mixed-volatile reactions involving tremolite that have been studied (Chernosky et al. 1998, Table 1) are 2–10 times larger than reactions 1 and 2; since these differences are not matched by correspondingly tighter experimental brackets, the mixed volatile reactions do a less-effective job of constraining the thermodynamic properties of tremolite. They are complex experiments to run, and not surprisingly, there are a number of interlaboratory differences in final results. In light of these considerations, we make no attempt to refine further the enthalpy of tremolite obtained above from the many experiments on reaction 1'. In general, our calculated isobaric $T$-$X_{CO_2}$ curves agree well with the experiments. Reaction 4 provides a typical illustration (Fig. 6); minerals were assumed to have end-member compositions, as in Chernosky et al. (1998). Our calculated curve for reaction 4 is consistent with experiments using synthetic tremolite (Metz 1983), but some experiments using the St. Gotthard tremolite (Slaughter et al. 1975; Chernosky et al. 1998) suggest a greater stability for tremolite, as in the case of reaction 2. However, there are other mixed-volatile experiments that suggest the reverse (Eggert and Kerrick 1981). The interlaboratory differences are at most 40 °C. Ln$K$ vs. $1/T$ plots showing the results of many additional unpublished experiments on mixed-volatile equilibria involving tremolite are given in Gottschalk (1997); these studies used synthetic tremolite or natural tremolites other than the St. Gotthard tremolite.

## CONCLUDING REMARKS

A consistent set of thermodynamic data for tremolite can be extracted from a large number of phase-equilibrium experiments that used synthetic tremolite, under the assumption that equilibrium mineral compositions pertain to the curve being bracketed. Experiments have not convincingly demonstrated a larger stability field for natural, near-end-member tremolite as compared to that of synthetic tremolite, which is known generally to contain more crystal defects and to be finer in grainsize. The crucial bracketing-type experiment is unattainable: growth of a true natural tremolite analog in an experimental reaction under $P$-$T$-$X_{CO_2}$ conditions known to reduce the amount of synthetic tremolite in favor of pyroxene products. The stable breakdown of tremolite corresponds to a tremolite with as much as 8 mol% Mg-cummingtonite in solid solution, depending on $P$ and $T$, and to pyroxenes of solvus compositions. With minerals in their standard states, the breakdown reaction 1 (metastable) is 9 °C higher.

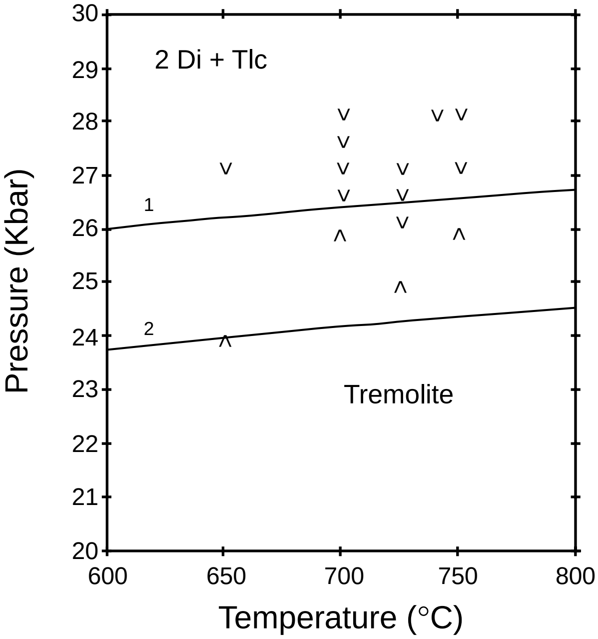

**FIGURE 5.** Reaction 3: experimental half-brackets for synthetic tremolite from Jenkins et al. (1991). Curve calculated using TWEEQU (Berman 1991) with end-member mineral compositions. Talc compressibility from 1: Chernosky et al. (1998), 2: Pawley et al. (1995).

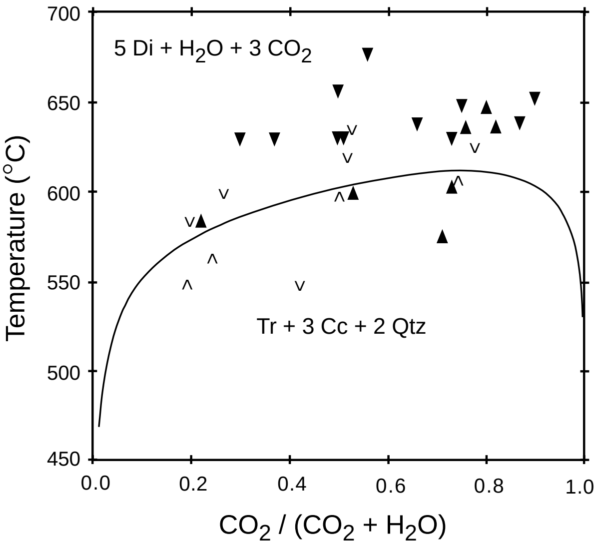

**FIGURE 6.** Reaction 4: experimental brackets at 5 kbar and curve calculated using TWEEQU (Berman 1991) with end-member mineral compositions, $H_2O$ data from Haar et al. (1984), $CO_2$ data from Mäder and Berman (1991), and $CO_2$-$H_2O$ mixing from Kerrick and Jacobs (1981). Open symbols, synthetic tremolite, from Metz (1983). Filled symbols, natural St. Gotthard tremolite, from Slaughter et al. (1975) and Chernosky et al. (1998).

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