

## Comparison of the high-temperature and high-pressure stability limits of synthetic and natural tremolite

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### ABSTRACT

Experiments were performed on two natural tremolite samples and compared with unpublished data of D. M. Jenkins, T.J.B. Holland, and A. K. Clare on synthetic tremolite to determine what, if any, differences exist between the upper-thermal and upper-pressure stability limits of synthetic and natural tremolite. The upper-thermal stability of natural tremolite, which was investigated with experimental reversals of the reaction tremolite = 2 diopside + 3 enstatite + quartz + H<sub>2</sub>O in the range of 1.5–7 kbar, is about 40 ± 20 °C higher than that of synthetic tremolite. Similarly, the upper-pressure stability of natural tremolite, investigated with the reaction tremolite = 2 diopside + talc, is about 1 kbar higher than that of synthetic tremolite. A thermodynamic analysis of the results for these two reactions indicates that one natural tremolite (TREM 12) has a Gibbs free energy that is 2.9 kJ/mol more negative than that of synthetic tremolite, whereas the other natural tremolite (TREM 8) is 0.4 kJ/mol more negative on a constant-entropy basis. Both values are much less than the 9.2-kJ/mol difference observed by Skippen and McKinstry (1985). Of the factors that can be quantified with some degree of accuracy at present, i.e., H<sub>2</sub>O fugacity, grain size, and composition, it appears that the compositional variation, in particular the F content, is sufficient to account for the higher stability and lower Gibbs free energy of natural tremolite. One need not invoke the presence of a high density of structural defects in synthetic tremolite to explain the observed differences. At least for hydrothermal processes, synthetic calcic amphiboles model closely the behavior of natural calcic amphiboles if differences in their compositions are considered.

### INTRODUCTION

Synthetic crystalline phases are often used in experimental studies of phase equilibria so that the experimentalist can exercise control over their composition and polymorphism. In most cases it is assumed that the results obtained with synthetic phases can be applied to nature if corrections are made for any compositional differences. Relatively little work has been done, however, to demonstrate whether differences in grain size or amount of structural defects between synthetic and natural phases could have a significant effect on phase equilibria. For example, calorimetric studies of quartz (Hemingway and Robie, 1977), tremolite (Nitkiewicz et al., 1984), and sillimanite (Salje, 1986) have shown that the enthalpy or heat capacity of a finely ground mineral can differ by 1–2% from that of its coarse-grained equivalent. The calculated effect of these heat-capacity differences on the position of a univariant boundary in *P-T* space can be quite large and would suggest that fine-grained synthetic materials, possibly with high defect densities, may give erroneous results. Experimentally observed differences in the position of a univariant boundary may in fact be much less if the rate of mineral recrystallization, involving both

grain coarsening and defect annealing, is faster than the rate of reaction among heterogeneous minerals. Direct experimental investigation of a given univariant reaction involving first a synthetic and then a natural mineral reactant should give a more realistic indication of the differences between synthetic and natural substances because all factors (e.g., recrystallization rate, reaction rate, surface energy, defect densities, etc.) are compared implicitly in this process.

Amphiboles may be especially susceptible to the influence of structural defects because planar, dislocation, and chain-width defects are fairly abundant in natural, particularly asbestiform, anthophyllite (Veblen, 1980), calcic amphiboles (Dorling and Zussman, 1987), and synthetic Mg-Mn amphiboles (Maresch and Czank, 1988). Skippen and McKinstry (1985) reported an increase of about 133 °C at 1 kbar in the location of the univariant boundary for the reaction

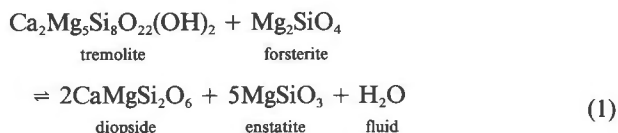


TABLE 1. Synthetic and natural phases used for investigating Reactions 2 and 3

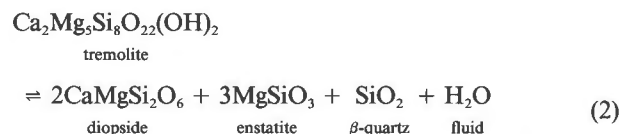
Phase (code no.)	Composition	Synthesis conditions				Starting mixtures**			
		T (°C)	P (kbar)	Form	t (h)	14	16	20	Re-action 3
Orthopyroxene (OPX 6-1)	(Mg <sub>0.99</sub> Ca <sub>0.01</sub> )MgSi <sub>2</sub> O <sub>6</sub>	930	6.3	oxides	54	X	X	X	0
Clinopyroxene (CPX 4-1)	(Ca <sub>0.98</sub> Mg <sub>1.02</sub> )MgSi <sub>2</sub> O <sub>6</sub>	925	5.9	oxides	95	X	X	0	0
Clinopyroxene (CPX 4-2)	(Ca <sub>0.98</sub> Mg <sub>1.02</sub> )MgSi <sub>2</sub> O <sub>6</sub>	930	5.2	oxides	191	0	0	X	0
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	1250	1 atm	glass	48	0	0	0	X
Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	700	17.5	oxides	26	0	0	0	X
Quartz	SiO <sub>2</sub>	790	2.0	oxide	16	X	X	X	0
Tremolite* (TREM 8)	(K <sub>0.01</sub> Na <sub>0.05</sub> )(Ca <sub>1.97</sub> Mg <sub>4.98</sub> Fe <sub>0.03</sub> <sup>2+</sup> Fe <sub>0.01</sub> <sup>3+</sup> Al <sub>0.06</sub> )Si <sub>7.94</sub> O <sub>22</sub> (OH <sub>1.85</sub> F <sub>0.09</sub> )					0	0	0	X
Tremolite* (TREM 12)	(K <sub>0.04</sub> Na <sub>0.16</sub> )(Ca <sub>1.89</sub> Mg <sub>4.93</sub> Fe <sub>0.07</sub> <sup>2+</sup> Al <sub>0.07</sub> )Si <sub>7.88</sub> O <sub>22</sub> (OH <sub>1.85</sub> F <sub>0.21</sub> )					X	X	X	0

\* Natural tremolite samples described in Jenkins (1987).

\*\* X = phase present in mixture, 0 = phase absent. The mixtures labeled 14, 16, and 20 refer to the starting mixtures for the experiments with the prefix 14, 16, or 20 in Table 2.

when natural tremolite was substituted for synthetic tremolite and with the H<sub>2</sub>O fugacity of the fluid controlled by the oxygen-buffering assemblage Ni + NiO. This observation casts considerable doubt on the relevance of experimental research involving synthetic calcic amphiboles to the phase equilibria of calcic amphiboles in nature.

In an attempt to corroborate the findings of Skippen and McKinsty (1985), two additional reactions were investigated using natural tremolite:



The results of these experiments are compared with those for the same reactions using synthetic tremolite (Jenkins, Holland, and Clare, unpublished data). Reactions 2 and 3 should reveal the differences between synthetic and natural tremolite better than Reaction 1 because the energetics of Reactions 2 and 3 are dictated by tremolite without the presence of any other reactant phase.

## EXPERIMENTAL METHODS

### Apparatus

Experiments performed below 8 kbar were conducted in internally heated gas vessels using Ar as the pressure medium. Pressures were monitored throughout each experiment with both a Bourdon-tube gauge and factory-calibrated manganin cell. The cited uncertainties in pressure measurement include both the accuracy of measurement ( $\pm 50$  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 po-

sitioned at either end of the capsule and the entire sample and thermocouple arrangement packed with ceramic wool in a cylindrical copper cup to minimize thermal gradients about the sample. Temperature uncertainties cited for the experiments include both the accuracy of the thermocouples ( $\pm 2$  °C) as well as any thermal gradients across the samples.

Experiments above 8 kbar were performed in piston-cylinder presses at the University of Chicago using 3/4-in.-diameter (1.905-cm-diameter) NaCl pressure media. Calibration of the sample pressure in this pressure medium was discussed in detail by Holland (1980) and Jenkins (1981). Sample pressures are believed to be accurate to  $\pm 300$  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. Individual experiments were performed by first pressurizing the NaCl assemblage at room temperature to several kbar 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 conform to either the hot or cold piston-out criteria described by Johannes et al. (1971) but has been shown to give results on the jadeite + quartz = albite calibration reaction that require virtually no additional "friction" correction (Holland, 1980; Jenkins, 1981).

### Starting materials and procedure

The phases and starting mixtures used for investigating Reactions 2 and 3 are in Table 1. All of the synthetic phases except for diopside were made hydrothermally in Au or Pt capsules. Diopside was made by annealing a glass of the composition CaMgSi<sub>2</sub>O<sub>6</sub> at about 1250 °C. The natural tremolite samples were described by Jenkins (1987) and were ground to an average grain size of about 60  $\mu\text{m}$  in the long dimension and 10  $\mu\text{m}$  in the shorter two dimensions. This is considerably larger than the grain size of synthetic tremolite, which, when made from oxides, has an average length of about 13  $\mu\text{m}$  and width of

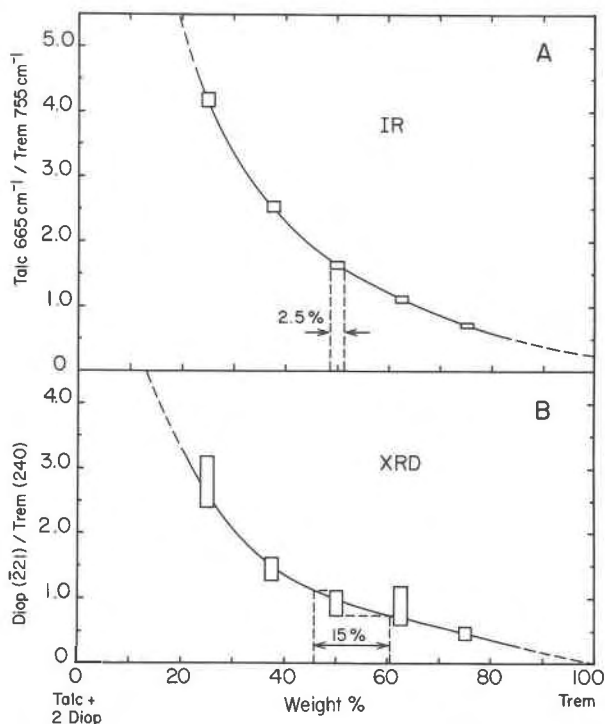


Fig. 1. (A) Variation in the peak-height ratio of the talc  $665\text{ cm}^{-1}$ /trem  $755\text{ cm}^{-1}$  IR absorption bands for several mechanical mixtures of natural talc, diopside, and tremolite prepared in accord with the stoichiometry of Reaction 3 in the text. (B) Variation in the peak-height ratio of the diop ( $\bar{2}21$ )/trem ( $240$ ) XRD peaks for the same mixtures. Abbreviations: Diop = diopside; Trem = tremolite.

$2\ \mu\text{m}$ . The starting mixtures for Reaction 2 consisted of reactants and products mixed in stoichiometric proportions while the starting mixture for Reaction 3 consisted of a 3:1 ratio of talc + diopside to tremolite. This ratio was chosen in order to make the intensities of the diopside ( $220$ ) and ( $\bar{2}21$ ) reflections about the same as those of tremolite ( $240$ ) and ( $151$ ) on an X-ray diffractometer pattern of the starting mixture. Notice in Table 1 that the pyroxene compositions used for studying Reaction 2 were those of coexisting orthopyroxene and clinopyroxene at about  $900\text{ }^{\circ}\text{C}$  and  $5\text{ kbar}$  in the system  $\text{CaO-MgO-SiO}_2$  (Lindsley et al., 1981). These compositions were chosen to minimize any reaction between the pyroxenes that was not related to Reaction 2.

Reactions 2 and 3 were investigated by sealing a portion of the appropriate starting mixture in platinum capsules with  $15\text{--}30\text{ wt}\%$   $\text{H}_2\text{O}$ . Each capsule was checked for leakage by examining the seams at the conclusion of an experiment and by weighing the capsule before and after each experiment.

#### Analytical methods

All experimental products were analyzed with a Norelco X-ray diffractometer using Ni-filtered Cu radiation.

The reaction direction for Reaction 2 could be readily determined from the relative peak heights of the X-ray reflections mentioned above. This was not the case for Reaction 3. Probably as a consequence of the much lower temperatures and smaller energetics (i.e.,  $\Delta S$  and  $\Delta H$ ), the extent of reaction for Reaction 3 was too small to discern via X-ray criteria within a few kbar of the univariant boundary. Greater sensitivity was achieved by examining the infrared (IR) spectra of the experimental products. Samples were prepared for IR spectroscopy by grinding about  $0.5\text{ mg}$  of the experimental products with  $360\text{ mg}$  of KBr and pressing this mixture under vacuum into a  $13\text{-mm}$ -diameter pellet. The IR spectra were collected in the linear absorption mode of either a Perkin-Elmer model 180 or 283B dual-beam spectrophotometer using a blank KBr pellet for reference. The spectra were obtained in the "lattice-stretching" range of  $800\text{--}550\text{ cm}^{-1}$  with a resolution of about  $1\text{ cm}^{-1}$ . Peak heights were measured from baselines drawn tangent to the background on either side of the peak. Figure 1A shows the variation in the peak-height ratios for the  $665\text{ cm}^{-1}$  to  $755\text{ cm}^{-1}$  vibrations of talc and tremolite, respectively, for five mechanical mixtures of natural talc, diopside, and tremolite prepared in accord with the stoichiometry of Reaction 3. Figure 1B shows the variation in the ratio of the diopside ( $\bar{2}21$ ) and tremolite ( $240$ ) X-ray diffraction (XRD) peak heights for the same five mechanical mixtures. The size of each symbol represents the precision (based on five measurements) in measuring a particular peak-height ratio. One can see from Figure 1 that the IR peak-height ratio is generally more sensitive than the XRD ratio at discerning the proportion of phases present in a given mixture. For example, the IR technique can indicate to within  $2.5\text{ wt}\%$  the true proportion of tremolite in a mixture consisting of  $50\text{ wt}\%$  tremolite, whereas the XRD technique can only distinguish within  $15\text{ wt}\%$ .

## RESULTS AND THERMODYNAMIC ANALYSIS

### Tremolite-enstatite-diopside-quartz- $\text{H}_2\text{O}$ equilibrium

The results of experiments performed in the range of  $1.5\text{--}7\text{ kbar}$  on Reaction 2 using natural tremolite (TREM 12 in Table 1) are in Table 2. Notice that most of the experiments were performed without any oxygen-buffering assemblage (group A), whereas the last four experiments were performed with an oxygen buffer (group B). The results in group A for natural tremolite are shown by the rectangular symbols in Figure 2 along with the unpublished results of Jenkins, Holland, and Clare for synthetic tremolite shown by the I-beam or bracket symbols. The symbols shown on Figure 2 include the maximum range of uncertainty in pressure and temperature measurement for each experiment, i.e., they have been "expanded" to include experimental uncertainties. One can readily see that natural tremolite has a higher thermal stability (minimum of about  $10\text{ }^{\circ}\text{C}$ ) than synthetic tremolite at any given pressure. This observation is in accord with the earlier study of Skippen and McKinstry (1985).

**TABLE 2.** Experimental results on Reaction 2 using natural tremolite (TREM 12)

Experiment no. (TREM)	T (°C)	P (kbar)	t (h)	Comments*
<b>Group A: Without an oxygen buffer</b>				
16-1	853(3)	1.52(5)	280	strong trem growth
16-13	868(3)	1.50(5)	112	trem growth
16-5	881(3)	1.48(5)	305	no apparent reaction
16-15	890(3)	1.50(5)	190	no apparent reaction
16-7	903(3)	1.56(5)	305	slight pyroxene growth
16-10	916(3)	1.50(5)	384	pyroxene growth
14-1	905(3)	2.9(1)	50	strong trem growth
14-6	917(3)	3.15(5)	289	trem growth
14-5	925(4)	2.98(7)	70	no apparent reaction
14-4	934(3)	3.04(7)	125	no apparent reaction
14-2	948(2)	3.05(5)	106	slight pyroxene growth
14-3	971(4)	3.00(5)	145	pyroxene growth
14-9	930(5)	5.05(10)	53	strong trem growth
14-12	940(3)	5.02(5)	306	trem growth
14-13	948(4)	4.98(5)	697	no apparent reaction
14-11	960(3)	5.10(5)	137	no apparent reaction
16-17	965(3)	5.25(5)	120	slight pyroxene growth
14-14	974(4)	5.08(5)	382	pyroxene growth
14-10	979(3)	5.10(5)	171	pyroxene growth
14-16	928(4)	7.1(2)	98	strong trem growth
16-3	940(6)	7.14(10)	26	trem growth
16-9	953(4)	7.0(25)	48	no apparent reaction
16-2	970(3)	7.1(15)	94	no apparent reaction
16-12	983(4)	7.15(15)	43	pyroxene growth
<b>Group B: With a Ni + NiO oxygen buffer</b>				
17-11**	865(6)	3.00(5)	58	trem growth
20-1	923(17)	3.01(5)	30	trem growth
20-2	939(7)	3.02(5)	29	no apparent reaction
20-5	950(5)	3.02(5)	20	slight pyroxene growth

Note: Experiments are arranged in order of increasing pressure. Group A experiments were not buffered, whereas group B were conducted in the presence of a Ni + NiO oxygen buffer. Uncertainty in the last digit is shown in parentheses.

\* Abbreviations as in Fig. 1.

\*\* This experiment involved synthetic tremolite made from the oxides, reacted for a period of 188 h at 740(5) °C and 2.0(1) kbar and then ground and reacted again for 214 h at 806(5) °C and 2.0(1) kbar. All other phases were the same as in mixtures 14 and 16 (Table 1).

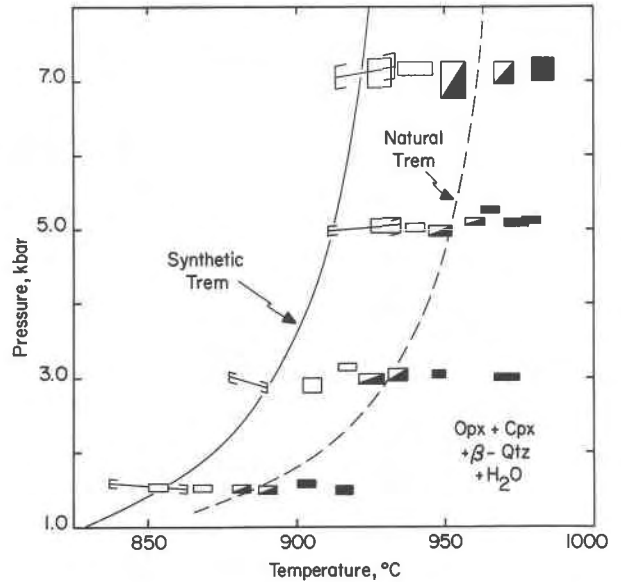


Fig. 2. Experimental results on the upper thermal stability of natural (dashed curve) and synthetic (solid curve) tremolite according to Reaction 2 in the text. Open rectangular symbols = tremolite growth; filled symbols = pyroxene growth; half-filled symbols = no apparent reaction; I-beam symbols = regions in which the univariant boundary for synthetic tremolite must lie according to the study of Jenkins et al. (1990). All symbols represent maximum uncertainty ranges in pressure and temperature. Calculation of univariant curves discussed in the text. Abbreviations: Cpx = clinopyroxene; Opx = orthopyroxene; Qtz = quartz; Trem = tremolite.

$$\text{where } \int_{P_0}^P \Delta V_T^{\text{solids}} dP \approx [\Delta V_{P_0, T_0} + \Delta(\alpha V)(T - T_0) - \Delta(\beta V)P/2]P.$$

However, the amount of increase in the thermal stability of natural tremolite (about 40 °C) is much less than the 133 °C reported by Skippen and McKinsty (1985).

A thermodynamic analysis of the data shown in Figure 2 was performed for the dual purpose of demonstrating internal consistency and for extracting Gibbs free-energy values for natural and synthetic tremolite to quantify their differences. A set of experimental data for a univariant reaction can be tested for internal consistency using the  $G'$  plot described by Day and Kumin (1980) and used by Jenkins (1983). Stated briefly, the condition that  $\Delta G$  of the reaction be zero at each  $P$ - $T$  point along a univariant boundary allows the following relationship to be written:

$$\begin{aligned} G' &= - \int_{T_0}^T \left( \int_{T_0}^T \frac{\Delta C_p}{T} dT \right) dT + \int_{P_0}^P \Delta V_T^{\text{solids}} dP \\ &\quad + nRT \ln f_{H_2O}^0 + RT \ln K \\ &= - \Delta G_{T_0, P_0}^0 + \Delta S_{T_0, P_0}^0 (T - T_0), \end{aligned}$$

The value of  $G'$  is calculated at the extreme  $P$  and  $T$  range of the experiments that bracket the location of the univariant curve using heat capacity ( $C_p$ ), volume ( $V$ ), expansivities ( $\alpha$ ), compressibilities ( $\beta$ ), and activity data (expressed in terms of the equilibrium constant,  $K$ ) for the phases participating in the reaction as well as data on the fugacity ( $f$ ) of  $H_2O$ . Internal consistency is demonstrated if a straight line can be drawn between the bracketing  $G'$  values on a plot of  $G'$  vs.  $(T - T_0)$ . The slope and intercept of this line are the  $\Delta S_{r, T_0, P_0}$  and  $-\Delta G_{r, T_0, P_0}$  values of the reaction, respectively.

Numerical evaluation of  $G'$  was performed in the following manner. Heat-capacity expressions for all of the phases as well as the volumes, expansivities, and compressibilities of the solid phases were those of Powell and Holland (1988). Fugacity data for  $H_2O$  were read or interpolated from the tables of Burnham et al. (1969) at pressures below 1.5 kbar, instead of being calculated from the equation for  $RT \ln f_{H_2O}$  given by Powell and Holland (1985), because the equation deviates strongly from the

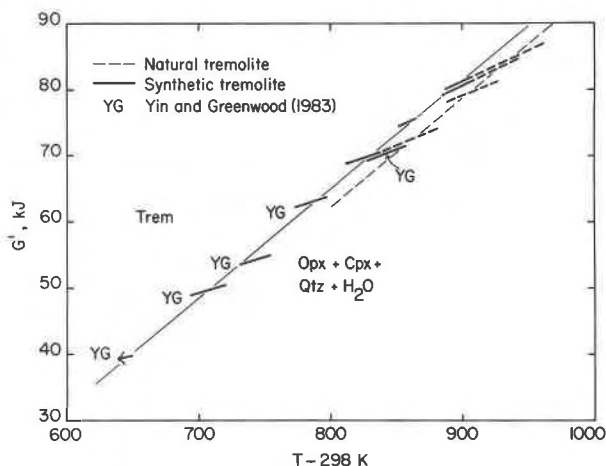


Fig. 3. Internal consistency analysis of the experimental data for Reaction 2 involving natural (dashed lines) and synthetic (solid lines) tremolite according to the  $G'$  technique described in the text. Short (thick) solid lines labeled YG are based on data from Yin and Greenwood (1983). Unlabeled short solid lines are from Jenkins et al. (1990). Unlabeled short (thick) dashed lines are from this study. All  $G'$  values were calculated with the maximum range of pressure and temperature uncertainties included. Abbreviations as in Fig. 2.

tabulated fugacity data in the pressure range of 1 kbar and below. The value of the equilibrium constant ( $K$ ) is assumed to be unity for several reasons. First, the compositions of the solid and fluid phases do not vary much, if at all, over the limited pressure and temperature range of the experiments for Reaction 2, and any compositional effects on the  $\Delta G_r$  of the reaction are essentially constant. By assuming  $K$  is unity, one forces any differences between natural and synthetic tremolite to be expressed by the differences in their derived values of  $\Delta G_r$ . Probable sources for these differences (i.e., composition, grain size, etc.) can then be sought for systematically. Second, well-documented activity vs. composition relationships are simply not available for calcic amphiboles.

Values of  $G'$  were determined for the experiments involving natural tremolite that bracket the univariant boundary for Reaction 2 [listed in Table 2 (group A)]. The extreme range of  $G'$  values, calculated by using the maximum pressure and temperature uncertainties, for each bracket plot as the four thick, short dashed lines (rather than rectangles) on the scale of the diagram in Figure 3. Internal consistency is demonstrated if at least one straight line can be drawn through each of the brackets, as is shown by the long, thin dashed line in Figure 3. Also shown in Figure 3 is an analysis of the experimental data for Reaction 2 involving synthetic tremolite that was reported by Yin and Greenwood (1983) and Yin (1988, personal communication) for the pressure range of 0.1 to 1.4 kbar and by Jenkins, Holland, and Clare (unpublished data) for the range of 1.5 to 7 kbar. The  $G'$  values for the

TABLE 3. Experimental results on Reaction 3 using natural tremolite (TREM 8)

Experiment no. (TR)	$T$ ( $^{\circ}\text{C}$ )	$P$ (kbar)	$t$ (h)	Comments*
22	725(5)	25.0(3)	48	trem growth
24	725(5)	26.0(3)	72	trem growth
28	725(5)	26.5(3)	72	trem growth
21	750(5)	26.0(3)	96	trem growth
19	750(5)	27.0(3)	27	trem growth
20	750(5)	28.0(3)	24	talc + diop growth

Note: Experiments are arranged in order of increasing temperature. Uncertainty in the last digit is shown in parentheses.  
\* Abbreviations as in Fig. 1.

experiments involving synthetic tremolite were calculated using the same data and method as for the experiments involving natural tremolite so that the two data sets can be compared directly. Notice that the greater temperature and pressure range for synthetic tremolite experiments places a much greater restriction on the choice of lines that can be drawn through the bracketing  $G'$  values (thick, short solid lines) in Figure 3. Indeed, it is not possible to draw one line through all of the experimental brackets, indicating a lack of internal consistency between the two sets of experiments for synthetic tremolite. With the exception of the highest temperature bracket of Yin and Greenwood (1983), a straight line can be drawn through the remaining  $7\frac{1}{2}$  brackets with slopes ranging between 164.59 and 166.60 J/K. The long solid line has the intermediate slope of 165.60 J/K and the associated intercept of  $-67.46$  kJ ( $= -\Delta G_{r,298\text{K},1\text{ bar}}^0$  of reaction). By forcing the reactions involving synthetic and natural tremolite to have the same  $\Delta S_{r,298\text{K},1\text{ bar}}^0$  of 165.60 J/K, one can derive the extreme range of  $\Delta G_r^0$  values from the intercepts of the two most widely spaced lines that can be drawn with this slope through all four natural tremolite brackets. The long dashed line in Figure 3 for the natural tremolite reaction data is drawn with an intercept of  $-70.39$  kJ which is intermediate between the extreme values of  $-69.24$  and  $-71.54$  kJ.

The experimental results and the thermodynamic analysis for Reaction 2 indicate that natural tremolite (TREM 12 in Table 1) is approximately  $40^{\circ}\text{C}$  more stable than synthetic tremolite which, on a constant-entropy basis, amounts to a difference of about  $-2.9 \pm 1.1$  kJ/mol in their  $\Delta G_r$  at 298 K and 1 bar. The univariant curves drawn in Figure 2 were calculated by reversing the thermodynamic analysis procedure described above and solving for  $P$  and  $T$  for a given  $\Delta S_{r,T_0,P_0}$  and  $\Delta G_{r,T_0,P_0}^0$ . Both curves were calculated for a  $\Delta S_{r,298\text{K},1\text{ bar}}^0$  of 165.60 J/K and a  $\Delta G_{r,298\text{K},1\text{ bar}}^0$  of 67.46 kJ (solid curve) or 70.39 kJ (dashed curve).

#### Tremolite-talc-diopside equilibrium

The results of experiments performed on Reaction 3 in the pressure range of 25–28 kbar and involving natural

tremolite (TREM 8 in Table 1) are listed in Table 3 and shown in Figure 4A. As seen in Figure 4A, the univariant boundary has only been bracketed at 750 °C; however, data at 725 °C indicate that the boundary must lie above 26.5 kbar. For comparison, only those experiments by Jenkins, Holland, and Clare (unpublished data) involving synthetic tremolite and the same diopside and talc as used in Figure 4A are shown in Figure 4B. Considering the pressure uncertainties associated with the experiments, there could be as little as 0- and as much as 2.6-kbar difference in the upper-pressure stabilities of natural and synthetic tremolite at 750 °C. The boundaries shown in Figures 4A and 4B are placed at the midpoints of the brackets and have the same  $dP/dT$  slope (22 bars/K), which is based on the larger data set of Jenkins, Holland, and Clare (unpublished data) for synthetic tremolite.

There are obviously insufficient data in Figures 4A and 4B to perform a  $G'$  analysis as was done in the previous section. A simple calculation of the difference in the  $\Delta G_r$  of reaction for the reactions involving natural and synthetic tremolite can be made using the expression

$$\begin{aligned} \Delta G_r(\text{Natural}) - \Delta G_r(\text{Synthetic}) &= \Delta V(P_1 - P_2) \\ &= \Delta G_r(\text{Natural}) - \Delta G_r(\text{Synthetic}), \end{aligned}$$

where  $P_1$  and  $P_2$  are the pressures of the univariant boundaries for natural and synthetic tremolite, respectively, at a constant temperature. As in the previous section,  $\Delta S$  and  $\Delta V$  of both reactions are assumed to be equal, and no adjustment is made for mineral solid solutions ( $K = 1$ ), which forces all differences between synthetic and natural tremolite to be expressed by the differences in  $\Delta G_r$ . Furthermore,  $\Delta V$  is assumed to be constant over the small pressure range of the calculation (~3 kbar). Using the volume, expansivity, and compressibility data of Powell and Holland (1988), one can calculate a  $\Delta V$  of  $-0.364$  J/bar at 27 kbar and 750 °C. Substituting this  $\Delta V$  into the above expression and noting that  $P_1 - P_2$  ranges from 0 to 2.6 kbar gives values of 0 to  $-0.95$  kJ for the difference between  $\Delta G_r$  for natural and synthetic tremolite. A value of  $-0.36$  kJ is obtained for the 1-kbar difference indicated in Figure 4.

#### SOURCES OF DISCREPANCY

The results indicate a real difference in the stability of natural and synthetic tremolite with the natural tremolite samples used in this study having the greater  $P$ - $T$  stability. This difference in stability corresponds to a  $\Delta G_r$  of natural tremolite that is about 0.4–2.9 kJ more negative than that of synthetic tremolite for a fixed entropy. The thermodynamic analysis performed by Skippen and McKinstry (1985) on their experimental data for Reaction 1 yielded a difference in  $\Delta G_r$  for natural and synthetic tremolite of  $-9.2 \pm 1.8$  kJ (for fixed entropy), which is at least three times greater than was observed in this study. It is important to consider possible sources of discrepancy between this study and that of Skippen and McKinstry (1985) that could explain these differences and,

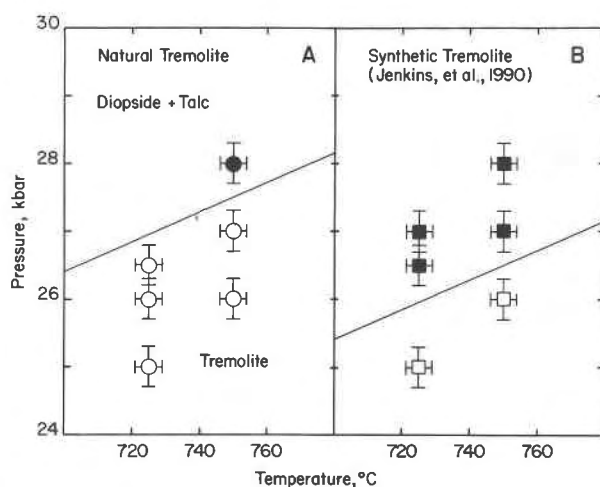


Fig. 4. Experimental results on the high-pressure stability of tremolite according to Reaction 3 in the text. (A) Results for natural tremolite from Table 3. (B) Results for synthetic tremolite, investigated with the same experimental apparatus and talc + diopside as for natural tremolite, from Jenkins, Holland, and Clare (unpublished data).

in the process, identify what factors are most likely controlling the difference in stability of natural and synthetic tremolite.

#### H<sub>2</sub>O fugacity

The largest difference in experimental technique between this study and that of Skippen and McKinstry (1985) is the use of H<sub>2</sub>O fugacity buffers. Skippen and McKinstry (1985) used both an oxygen buffer (Ni-NiO) and hydrogen buffer (C-CH<sub>4</sub>) to buffer indirectly the H<sub>2</sub>O fugacity in their experiments and so eliminated this as a variable in their experiments. A relatively high fugacity of oxygen (as with pure H<sub>2</sub>O) may affect the relative stabilities of natural and synthetic tremolite if the minor amounts of Fe (<0.7 wt% FeO in both studies), Mn (<0.1 wt% MnO), or Ti (<0.04 wt% TiO<sub>2</sub>) in natural tremolite are oxidized and increase its stability via a magnesiohastingsite (Semet and Ernst, 1981), magnesioriebeckite (Ernst, 1960), or oxyhornblende component.

Several experiments were performed in this study using the Ni-NiO oxygen buffer to bracket the location of Reaction 2, involving natural tremolite at 3 kbar. The results of these experiments are in Table 2 (group B). It should be noted that the experiment durations were purposely kept short to minimize expenditure of the buffer resulting from the rapid diffusion of H<sub>2</sub> through the wall of the outer Au capsule at temperatures of 900–950 °C (Chou, 1986). Also notice that the larger, double-capsule configuration used in these experiments resulted in a larger thermal gradient across the capsule and therefore larger uncertainty in the temperature measurement. As shown in Table 2, there is essentially no difference between the results obtained with the buffered and unbuffered exper-



iments at 3 kbar, indicating that the buffer does not significantly influence the upper-thermal stability of natural tremolite. An additional experiment was performed with a synthetic tremolite-bearing mixture using the Ni-NiO buffer (17-11 in Table 2) to see if the buffer might lower the stability of synthetic tremolite. Definite tremolite growth occurred at 865 °C and 3 kbar, which agrees with the univariant boundary for synthetic tremolite shown in Figure 2 and shows that any displacement in this curve to lower temperatures must be less than 20 °C.

### Grain size

Differences in the grain size, and attendant differences in surface areas, of natural and synthetic tremolite might account for the differences in their  $\Delta G_f$  in terms of their surface free energies. Qualitatively, this reasoning is correct because the synthetic tremolite used in this study and that of Skippen and McKinstry (1985) has a finer grain size (greater surface area per mole of tremolite) and a greater surface free energy (always positive) than natural tremolite. Quantitatively, it appears that surface free energy alone is not sufficient to account for the observed differences. No effort was made in this study to perform any sieving of the tremolite in order to restrict the grain-size range of the starting material because of the extremely fine grain size and limited quantity of the synthetic tremolite. Instead it was assumed that thorough grinding of the natural tremolite would yield a range of grain sizes comparable to the range of grain sizes obtained in the synthesis of tremolite. This was not quite the case. A survey was made of the grain sizes of the natural and synthetic tremolite used in the starting mixtures with the petrographic microscope. The largest synthetic tremolite grains were 30  $\mu\text{m}$  long and 5  $\mu\text{m}$  wide (assumed equal to depth) with the average length being about 13  $\mu\text{m}$  and width being 2  $\mu\text{m}$ . The largest natural tremolite grains were 110  $\mu\text{m}$  long and 30  $\mu\text{m}$  wide, with the average being about 56  $\mu\text{m}$  long and 10  $\mu\text{m}$  wide. The aggregate surface area can be calculated to a first approximation by assuming that all tremolite grains have the same dimensions as the average grain sizes listed above. Knowing the density of tremolite (2.98 g/cm<sup>3</sup>), one can calculate that synthetic tremolite has a surface area of 7220 cm<sup>2</sup>/g (587 m<sup>2</sup>/mol) whereas natural tremolite has a surface area of 1460 cm<sup>2</sup>/g (119 m<sup>2</sup>/mol). A reasonable range of surface free energies for surface-fluid interfaces is 0.1–0.6 J/m<sup>2</sup> (Ridley and Thompson, 1986). Applying the maximum value of 0.6 J/m<sup>2</sup> to the surface areas above yields surface free energies of 0.35 kJ/mol and 0.07 kJ/mol for synthetic and natural tremolite, respectively. The maximum difference of 0.28 kJ/mol attributed to surface free energy is not quite enough to account for the observed differences of 0.4–2.9 kJ/mol.

### Composition

The natural and synthetic tremolite used in this study are similar but not identical in composition (Table 1). Seemingly minor differences in their compositions may

have a noticeable effect on their thermal stabilities. One element that could account for an increase in the stability of natural tremolite is F. The experimental data on the upper-thermal stability of synthetic F end-member tremolite (Gilbert et al., 1982) indicate that it is stable up to about 1190 °C at 5 kbar (midrange of this study). From Figure 2 it can be seen that OH end-member tremolite is stable to 910 °C at 5 kbar. Combining these observations gives a linear increase of 60 °C per wt% F in the stability of tremolite. The natural tremolite used to investigate Reaction 2 (TREM 12) has 0.5 wt% F, which corresponds to a calculated 30 °C increase in its thermal stability. This is very close to the observed increase of 40 °C at 5 kbar.

A comparison of the upper-pressure stabilities of OH end-member tremolite and F end-member tremolite is not so meaningful, because the high-pressure breakdown of F end-member tremolite does not involve talc (owing to the apparent instability of F end-member talc), but involves instead the assemblage orthopyroxene, clinopyroxene, coesite, and fluorite (Gilbert et al., 1982). Nevertheless, the stability of F end-member tremolite at 700 °C is 7 kbar greater than that of OH end-member tremolite, which is in qualitative agreement with the increased stability of the F-bearing natural tremolite (TREM 8) used for studying Reaction 3.

Composition can also account for the differences in the derived values for  $\Delta G_f$  of natural and synthetic tremolite. If one adopts a simple ideal-mixing model for the component  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  (= TR) in tremolitic amphibole, then the resultant activity expression for the TR component is

$$a_{\text{TR}}^{\text{amph}} = (X_{\square}^{\text{O}})(X_{\text{Ca}}^{\text{M4}})^2(X_{\text{Mg}}^{\text{M1,2,3}})^5(X_{\text{Si}}^{\text{T1,2}})^8(X_{\text{OH}}^{\text{O3}})^2,$$

where  $X_i^k$  is the mole fraction of cation  $i$  on site  $k$  and  $\square$  = vacancy. Notice that the octahedral-cation distribution is averaged over the M1, M2, and M3 sites (M1, 2, 3), and the tetrahedral-cation distribution is averaged over the T1 and T2 sites (T1, 2). Differences in the derived values of  $\Delta G_f$  of pure OH end-member tremolite can now be related to the deviations that natural and synthetic tremolite have from the ideal composition by the relationship

$$G_{\text{TR}}^{\text{amph}} - G_{\text{TR}}^{\text{O}} = RT \ln a_{\text{TR}}^{\text{amph}}.$$

The composition of synthetic tremolite deviates from the ideal by having 10% excess Mg in the M4 site (Jenkins, 1987) giving  $a_{\text{TR}}^{\text{amph}} = 0.81$ . Using the compositions cited in Table 1 for the natural tremolites and the site-occupancy scheme of Leake (1978), one obtains values of 0.70 and 0.53 for the  $a_{\text{TR}}^{\text{amph}}$  of TREM 8 and TREM 12, respectively. The difference between TREM 12 and synthetic tremolite at the mean temperature of 930 °C for the upper-thermal stability of tremolite at 5 kbar is

$$\begin{aligned} G_{\text{TR}}^{\text{amph}}(\text{TREM 12}) - G_{\text{TR}}^{\text{amph}}(\text{Synthetic}) \\ = RT \ln a_{\text{TR}}^{\text{amph}}(\text{TREM 12}) - RT \ln a_{\text{TR}}^{\text{amph}}(\text{Synthetic}), \end{aligned}$$

which is  $-4.24$  kJ/mol. A similar calculation for synthetic and natural tremolite TREM 8 at 750 °C, the tem-

perature at which the calculations for Reaction 3 were made, gives a difference of  $-0.92$  kJ/mol. These calculated values are slightly greater than the observed values of  $-2.9$  and  $-0.4$  kJ/mol for Reactions 2 and 3, respectively. The main point, however, is that rather minor differences in the compositions of natural and synthetic tremolite are more than enough to account for the differences in their thermochemical properties if ideal mixing is assumed.

The exact chemical substitutions that are giving rise to the reduced activity of the TR component in natural tremolite and the corresponding increase in its  $P$ - $T$  stability are not known. For example, ideal mixing of tremolite with either fluortremolite, richterite (Na), pargasite (Na,Al), or magnesiohastingsite (Na,Al,Fe<sup>3+</sup>) will increase its thermal stability at the rate of 2–3 °C per mol% of the amphibole component (see review by Gilbert et al., 1982). If the observed increase in the thermal stability of natural tremolite is attributed to its F content, then it is important to briefly consider the rate of chemical reaction vs. the rate of exchange of F<sup>-</sup> for OH<sup>-</sup> between the crystal and ambient hydrothermal solution. The rate of chemical reaction for the dehydration of tremolite via Reaction 2 can be calculated from the procedure of Walther and Wood (1984). The univariant boundary involving synthetic tremolite for Reaction 2 lies at 870 °C at a pressure of 2 kbar. For a 5 °C overstep of this boundary, the  $\Delta G_r$  of reaction is  $-0.51$  kJ and the corresponding reaction rate,  $dm/dt$ , is  $2.25 \times 10^{-11}$  mol/(cm<sup>2</sup>·s) of oxygen. The time necessary to completely break down a sphere of tremolite with a radius of 50  $\mu$ m and an oxygen "density" of 0.085 mol/cm<sup>3</sup> is 220 d. Recent investigation in this laboratory into the kinetics of F-OH interdiffusion in tremolite by D. Brabander (personal communication) indicates a maximum diffusion rate of  $2.5 \times 10^{-13}$  cm<sup>2</sup>·s<sup>-1</sup> at 875 °C. Substituting this value into the equation for diffusion from a source of limited extent (Crank, 1975, p. 15), one can calculate the rate at which F diffuses from a 50- $\mu$ m-radius sphere of tremolite, whose initial concentration is 0.5 wt% F throughout, into the ambient aqueous fluid. After 220 d, this sphere would have lost only 23% of its total F. It is clear that the rate of chemical reaction (complete in 220 d) is much faster than the rate of F-OH interchange and that a F-bearing tremolite crystal is effectively impervious to any significant F-OH exchange between the crystal and fluid on the time scale of the experiments performed in this study.

### CONCLUSIONS

The main observation of this study is that natural and synthetic tremolite do indeed have different upper-thermal and upper-pressure stabilities, with natural tremolite having the greater stability. The extent to which they differ, however, is not nearly so large as indicated by the study of Skippen and McKinstry (1985). Of the factors that can be quantified with some degree of accuracy, i.e., H<sub>2</sub>O fugacity, grain size, and composition, it appears that compositional variation is adequate to account for the

higher stability and associated lower  $\Delta G_r$  of natural tremolite. Minor differences in F content, for example, could account for the different thermal and (perhaps) pressure stabilities of natural and synthetic tremolite.

The reasons for the conflicting results between this study and that of Skippen and McKinstry (1985) are not known. Based on the study of Reaction 1 by Jenkins (1983), Skippen and McKinstry (1985) suggested that tremolite synthesized at high pressures (> 15 kbar), might be structurally closer to that of natural tremolite. This is not substantiated because the synthetic tremolite used in this study was made at 2 kbar (Table 2), the same pressure used by Skippen and McKinstry (1985). It is clear from their own analysis and from the arguments given here that compositional differences would account for some, but certainly not all, of the approximately 133 °C difference in thermal stability that they observed. One important observation made in this study that may offer an explanation is that the (isobaric) experimental brackets for synthetic tremolite are much tighter (22 °C on the average) than those for natural tremolite (41 °C on the average). This probably arises from the slightly more complex composition of natural tremolite imparting a divariant nature on a nominally univariant reaction. The overall effect is to make it more difficult to interpret at what temperature tremolite grows or breaks down.

At this time there is little information available on the type or amount of structural defects in synthetic and natural tremolitic amphiboles. Even if such information were available, it would not be obvious what influence such defects would have on the macroscopic properties of amphiboles. In view of the effect that composition can have, there is no immediate reason to assume that structural defect density is dominating the behavior of amphiboles. At least in hydrothermal processes, synthetic calcic amphiboles closely model the behavior of natural calcic amphiboles if differences in composition are taken into consideration.

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