

Synthesis and characterization of tremolite in the system $\text{H}_2\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2$

DAVID M. JENKINS

Department of Geological Sciences and Environmental Studies, State University of New York–Binghamton, Binghamton, New York 13901, U.S.A.

ABSTRACT

Attempts at synthesizing tremolite of the composition $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (= TR) in this and previous studies have repeatedly resulted in good but incomplete yields. This investigation was performed to determine whether the incomplete synthesis of tremolite is the result of sluggish growth rates or is the result of synthetic tremolite not having the ideal composition. The growth rate of tremolite at typical synthesis conditions (800°C, 2 kbar, 10 d) does *not* appear to be a limiting factor, as demonstrated by the partial breakdown and essentially complete regrowth (as discerned from X-ray diffraction patterns) of both natural and synthetic tremolite with $\text{Ca}/(\text{Mg} + \text{Fe})$ ratios less than 2/5 that were grown in response to variable silica content in the ambient aqueous fluid. This observation also reveals the pronounced effect that the aqueous silica content has on the synthesis of tremolite. Tremolite was synthesized from a series of bulk compositions at 5 mol% increments along part of the join TR-MC (MC = $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$) at 850°C and 6 kbar and at 750°C and 13 kbar in order to determine if the Ca/Mg ratio of the starting material affects the synthesis of tremolite. The 6-kbar series (with additional quartz) produced the maximum yield of tremolite from the $\text{TR}_{90}\text{MC}_{10}$ bulk composition. Similar results were obtained at 13 kbar but were rendered less useful by the spontaneous nucleation of talc in the Mg-rich mixtures. The phase relations along this join indicate that synthetic tremolite either has the fixed composition of $\text{TR}_{90}\text{MC}_{10}$ or a very narrow compositional range about this value. Attempts at varying the Ca/Mg ratio of synthetic tremolite were unsuccessful. A survey of the purest natural tremolites reported in the literature confirmed that Mg enrichment is common. It is calculated that the presence of 10 mol% additional Mg on the M4 site of synthetic tremolite will increase values of ΔG° for the TR component derived from phase equilibria by up to 2 kJ/mol.

INTRODUCTION

Many experimental studies involving calcic amphiboles have dealt with tremolite because of its relatively simple chemistry. Somewhat surprisingly, few (if any) studies have ever reported that a complete yield of amphibole could be obtained from a starting mixture of the composition $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (or simply TR). Investigators who have documented the synthesis of tremolite in some detail (Boyd, 1959; Troll and Gilbert, 1972; Wones and Dodge, 1977; Oba, 1980; Skippen and McKinstry, 1985) have all indicated difficulties in obtaining pure yields of tremolite. Usually a mixture of phases is obtained consisting of about 90 wt% tremolite and 10 wt% diopsidic pyroxene with or without quartz. This rather consistent observation gives rise to several questions. Have the “right” conditions for synthesizing pure tremolite simply not been found? Does tremolite growth become prohibitively slow (i.e., kinetically controlled) after the synthesis is about 90% complete, or is the equilibrium composition of the tremolite formed at typical synthesis conditions enriched in Mg thereby caus-

ing calcic pyroxene plus quartz to form as well? If tremolite has a range of compositions, can this compositional range be correlated with specific geologic conditions of pressure and temperature? What effect does variable tremolite composition have on the thermochemical properties of the tremolite derived from experimental investigations?

A number of experiments have been performed in this study to address these questions. First, the results of tremolite syntheses from a fixed bulk composition over a wide range of pressures and temperatures are examined in terms of the phases observed and amount of amphibole obtained. Second, a series of experiments is described that was conducted with natural and synthetic tremolite in order to investigate the growth rate of tremolite under typical synthesis conditions. Third, the results of two isothermal, isobaric syntheses of tremolite over a range of bulk compositions are presented in order to determine the effect of bulk composition on the synthesis of tremolite. Finally, several attempts were made to induce a shift in the composition of synthetic tremolite (i.e., reverse

TABLE 1. Natural tremolites used in this study

Oxides (wt%)	TREM 8*	TREM 12**	Cations	TREM 8* (24O, OH,F)	TREM 12** (23O,F)
SiO ₂	58.2	58.9	Si	7.936	7.888
TiO ₂	0.04	0.04	Ti	0.004	0.004
Al ₂ O ₃	0.53	0.43	Al	0.085	0.068
Fe ₂ O ₃	0.08	—	Fe ³⁺	0.008	—
FeO	0.24	0.66†	Fe ²⁺	0.027	0.074†
MgO	24.5	24.7	Mg	4.980	4.931
MnO	0.01	0.08	Mn	0.001	0.009
CaO	13.5	13.2	Ca	1.972	1.894
Na ₂ O	0.20	0.60	Na	0.053	0.156
K ₂ O	0.04	0.24	K	0.007	0.041
P ₂ O ₅	<0.01	<0.01‡	P	—	—
H ₂ O ⁺	2.03	—	OH	1.846	—
H ₂ O ⁻	0.01	—	—	—	—
Cl	<0.01	<0.01‡	Cl	—	—
F	0.21	0.5‡	F	0.091	0.212
(-O = F)	(-0.09)	(-0.21)			
Total	99.50	99.14			

* Sample: Mass. 918-1, analysis and sample provided by E-an Zen, USGS.

** Sample: Barrie Township, Ontario, analysis provided by Ian M. Steele, University of Chicago.

† Total Fe reported as FeO.

‡ P, Cl, and F analyses provided by Richard L. Hervig, Arizona State University.

the composition) in order to detect what, if any, compositional dependency tremolite may have on temperature.

EXPERIMENTAL METHODS

Apparatus

Three different apparatus were used in this study: piston-cylinder presses, internally heated gas vessels, and cold-seal vessels. All experiments above 8 kbar were performed in a piston-cylinder apparatus at the University of Chicago using 3/4-in. O.D. NaCl pressure media. A detailed discussion of the calibration of the sample pressure in this assemblage is given in Jenkins (1981). In brief, sample pressure measurements are believed to be accurate to ± 300 bars, and temperature measurements (with chromel-alumel thermocouples) to $\pm 5^\circ\text{C}$. Individual experiments were performed by first pressurizing the NaCl assemblage at room temperature to several kilobars below the desired pressure and then using the (well-calibrated) thermal expansion of NaCl to obtain the desired pressure upon heating. Experiments in the pressure range of 2–8 kbar were performed in internally heated gas vessels of identical design at either the University of Chicago or SUNY-Binghamton. The pressure medium in these vessels was Ar, and its pressure was monitored throughout each experiment by both a bourdon-tube gauge and manganin cell. The precision of pressure measurement is ± 15 bars, and the accuracy is about ± 50 bars. Temperatures in the internally heated vessels were monitored with two inconel-sheathed, chromel-alumel thermocouples whose tips were positioned at either end of the sample capsule, as described by Jenkins (1983), allowing direct measurement of the thermal gradient across the sample. Temperature uncertainties associated with experiments performed in the internally heated gas vessels include both the accuracy (generally $\pm 2^\circ\text{C}$) as well as the thermal gradient across the sample ($2\text{--}5^\circ\text{C}$). Experiments at 2 kbar or less were performed in cold-seal vessels at SUNY-Binghamton using water as the pressure

medium. The vessels were constructed of René 41 and were operated horizontally with a tight-fitting filler rod of Stellite. Temperatures were measured with inconel-sheathed, chromel-alumel thermocouples calibrated against the freezing point of NaCl (800.5°C). Each thermocouple was located in an external thermocouple well with the tip positioned near the sample. A calibration of the sample temperature inside the vessel was made using the reaction talc = 3 enstatite + quartz + H₂O. Talc, enstatite, and quartz were synthesized individually from the oxides MgO, SiO₂, and H₂O and were mixed in the stoichiometric proportions of the reaction. At 2.0 ± 0.1 kbar, strong growth of talc was observed at $718 \pm 5^\circ\text{C}$, whereas strong growth of enstatite + quartz was observed at $741 \pm 5^\circ\text{C}$. These results are in excellent agreement with a temperature of 731°C for the univariant boundary at 2 kbar, which was determined by Chernosky et al. (1985) using all extant experimental data, and indicate that the temperature measured at the thermocouple well is within at least 10°C of the internal (sample) temperature. Pressures were measured intermittently with a bourdon-tube gauge calibrated against both a 50 000 and 75 000 psi Heise gauge. Pressure measurements are considered accurate to ± 100 bars.

Starting materials

All synthetic phases were made from mixtures of reagent-grade oxides. Calcium oxide was obtained by weighing CaCO₃ (Baker and Adamson, lot C224, or Mallinckrodt, JPX), because of its ease in handling, into the mixture and then decarbonating to CaO by heating to 800–900°C in air for 15–30 min. Magnesium oxide from three sources was used: (1) single-crystal chips of MgO (Muscle Shoals Electrochemical Corp.), (2) finely powdered MgO (Fisher, lot 706058), or (3) MgO fired from hydrous magnesium carbonate (Bakers, lots 91507 and 36416). In each case the MgO was fired to at least 1000°C for several hours prior to weighing. Several forms of SiO₂ were used: natural vein quartz from Lisbon, Maryland (provided by J. R. Goldsmith), ground fused silica, and cristobalite made by firing silicic acid (Bakers, lot 28298, or Fisher, lot 706058) in air at 1000°C for several days. Starting mixtures were prepared in 2-g batches, and each reagent was weighed to a precision of at least ± 0.1 wt%. With this precision, mixtures could be prepared to within ± 0.001 of the ideal Ca/Mg ratio of 0.400. No pronounced effect on the rate of growth or the morphology of synthetic amphibole crystals was observed with the use of these various forms of MgO or SiO₂.

Two natural tremolites were used in this study. One was from a dolomite marble (Mass. 918-1) collected by E-an Zen (USGS) and kindly donated to J. R. Goldsmith (University of Chicago), from whom a portion of the rock was obtained. The other was from a calcite marble in Barrie Township, Ontario, and was obtained from Wards Scientific. Particular care was taken to hand pick crystals that were as free of carbonate as possible; however, both samples had to be treated with cold 1.2M HCl to remove all carbonate from their X-ray patterns. The tremolites were also found to be free of talc by looking for the distinctive (002) reflection at $d = 9.35 \text{ \AA}$ in the X-ray pattern. Chemical analyses of these tremolites are given in Table 1.

Procedure

Synthesis experiments were performed by sealing a portion of the oxide starting mixture with an additional 15–50 wt% distilled H₂O in a Pt or Au capsule. Some amphibole synthesis experiments were performed with an extra 1–10 wt% SiO₂ in the starting mixture in order to saturate the ambient fluid in SiO₂ and, thereby, halt the dissolution of this component from the syn-

thetic amphibole. Further discussion of this phenomenon is given below.

The integrity of a sealed capsule was checked at the conclusion of an experiment in two ways: first by examining the capsule seams for the appearance of water while compressing the capsule with a pair of pliers, and second by checking the capsule weight before and after the experiment.

Analytical methods

All experimental products were examined under the petrographic microscope. An oil of refractive index 1.604 (α of tremolite) proved to be most useful for discerning minor amounts of enstatite ($\alpha = 1.650$), diopside ($\alpha = 1.664$), and quartz ($\epsilon = 1.553$) coexisting with tremolite. All products were also characterized with a Norelco X-ray diffractometer using Ni-filtered Cu radiation. Unit-cell refinements were obtained from diffractometer patterns at a scan rate of $1/4^\circ 2\theta/\text{min}$ using an internal standard of synthetic corundum ($a = 4.7593 \pm 0.0003 \text{ \AA}$; $c = 12.991 \pm 0.001 \text{ \AA}$) and the least-squares program of Appleman and Evans (1973). Several experimental charges were examined with an AMR 900 scanning-electron microscope (SEM). Modal amounts of phases were estimated from X-ray diffraction peak-height ratios; reproducibility was hindered, however, by preferred orientation of amphibole grains.

RESULTS

Tremolite synthesis attempts

A number of attempts were made at the outset of this study to synthesize tremolite from the bulk composition TR over a wide range of pressures, temperatures, and with a variety of starting materials. The starting materials used in these hydrothermal synthesis experiments involved the following: oxide mixture, oxide mixture with excess silica, oxide mixture seeded with 5 wt% natural tremolite, gel seeded with natural tremolite, mixture of synthetic talc plus $\text{Ca}(\text{OH})_2$ plus quartz, and an oxide mixture encapsulated with a 0.2M CaI_2 solution instead of distilled water (H. A. Yin, 1983, pers. comm.). Between 750 and 850°C, clinopyroxene formed with tremolite, whereas at or below 750°C, talc often nucleated with tremolite and clinopyroxene. These results are summarized in Figure 1. In short, no synthesis attempt yielded 100% tremolite when the starting mixture had the bulk composition TR or a Ca/Mg ratio of 2/5 or greater.

Tremolite growth rate

The approach adopted here for determining the rate of tremolite growth does not involve a numerical assessment of reaction-rate laws but, instead, a simple demonstration that the partial dissolution and essentially complete regrowth of tremolite is possible under typical synthesis conditions and durations.

It was found that the hydrothermal treatment of natural tremolite can lead to its incongruent dissolution by the reactions

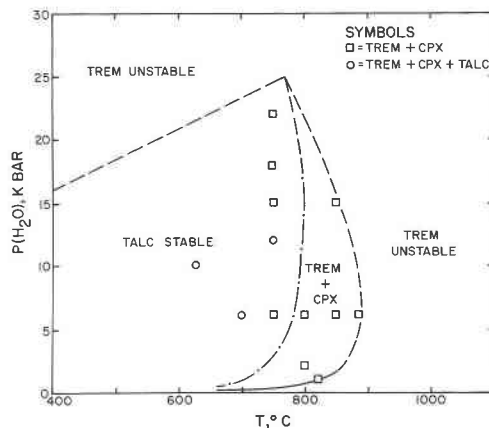
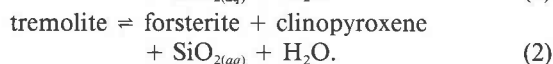
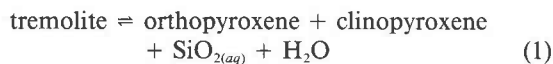


Fig. 1. Tremolite synthesis attempts from various starting materials of the bulk composition $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, with and without excess SiO_2 or Ca^{2+} . Dash-dot curve is the upper stability of talc from Chernosky et al. (1985). Solid curve is the upper stability of tremolite from Yin and Greenwood (1983). Dashed curves are approximated. Abbreviations as in Table 2.

Both reactions indicate that silica is preferentially dissolved from tremolite, leaving clinopyroxene and either orthopyroxene or forsterite as the residual solids. Whether Reaction 1 or 2 occurs appears to depend on the degree of silica undersaturation in the aqueous fluid, such that Reaction 1 occurs in mildly undersaturated fluids, whereas Reaction 2 occurs in strongly undersaturated fluids. This phenomenon of silica dissolution was used to show that two modally pure natural tremolites and a modally pure synthetic tremolite ($\text{Ca}/\text{Mg} = 1.8/5.2$) can be partially decomposed by hydrothermal treatment and then completely reformed to 100% amphibole (as discerned from X-ray patterns) *as long as the assemblage is saturated in silica*. Experimental results are listed in Table 2, and X-ray diffraction patterns for the synthetic tremolite experiments are shown in Figure 2. Figure 3a shows an SEM image of the surface of natural tremolite sample TREM 12 after hydrothermal treatment at 800°C and 2 kbar for 115 h with a water/tremolite ratio of 3.6/1.0 (by weight). Notice that the individual crystals have relatively smooth and often euhedral terminations, apparently as a result of both dissolution and recrystallization of cleavage fragments. Minor amounts of forsterite and clinopyroxene (not seen in Fig. 3a) formed as a result of hydrothermal treatment. Figure 3b shows a relatively large crystal of tremolite (TREM 12) from experiment no. TREM 12-6 in Table 2. In this experiment, orthopyroxene and clinopyroxene almost completely reacted with added quartz to form tremolite overgrowths on remnant tremolite from a previous hydrothermal treatment. One can see the jagged and uneven terminations resulting from columnar growth parallel to the Z axis. In transmitted light, the tremolite overgrowths are in optical continuity with the remnant tremolite grains.

It is emphasized that the modal abundances of the phases have been determined primarily from X-ray dif-

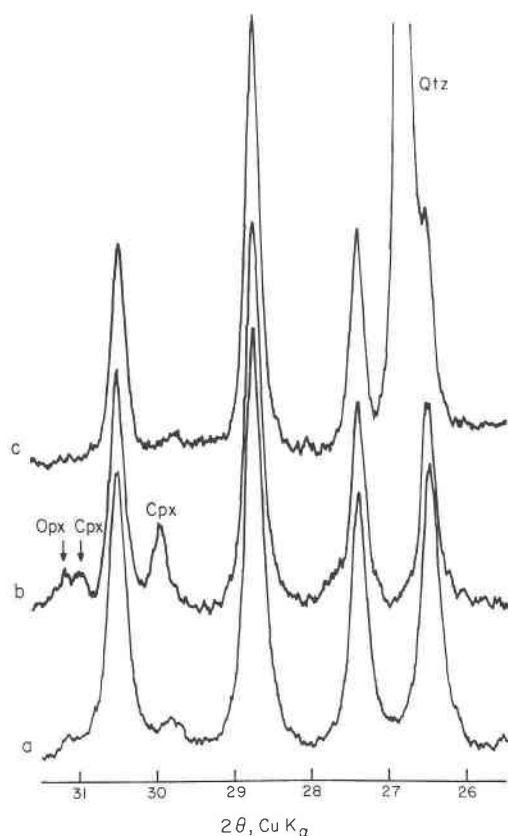


Fig. 2. X-ray diffractometer scans of synthetic tremolite of the composition $\text{Ca}_{1.8}\text{Mg}_{5.2}\text{Si}_8\text{O}_{22}(\text{OH})_2$. (a) Tremolite synthesized first at 2 kbar, 796°C, 285 h, and then at 1 kbar, 825°C, 389 h. (b) The tremolite of spectrum (a) treated at 2 kbar, 806°C, 144 h with a 5/1 ratio of water/tremolite (by weight). Note the presence of clinopyroxene (Cpx) and orthopyroxene (Opx). (c) The assemblage of spectrum (b) treated at 2 kbar, 800°C, 310 h with excess quartz. Notice the disappearance of Cpx and Opx and the appearance of quartz (Qtz) in the pattern.

fraction peak heights. Phases present at levels below about 5 wt% are generally not detectable. Careful examination of the experimental products with the petrographic microscope shows that there are minor amounts (<2 vol%) of clinopyroxene present in the experiments involving natural tremolite (TREM 8-2; TREM 12-6) and virtually no clinopyroxene present in the experiment involving synthetic tremolite (TREM 5-16). This can be explained in part by the variable compositions of the three tremolites investigated. Both of the natural tremolites have a higher Ca/(Mg + Fe) ratio (1.97/5.01 for TREM 8-2; 1.89/5.01 for TREM 5-16) than the synthetic tremolite (1.8/5.2). If there is any tendency toward Mg enrichment in tremolite at high temperatures, as discussed below, then there should be more clinopyroxene remaining unreacted in the natural as compared to the synthetic tremolite experiment, as is observed.

From these experiments, it can be concluded that small amounts of pyroxenes can be formed from, and readily

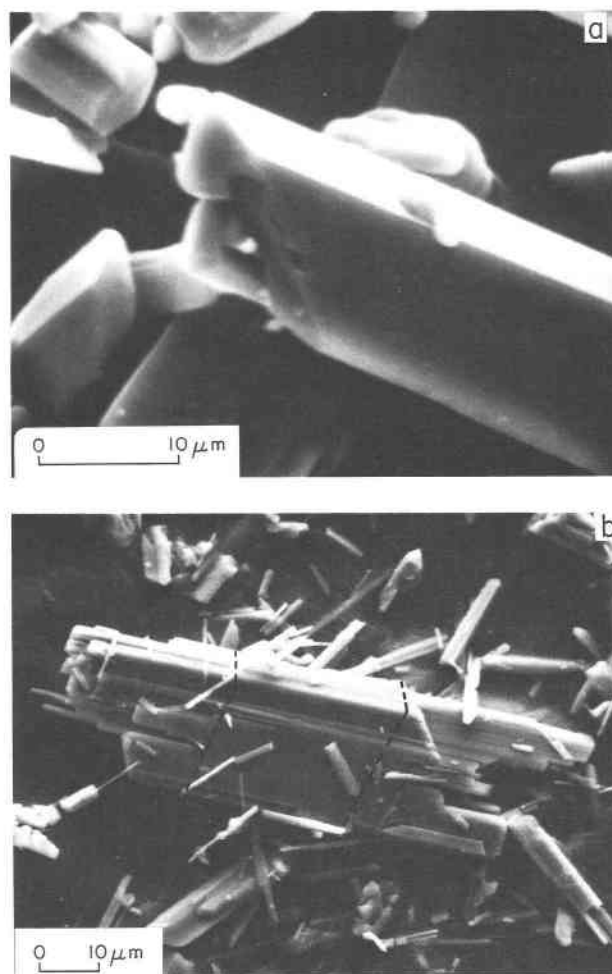


Fig. 3. SEM images of natural tremolite TREM 12. (a) Surface textures resulting from hydrothermal treatment of cleavage fragments at 2 kbar, 800°C, 115 h, water/tremolite ratio of 3.6/1.0 (by weight). Notice the relatively smooth, rounded edges of the partially dissolved and recrystallized cleavage fragments. (b) Surface textures resulting from hydrothermal treatment of partially dissolved tremolite fragments plus excess quartz at 2 kbar, 795°C for 217 h. Notice the sharp, protruding edges resulting from tremolite overgrowths parallel to the Z axis of the relic tremolite (approximate boundary is dashed).

react to, tremolite depending on the activity of SiO_2 in the ambient fluid. There is no indication that the kinetics at 800–880°C and 2–6 kbar are inhibiting the growth of tremolite, particularly when abundant tremolite nuclei are present. Instead, it is the composition of the system that exerts the dominant control.

The join $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ - $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$

Syntheses using a series of bulk compositions along the join $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ - $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ (TR-MC) were performed to determine how variation in the Ca/Mg ratio of the bulk composition affects tremolite formation. Mixtures were prepared from the oxides in 5 mol% increments between TR₇₅MC₂₅ and TR₁₀₀MC₀. Two series of

TABLE 2. Experimental results on the dissolution and regrowth of natural and synthetic tremolite

Code no.	P (kbar)	T (°C)	t (h)	Starting material (wt%)	Products*
Natural tremolite					
TREM 8-1	5.95 ± 0.05	885 ± 3	53	73% TREM 8 + 27% H ₂ O	trem + opx + cpx
TREM 8-2	6.36 ± 0.05	882 ± 3	68	56% TREM 8-1 + 7% qtz + 37% H ₂ O	trem + qtz + [cpx]
TREM 12-3	2.0 ± 0.1	795 ± 5	96	2% TREM 12 + 98% H ₂ O**	cpx + fo + trem
TREM 12-4	2.0 ± 0.1	790 ± 5	88	1.0% TREM 12-3 + 0.5% qtz + 98.5% H ₂ O**	trem + cpx + opx
TREM 12-6	2.0 ± 0.1	795 ± 5	217	39% TREM 12-4 + 8% qtz + 53% H ₂ O	trem + qtz + [cpx]
Synthetic tremolite					
TREM 5-13	2.0 ± 0.1	796 ± 5	285	63% trem oxide mix with Ca/Mg = 1.8/5.2 (moles) + 37% H ₂ O	trem (poorly crystalline)
TREM 5-14	1.0 ± 0.1	825 ± 10	389	51% TREM 5-13 + 49% H ₂ O	trem
TREM 5-15	2.0 ± 0.1	806 ± 5	144	17% TREM 5-14 + 83% H ₂ O	trem + cpx + opx
TREM 5-16	2.0 ± 0.1	800 ± 5	310	36% TREM 5-15 + 17% qtz + 47% H ₂ O	trem + qtz

* Abbreviations: cpx = clinopyroxene; fo = forsterite; opx = orthopyroxene; trem = tremolite; qtz = quartz.

** The starting material was placed in a crimped (not sealed) Pt capsule to expose the material to the distilled-water pressure medium.

experiments were performed: one at 6 kbar and 850°C and the other at about 13 kbar and 750°C. An additional 2–10 wt% quartz was added to each of the starting mixtures in the 6-kbar series in order to saturate the fluid in silica and drive Reactions 1 and 2 to the left. The results of these experiments are listed in Table 3, and the 6-kbar results are shown in Figure 4. At 6 kbar, mixtures at TR₁₀₀MC₀ and TR₉₅MC₅ yielded the assemblage tremolite + clinopyroxene + quartz, that at TR₉₀MC₁₀ yielded

tremolite + quartz, and those at TR₈₅MC₁₅, TR₈₀MC₂₀, and TR₇₅MC₂₅ yielded tremolite + orthopyroxene + quartz. Only the mixture at TR₉₀MC₁₀ yielded amphibole without coexisting pyroxene. The experiments at 13 kbar, which were performed without excess SiO₂, yielded results similar to those at 6 kbar. The TR₁₀₀MC₀ and TR₉₅MC₅ mixtures yielded tremolite + clinopyroxene without orthopyroxene, and the TR₈₅MC₁₅ and TR₈₀MC₂₀ mixtures yielded tremolite + orthopyroxene without cli-

TABLE 3. Synthesis results from mixtures along the join Ca₂Mg₅Si₈O₂₂(OH)₂-Mg₇Si₆O₂₂(OH)₂ (TR-MC)

Mol% TR in mixture	Run code	P (kbar)	T (°C)	t (h)	Products
With excess quartz					
100	TREM 1-9*	6.00 (± 0.05)	851 (± 2)	135	trem + cpx + qtz
95	TREM 6-12	6.00	852	241	trem + [cpx] + qtz
90	TREM 5-9	5.93	850	215†	trem + qtz
85	TREM 7-8	6.00	851	135†	trem + [opx] + qtz
80	TREM 10-1	5.93	850	215†	trem + opx + qtz
75	TREM 11-1**	6.00	850	166	trem + opx
		6.05	849	240	trem + opx
Without excess quartz					
100	TREM 1-3	15.0	750	44	trem + cpx
		18.0	750	61	
		(± 0.3)	(± 5)		
95	TREM 6-6	13.0	750	52	trem + cpx
		13.0	750	41†	
90	TREM 5-3	13.0	750	36	trem + opx + cpx + talc
		13.0	760	51	
		13.0	750	25†	
85	TREM 7-2	13.0	750	52	trem + opx + talc
		13.0	750	69†	
80	TREM 4-5	13.0	760	48	trem + opx
		13.0	760	40	
		13.0	755	76†	

Note: Abbreviations as in Table 2.

* Unit-cell dimensions of the tremolite are $a = 9.806 \pm 0.003$; $b = 18.046 \pm 0.006$; $c = 5.278 \pm 0.002$ Å; $\beta = 104.55^\circ \pm 0.04^\circ$; $V = 904.1 \pm 0.4$ Å³.

** Unit-cell dimensions of the tremolite are $a = 9.804 \pm 0.002$; $b = 18.047 \pm 0.004$; $c = 5.280 \pm 0.001$ Å; $\beta = 104.53^\circ \pm 0.02^\circ$; $V = 904.3 \pm 0.3$ Å³.

† The multiple sets of conditions indicate multiple hydrothermal treatment of the same material with intermediate grinding.

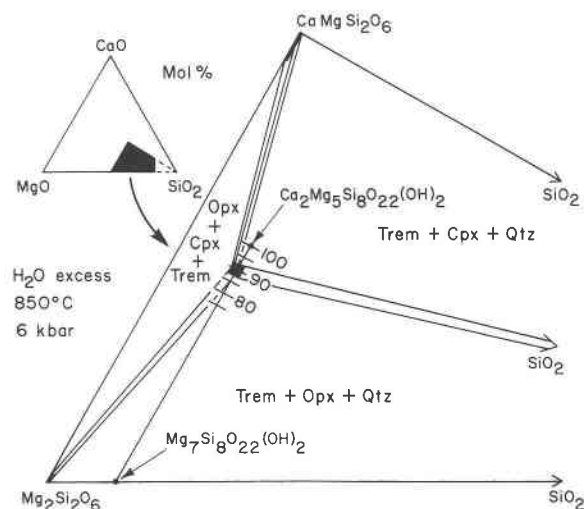


Fig. 4. Phase relations in a portion (shaded region in inset) of the system $\text{H}_2\text{O}-\text{CaO}-\text{MgO}-\text{SiO}_2$ projected from H_2O onto the ternary diagram $\text{CaO}-\text{MgO}-\text{SiO}_2$. Numbers refer to the mol% of $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ in mixtures along the join $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2-\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. Tie lines between Opx, Cpx, and Trem have been inferred. Pyroxene compositional ranges from Lindsley and Dixon (1976). Abbreviations given in Table 2.

nopyroxene. However, the nucleation of talc in two of the experiments and the almost certain loss of silica to the ambient fluid hinders direct comparison with the 6-kbar results. From Figure 4 one can see that tremolite synthesized from a bulk composition of $\text{TR}_{100}\text{MC}_0$ will have an estimated maximum of 93 mol% of the TR component.

The synthesis experiments limit the extent of tremolite solid solution to the compositional range of 90 ± 3 mol% TR. An even narrower range of solid solution, i.e., a single composition, is suggested by the unit-cell dimensions of the tremolites produced in the most calcic ($\text{TR}_{100}\text{MC}_0$) and the least calcic ($\text{TR}_{75}\text{MC}_{25}$) bulk compositions investigated. These unit-cell dimensions are given in the footnotes to Table 3. Notice that both tremolites have the same unit cells within the limits of uncertainty. If there was significant solid solution, one would anticipate the a dimension to increase by $0.0035 \text{ \AA/mol\% TR}$, or the volume by $0.26 \text{ \AA}^3/\text{mol\% TR}$, on the basis of a linear interpolation between the unit-cell dimensions of tremolite (Borg and Smith, 1969) and the hypothetical phase magnesio-cummingtonite extrapolated from the data of Viswanathan and Ghose (1965). Using these values, one finds that the *maximum* compositional range allowed by the unit-cell dimensions (and their uncertainties) in Table 3 is 2 mol% TR.

Several attempts were made to obtain direct chemical analyses on individual synthetic tremolite crystals using both an electron microprobe to analyze polished grain mounts and an SEM (equipped with a quantitative energy-dispersive unit) to analyze grains dispersed on a graphite

substrate. In general the analyses yielded very low totals because of the small grain sizes and, therefore, substandard analyses. However, the Ca/Mg ratio was consistently lower than that of ideal tremolite and tended to lie within the range 1.75/5.25 to 1.9/5.1 for those grains that gave the highest total weight percentages. The general indication is that direct chemical analyses confirm the low Ca/Mg ratio in synthetic tremolite.

Ca/Mg reversal attempts

The evidence presented so far indicates that tremolite synthesized from a variety of starting mixtures is Mg enriched. It remains to be shown, however, that this is the equilibrium composition of tremolite. Ideally, one would like to demonstrate that a Ca-enriched and a Mg-enriched tremolite converge to, or narrowly bracket, a specific composition at a given P and T . Unfortunately, this is not possible for a substance that displays virtually no solid solution (Fig. 4). An alternative approach is to change the composition of tremolite by reacting it with other phases to produce a more calcic or more magnesian tremolite and thus to demonstrate that *this* process is reversible.

It was noted by Robinson et al. (1982, Fig. 51) that tremolite in ultramafic rocks shows a tendency toward Ca enrichment at lower metamorphic grades. Accordingly, several experiments were performed at 490°C with a tremolite that was synthesized at 800°C in order to induce an increase in its Ca/Mg ratio by reaction with clinopyroxene and quartz (Fig. 4). A mixture of synthetic tremolite, diopside, and quartz was hydrothermally treated at 490°C and 2.5 kbar for 2166 h with grinding after 531 h. No perceptible reaction occurred. An additional treatment of the same material with a 0.2M CaI_2 solution for 679 h also yielded no reaction. Talc was not observed. Additional experiments at pressures above 8 kbar might prove successful in view of the enhanced reaction rates at higher pressures (e.g., Goldsmith and Newton, 1974), but such experiments have not yet been performed because of the extreme durations involved.

In summary, experimental proof of the Mg enrichment of synthetic tremolite or of any variation in its Ca/Mg ratio with temperature has yet to be obtained. The only argument that can be made at present for the stable existence of Mg enrichment in synthetic tremolite is that many different starting materials (i.e., oxide mixture, gel, crystalline phases) produce the same assemblage of tremolite plus clinopyroxene at temperatures of $750\text{--}850^\circ\text{C}$ and that the process does not appear to be path dependent.

DISCUSSION

Applications to natural tremolite

The presence of Mg enrichment, or at least Ca depletion relative to octahedral cations, in natural tremolites has been noted by Wones and Dodge (1977) and Robinson et al. (1982) based on surveys of numerous calcic

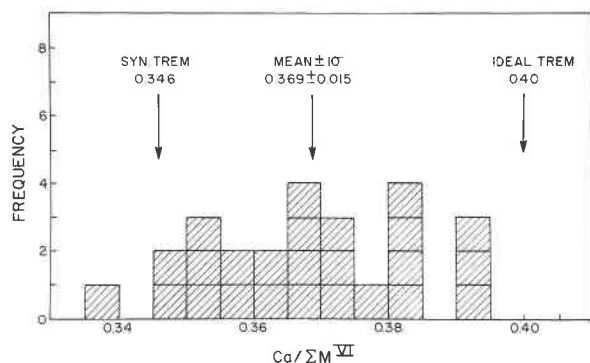


Fig. 5. Histogram of the ratio of Ca to the sum of all cations assigned to octahedral sites ($\text{Ca}/\Sigma\text{M}^{\text{VI}}$) of 25 natural tremolites selected according to the criteria discussed in the text. Arrows indicate the values for synthetic tremolite (0.346), mean for the natural tremolites (0.369), and ideal tremolite (0.40).

amphibole analyses. A survey of natural tremolite compositions was also performed in this study in order to determine the range of cation variations within the "purest" tremolites reported in the literature. Out of a total of 123 tremolite analyses surveyed from the literature (Deer et al., 1963; Leake, 1968; Ross et al., 1969; Trommsdorff and Evans, 1972; Frost, 1975; Misch and Rice, 1975; Slaughter et al., 1975; Vance and Dungan, 1977; Valley and Essene, 1980; Sanford, 1982), only 25 were found to obey the following criteria: $\text{Al}_2\text{O}_3 \leq 1.0$ wt%, $\text{FeO} \leq 2.0$ wt% ($\text{Na}_2\text{O} + \text{K}_2\text{O} \leq 0.5$ wt%, $\text{Fe}_2\text{O}_3 \leq 1.0$ wt% (if given), and the sum of Ca plus the cations $\text{Mg} + \text{Fe}^{2+} + \text{Ni} + \text{Mn} + \text{Ti} + \text{Fe}^{3+} + \text{Cr} + \text{Al}$ ($= \Sigma\text{M}^{\text{VI}}$) being 7.0 ± 0.1 on the basis of 23 oxygens. The assignment of cations to the octahedral sites was made in accord with the assignment scheme of Leake (1978) with the exception that the total number of octahedral cations could exceed 5.0 and that Na, K, and Ca could not be assigned to octahedral sites. These selection criteria were used in order to identify tremolites that are as free as possible of non-tremolite components and that have full occupancy of the M1 to M4 sites. A histogram of the $\text{Ca}/\Sigma\text{M}^{\text{VI}}$ ratios for these 25 analyses is shown in Figure 5, as well as the ratios for the ideal tremolite composition ($2.0/5.0 = 0.4$) and the synthetic tremolite ($1.8/5.2 = 0.346$). Although the database is admittedly small, Figure 5 shows that *none* of the natural tremolites considered here has the ideal ratio of 2/5 and that most have values lying midway between ideal and synthetic tremolite. In other words, even the purest tremolites in nature frequently possess an excess of cations assigned to the octahedral sites, indicating the presence of (mostly) Mg and Fe^{2+} on M4 sites.

There are several lines of evidence to suggest that the $\text{Ca}/\Sigma\text{M}^{\text{VI}}$ ratio of tremolite varies inversely with temperature. First, synthetic tremolite has a smaller $\text{Ca}/\Sigma\text{M}^{\text{VI}}$ ratio than that of the most natural tremolites (Fig. 5). It is reasonable to assume that tremolite synthesized in the range 750–850°C has formed at temperatures much higher

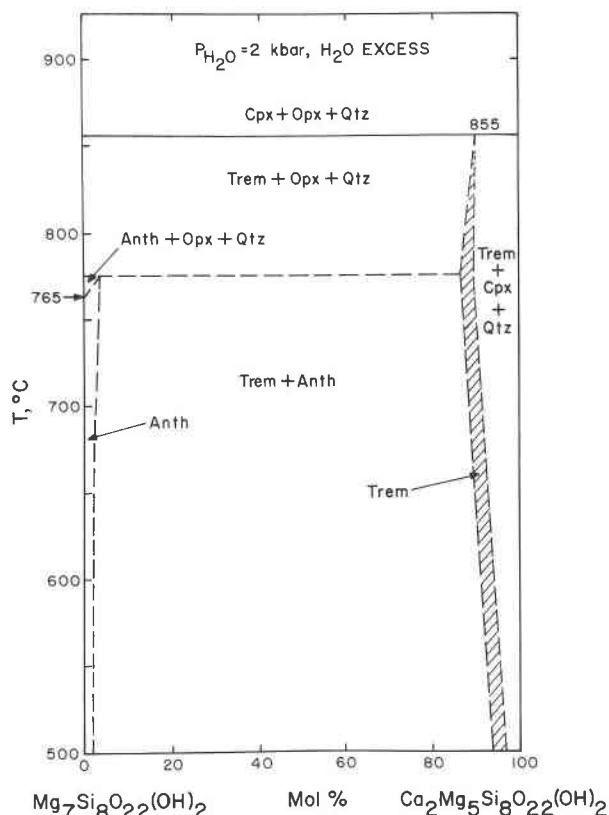


Fig. 6. Approximate phase diagram for the pseudobinary join $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ - $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ in the system H_2O - CaO - MgO - SiO_2 at $P_{\text{H}_2\text{O}} = 2$ kbar. H_2O is present in all fields. Shaded region denotes range of tremolite solid solution. Dashed lines are approximate boundaries. Upper thermal stability of pure anthophyllite (Anth) is from Chernosky et al. (1985). Upper thermal stability of tremolite is from Fig. 1. Other abbreviations as in Table 2.

than those of natural tremolites from greenschist or lower-amphibolite facies mafic, ultramafic, or siliceous carbonate rocks. Second, the experimental study by Cameron (1975) on cummingtonite-actinolite phase relations in the system H_2O - CaO - MgO - FeO - SiO_2 at 2 kbar and 500–800°C suggested that the $\text{Ca}/(\text{Mg} + \text{Fe})$ ratio of actinolite decreased with increasing temperature. Third, Robinson et al. (1982) observed a decrease in the $\text{Ca}/\Sigma\text{M}^{\text{VI}}$ ratio of calcic amphiboles with increasing metamorphic grade in progressively metamorphosed ultramafic rocks. Combining these observations with the information on tremolite compositions obtained in this study, one can approximate the phase relations along the pseudobinary join MC-TR, as shown in Figure 6. The critical feature to be noted in this diagram is the very narrow range of solid solution indicated for tremolite (shaded region). Unlike the analogous single-chain silicate join $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ (enstatite-diopside), there is no indication of a range of extensive solid solution for amphiboles along this join at high temperatures. This is rather surprising in view of the general similarities be-

tween the pyroxenes and amphiboles as demonstrated, for example, by their similar structural transformations (Carpenter, 1982). Nevertheless, the experimental evidence does not support the presence of an extensive range of solid solution near the maximum temperatures of amphibole stability (750–850°C).

Thermodynamic considerations

Mg enrichment in synthetic tremolite will affect the thermodynamic properties of the TR component derived from phase equilibria. At a given temperature and pressure, the change in the chemical potential of the TR component (μ_{TR}) resulting from solid solution in amphibole (amph) is given by the relation

$$\mu_{\text{TR}}^{\text{amph}} - \mu_{\text{TR}}^0 = RT \ln a_{\text{TR}}^{\text{amph}} = \Delta\mu_{\text{TR}}, \quad (3)$$

where μ_{TR}^0 is the chemical potential of the pure phase of composition TR and $a_{\text{TR}}^{\text{amph}}$ is the activity of TR in the amphibole solid solution. At present there is little experimental information on the activity-composition relations of amphiboles. However, one can examine several possible activity expressions and from them ascertain a range of variation in derived thermochemical properties.

The simplest assumption for activity is that of ideal mixing of unlike cations on each crystallographic site. In the case of tremolite, the ideal activity expression is

$$a_{\text{TR}}^{\text{amph}} = (X_{\text{Ca}}^{\text{A}})(X_{\text{Ca}}^{\text{M4}})^2(X_{\text{Mg}}^{\text{M3}})(X_{\text{Mg}}^{\text{M2}})^2(X_{\text{Mg}}^{\text{M1}})^2(X_{\text{Si}}^{\text{T1}})^4(X_{\text{Si}}^{\text{T2}})^4(X_{\text{OH}}^{\text{O3}})^2, \quad (4)$$

where X_i^k is the mole fraction of species i on site k , $\square$ stands for vacancy, and site nomenclature is that of Hawthorne (1981). The reader is directed to Wood and Fraser (1976, Chap. 3) or Nordstrom and Munoz (1985, App. C) for the theory behind the derivation of ideal activity expressions. For the system investigated in this study, all values of X_i^k in Equation 4 are unity except $X_{\text{Ca}}^{\text{M4}}$, which is 0.9 because of the 10% additional Mg in synthetic tremolite. Thus, Equation 4 simplifies to

$$a_{\text{TR}}^{\text{amph}} = (X_{\text{Ca}}^{\text{M4}})^2 = (0.9)^2 = 0.81. \quad (5)$$

At 800°C, for example, this activity yields a $\Delta\mu_{\text{TR}}$ of -1.88 kJ/mol.

An alternative activity expression was proposed by Powell (1975), who treated natural amphiboles as regular solutions (e.g., Wood and Fraser, 1976) of eight components. Using a suite of coexisting cummingtonite-hornblende pairs from New Zealand rhyolites, Powell (1975) was able to derive a set of seven mixing parameters by knowing the compositions of the amphiboles and their temperature of equilibration as determined by Fe-Ti oxide geothermometry. Application of Equations 6 and 8 of Powell (1975) to the synthetic tremolite of this study yields the following expressions for the mole fraction ($X_{\text{TR}}^{\text{amph}}$), activity coefficient ($\gamma_{\text{TR}}^{\text{amph}}$), and activity of the TR component:

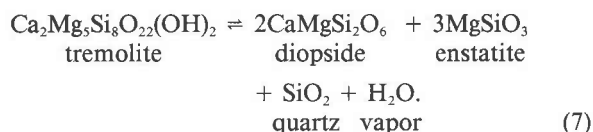
$$X_{\text{TR}}^{\text{amph}} = (X_{\text{Ca}}^{\text{M4}})^2 \quad (6a)$$

$$RT \ln \gamma_{\text{TR}}^{\text{amph}} = 2(X_{\text{Mg}}^{\text{M4}})^2(25.095 \text{ kJ/mol}) \quad (6b)$$

$$a_{\text{TR}}^{\text{amph}} = (X_{\text{TR}}^{\text{amph}})(\gamma_{\text{TR}}^{\text{amph}}). \quad (6c)$$

At 800°C, Equations 6a–6c yield $a_{\text{TR}}^{\text{amph}} = 0.857$, which in turn, yields a $\Delta\mu_{\text{TR}}$ of -1.38 kJ/mol.

It is apparent from the above discussion that reasonable choices for $a_{\text{TR}}^{\text{amph}}$ will increase the derived Gibbs free energy of formation, ΔG_f^0 , of stoichiometric tremolite by up to 2 kJ/mol. At present, this adjustment is much smaller than the range in the reported values of ΔG_f^0 (298 K, 1 bar) of tremolite, which vary from -11592.55 kJ/mol (Helgeson et al., 1978) to -11627.91 ± 17 kJ/mol (Robie et al., 1978). However, a 2-kJ increase in the ΔG_f^0 of tremolite translates to a decrease of 20–30°C in the calculated position of the reaction



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