

## X-ray structure refinements of tremolite at 140 and 295 K: Crystal chemistry and petrologic implications

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### ABSTRACT

A near-end-member natural tremolite,  $\text{Na}_{0.01}\text{Ca}_{1.97}\text{Mg}_{4.98}\text{Fe}_{0.03}\text{Al}_{0.01}\text{Si}_{8.00}\text{O}_{22}(\text{OH})_2$ , was studied by single-crystal X-ray diffraction at 140 and 295 K to seek a possible crystal-chemical explanation for the typically low  $\text{Ca}/\Sigma \text{M}$  ratios, relative to the ideal ratio of 2/5, observed in both natural and synthetic tremolite samples. Difference-Fourier maps revealed the presence of a residual electron density close to the M4 site along the diad axis toward the octahedral strip. Structure refinements indicated that the M4 and M4' sites are occupied by  $\text{Ca} + \text{Na}$  and  $\text{M}(\text{Fe} + \text{Mg})$ , respectively. In comparison with the configuration of the M2 coordination polyhedron in diopside, the degree of distortion and the volume of the M4 coordination polyhedron in tremolite are relatively large and the M4 cation is slightly underbonded. These two factors contribute to an energetic drive toward M-enriched tremolite. The average unit-cell volume of  $906.6(2) \text{ \AA}^3$  determined at 295 K for nearly pure tremolite in this study suggests an end-member reference-state volume for tremolite of  $907 \text{ \AA}^3$ . This indicates that cell volumes of synthetic tremolite of  $904.2(4) \text{ \AA}^3$  reflect 8–10% cummingtonite solid solution, as previous authors have claimed. Similarly,  $\beta$  angles of  $104.53\text{--}104.58^\circ$  for synthetic tremolite suggest similar amounts of cummingtonite, when compared to  $\beta = 104.76(2)^\circ$  for near-end-member tremolite and  $104.75(5)^\circ$  for many natural tremolite samples from calc-silicate parageneses.

The compositions of natural and synthetic tremolite samples are consistent with theoretical constraints on the  $\text{Ca}/\Sigma \text{M}$  ratio of tremolite. Decreasing temperature increases the  $\text{Ca}/\Sigma \text{M}$  ratio of tremolite in both Mg-saturated (+ talc, anthophyllite, cummingtonite, or enstatite) and Ca-saturated (+ diopside, quartz,  $\text{H}_2\text{O}$ ) parageneses. Stabilization of cummingtonite-tremolite solid solution caused by M4-site splitting (M on M4') is small in comparison with the enthalpic consequence of size mismatch. The configurational entropy term (mixing of Ca and Mg) accounts for the coexistence of cummingtonite-bearing tremolite with diopside, quartz, and  $\text{H}_2\text{O}$ , and for the problem of achieving 100% synthesis of tremolite of ideal composition.

### INTRODUCTION

Tremolite,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , is an important calcic amphibole occurring in a variety of metamorphic and altered igneous rocks. Because of its end-member status, tremolite has been the subject of many experimental studies designed to define its stability and derive the thermodynamic data necessary for calcic amphibole to be used as a petrogenetic indicator. However, as noted by many workers (e.g., Wones and Dodge 1977; Robinson et al. 1982; Jenkins 1987; Skogby and Ferrow 1989; Graham et al. 1989; Welch and Pawley 1991), tremolite with the ideal  $\text{Ca}/\Sigma \text{M}$  ratio of exactly 2/5 ( $\Sigma \text{M} = \text{Mg} + \text{Fe}^{2+} + \text{Mn} + \text{Ni} + \text{Ti} + {}^{60}\text{Fe}^{3+} + {}^{60}\text{Cr} + {}^{60}\text{Al}$ ) has not been found in nature or synthesized experimentally; all trem-

olite is somewhat depleted in Ca and enriched  $\Sigma \text{M}$ . On the basis of certain selection criteria, Jenkins (1987) found that all natural tremolite samples have  $\text{Ca}/\Sigma \text{M}$  ratios  $< 0.4$ , with a mean value of  $0.369 \pm 0.015$ . Experimental studies have shown that synthetic tremolite appears to contain 8–10% cummingtonite component in solid solution (Boyd 1959; Troll and Gilbert 1972; Wones and Dodge 1977; Oba 1980; Skippen and McKinstry 1985; Jenkins 1987; Graham et al. 1989; Welch and Pawley 1991; Pawley et al. 1993; Hoschek 1995). The off-composition nature of synthetic tremolite is one of several factors with the potential to create discrepancies among derived thermodynamic properties. Jenkins (1987) investigated the problem of the nonideal  $\text{Ca}/\Sigma \text{M}$  ratio in synthetic tremolite in terms of growth rate, bulk composition, pressure, and temperature and concluded that none of them is a limiting factor in attempts to synthesize "pure" tremolite. Using high-resolution transmission

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TABLE 1. Chemical composition of tremolite CG-1

|                                | This study | Welch and Pawley (1991) |
|--------------------------------|------------|-------------------------|
|                                | wt%        |                         |
| SiO <sub>2</sub>               | 59.19      | 58.61                   |
| TiO <sub>2</sub>               | 0.01       | 0.02                    |
| Al <sub>2</sub> O <sub>3</sub> | 0.04       | 0.03                    |
| Cr <sub>2</sub> O <sub>3</sub> | n.d.       | 0.01                    |
| FeO                            | 0.25       | 0.43                    |
| MgO                            | 24.74      | 25.01                   |
| MnO                            | 0.02       | 0.03                    |
| CaO                            | 13.63      | 13.65                   |
| Na <sub>2</sub> O              | 0.05       | 0.02                    |
| K <sub>2</sub> O               | 0.01       | 0.02                    |
| H <sub>2</sub> O               | 2.22*      | 2.19                    |
| F                              | n.d.       | 0.05                    |
| less O = F                     |            | 0.02                    |
| Total                          | 100.16     | 100.05                  |
| Formula (O + OH + F = 24)      |            |                         |
| Si                             | 7.997      | 7.947                   |
| Ti                             | 0.001      | 0.002                   |
| Al                             | 0.006      | 0.005                   |
| Fe                             | 0.028      | 0.049                   |
| Mg                             | 4.983      | 5.055                   |
| Mn                             | 0.002      | 0.003                   |
| Ca                             | 1.973      | 1.983                   |
| Na                             | 0.013      | 0.005                   |
| K                              | 0.002      | 0.003                   |
| F                              | —          | 0.021                   |
| OH                             | 2.001      | 1.981                   |
| Σ cations                      | 15.005     | 15.052                  |

Note: n.d. = not determined.

\* Ideal H<sub>2</sub>O.

electron microscopy, Ahn et al. (1991) found that synthetic tremolite commonly contains chain-multiplicity faults, whereas natural tremolite is largely free of them. They concluded that the presence of intergrown wide-chain lamellae is one of the factors causing the bulk composition of synthetic tremolite to deviate from the ideal Ca/Mg ratio, but that their abundance is insufficient to account for the noticeably low Ca/Mg ratios of synthetic tremolite (0.346–0.356). Similar conclusions were made by Skogby and Ferrow (1989) and by Smelik et al. (1994). On the other hand, Maresch et al. (1994) argued that their synthetic tremolite samples correspond closely to end-member tremolite, and that chain-multiplicity faults play a significant role in the apparent compositional shift of synthetic tremolite, such that the genuine magnesio-cummingtonite component may be much less than 10 mol%.

To seek a possible crystal-chemical explanation for the nonideal Ca/Σ M ratio in tremolite, we performed X-ray structure refinements of a natural tremolite crystal (Welch and Pawley 1991; here labeled CG-1) at 140 and 295 K, with particular interest on the configuration of the M4 site because it plays a critical role in amphibole structures [see Hawthorne (1983) for a thorough review]. The reason for undertaking the low-temperature measurements is to minimize atomic thermal vibrations so that high quality data can be obtained and more detailed features of the structure revealed.

The crystal structure of tremolite is characterized by double silicate chains linked together by strips of M<sup>2+</sup> cations occupying three octahedral sites (M1, M2, and

M3) and an eightfold-coordinated polyhedral site (M4). In an ideal tremolite structure there is no atomic disorder among the various distinct sites: The M1, M2, and M3 sites are fully occupied by Mg, and the M4 site by Ca. A two-dimensional refinement of the tremolite structure was reported by Zussman (1959). Papike et al. (1969) conducted a detailed X-ray structure refinement of a fairly pure tremolite (G-21) from Gouverneur, New York. The structure of a tremolite crystal from the same sample used by Papike et al. (1969) was investigated at 673 and 973 K by Sueno et al. (1973) using single-crystal X-ray diffraction. Hawthorne and Grundy (1976) refined the crystal structure of a slightly edenitic tremolite by X-ray and neutron diffraction techniques.

### EXPERIMENTAL PROCEDURES

The natural tremolite sample used in this study is from the collection of the University of Edinburgh, but its locality is unknown. Welch and Pawley (1991) showed that it has a nearly ideal tremolite composition, with Ca/Σ M = 0.387, and is free of chain-width disorder, stacking faults, and mineral inclusions. Our electron microprobe analysis (Table 1) confirmed the near-perfect stoichiometry of this tremolite, and it avoids the need to place Fe in a tetrahedral site and some Ca in the A site, features of the earlier analysis (which are not necessarily wrong). The average composition presented in Table 1 was used in the structure refinements. A nearly cube-shaped single crystal (0.16 × 0.16 × 0.14 mm) was selected and mounted on a glass fiber with a cyanoacrylate glue. The experimental procedures for the collection of X-ray intensity data from this crystal at 140 and 295 K are similar to those used by Yang and Smyth (1996).

Unit-cell dimensions and X-ray diffraction intensities of the crystal were measured at 140 and 295 K. Unit-cell dimensions were determined by the least-squares refinement of 28 reflections with 15° < 2θ < 30°. Reflections violating the C2/m space group were searched for at 140 K, but none was found. The X-ray diffraction intensities of monoclinic-equivalent reflection pairs *hkl* and *h $\bar{k}$ l* in the Laue group 2/m were collected using the ω-scan mode and variable scan speeds (3–30°/min) with 2° ≤ 2θ ≤ 60°. Three standard reflections were monitored after every 97 reflection measurements, and no significant or systematic variations in the standard reflection intensities were observed. All X-ray intensity data, after correction for Lorentz and polarization effects and for absorption by the analytical method, were merged and reduced to structure factors. Reflections with intensities greater than 4σ<sub>F</sub> were considered as observed and included in the refinements, where σ<sub>F</sub> is the standard deviation determined from the counting statistics.

The initial atomic positional and displacement parameters of tremolite were taken from Papike et al. (1969). Weighted (w = 1/σ<sub>F</sub><sup>2</sup>) full-matrix least-squares refinements were performed using an updated version of RFINE4 (Finger and Prince 1975) in the space group C2/m for all observed reflections. The structure refinement at 295 K was started with the bulk chemical composition con-

**TABLE 2.** Crystal data and refinement statistics for tremolite at 140 and 295 K

|                               | 140 K       | 295 K       | 295 K*     |
|-------------------------------|-------------|-------------|------------|
| <i>a</i> (Å)                  | 9.8293(13)  | 9.8356(12)  | 9.8385(4)  |
| <i>b</i> (Å)                  | 18.0307(24) | 18.0557(22) | 18.0554(8) |
| <i>c</i> (Å)                  | 5.2752(6)   | 5.2785(6)   | 5.2778(4)  |
| $\beta$ (°)                   | 104.846(9)  | 104.782(9)  | 104.751(5) |
| <i>V</i> (Å <sup>3</sup> )    | 903.4(2)    | 906.4(2)    | 906.6(1)   |
| Total reffs.                  | 2777        | 2785        |            |
| Unique reffs.                 | 1366        | 1372        |            |
| Reffs. >4 $\sigma$ (F)        | 1198        | 1214        |            |
| <i>R</i> <sub>merge</sub> (%) | 1.8         | 1.8         |            |
| <i>R</i> <sub>w</sub> (%)     | 2.7         | 2.6         |            |
| <i>R</i> (%)                  | 2.3         | 2.3         |            |

\* Results are from use of the Rietveld powder method by D.L. Bish (personal communication, 1995).

strained to that determined from microprobe analysis, ignoring the small amounts of Al, Mn, Ti, and K; Ca and Na were assigned to the M4 site, and the site occupancies of Mg and Fe among the M1, M2, M3, and M4 sites were allowed to vary. The following parameters were refined simultaneously: an overall scale factor, a type-II isotropic extinction factor (Becker and Coppens 1975), site occupancies of Mg and Fe in the M1, M2, M3, and M4 sites, atomic positional coordinates, and anisotropic displacement parameters (except for H). The crystal structure at 140 K was refined using the parameters derived from the refinement at 295 K. Because of the very small amount of Fe in M1, M2, and M3, these sites were assumed to be filled completely by Mg in the subsequent refinements. Difference-Fourier maps obtained at convergence of the refinements for both the 140 and 295 K data sets revealed no significant positive or negative peaks at the A- or O3-site position, indicating full vacancy of the A site and the absence of a significant amount of F in the O3 site; however, an appreciable residual electron density near the M4 site was detected: 0.24 and 0.22 e/Å<sup>3</sup> for the data at 140 and 295 K, respectively. The position of the electron-density residue is displaced along the diad axis toward the octahedral strips and has been called the M4' site by Ungaretti et al. (1981). The total electron density in the position of the residual peak corresponds to a site fraction of approximately 0.009 Fe. Considering the experimental uncertainties, this amount of Fe is equal to the refined Fe site occupancy (0.007) in the M4 + M4' site, which is consistent with occupancy of the M4' site by Fe. However, in a sample as rich in Mg as CG-1, equilibrium intrasite fractionation of Mg and Fe (e.g., Hirschmann et al. 1994, Fig. 4) would require us to infer that a sizeable fraction of the M on M4' be Mg. We note that a site fraction up to 0.02 Mg has been determined in M4 in several actinolite samples, especially those reequilibrated at high temperature (Skogby and Annersten 1985; Skogby 1987; Yang and Evans, unpublished data).

The above observations are in agreement with those of Ungaretti et al. (1981) and Oberti et al. (1993), who showed that the M4' site in calcic and sodic-calcic amphiboles is primarily occupied by relatively small cations, such as Fe, Mn, and Mg. A split M4-site model was there-

**TABLE 3.** Atomic positional coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for tremolite at 140 and 295 K

| Site         | x           | y          | z           | B        |
|--------------|-------------|------------|-------------|----------|
| <b>140 K</b> |             |            |             |          |
| M1           | 0           | 0.08775(4) | 0.50000     | 0.29(1)  |
| M2           | 0           | 0.17639(4) | 0           | 0.31(1)  |
| M3           | 0           | 0          | 0           | 0.29(2)  |
| M4           | 0           | 0.27822(3) | 0.50000     | 0.36(1)  |
| M4'          | 0           | 0.259(2)   | 0.50000     | 1.7(9)   |
| T1           | 0.28039(4)  | 0.08416(2) | 0.29742(8)  | 0.26(1)  |
| T2           | 0.28824(4)  | 0.17133(2) | 0.80493(8)  | 0.28(1)  |
| O1           | 0.11179(11) | 0.08596(6) | 0.21767(22) | 0.39(2)  |
| O2           | 0.11860(11) | 0.17124(6) | 0.72418(21) | 0.40(2)  |
| O3           | 0.11027(16) | 0          | 0.71599(31) | 0.43(3)  |
| O4           | 0.36514(12) | 0.24820(6) | 0.79245(22) | 0.43(2)  |
| O5           | 0.34644(11) | 0.13458(6) | 0.10096(21) | 0.41(2)  |
| O6           | 0.34384(11) | 0.11833(6) | 0.59009(21) | 0.39(2)  |
| O7           | 0.33726(16) | 0          | 0.29140(31) | 0.45(3)  |
| H            | 0.207(4)    | 0          | 0.780(7)    | 2.3(9)   |
| <b>295 K</b> |             |            |             |          |
| M1           | 0           | 0.08769(4) | 0.50000     | 0.47(2)  |
| M2           | 0           | 0.17653(4) | 0           | 0.48(2)  |
| M3           | 0           | 0          | 0           | 0.47(2)  |
| M4           | 0           | 0.27812(3) | 0.50000     | 0.66(1)  |
| M4'          | 0           | 0.261(2)   | 0.50000     | 2.7(1.0) |
| T1           | 0.28006(4)  | 0.08408(2) | 0.29689(7)  | 0.39(1)  |
| T2           | 0.28825(4)  | 0.17112(2) | 0.80447(8)  | 0.41(1)  |
| O1           | 0.11186(11) | 0.08605(6) | 0.21749(19) | 0.52(2)  |
| O2           | 0.11871(10) | 0.17120(6) | 0.72414(19) | 0.55(2)  |
| O3           | 0.11036(16) | 0          | 0.71619(28) | 0.65(3)  |
| O4           | 0.36531(11) | 0.24781(7) | 0.79313(19) | 0.65(2)  |
| O5           | 0.34592(11) | 0.13402(6) | 0.09930(19) | 0.64(2)  |
| O6           | 0.34355(11) | 0.11863(6) | 0.58847(19) | 0.64(2)  |
| O7           | 0.33662(16) | 0          | 0.29264(29) | 0.72(3)  |
| H            | 0.206(3)    | 0          | 0.771(6)    | 2.3(1.0) |

Note: Refined parameters are for the split-site model. M4 and M4' refined independently.

fore adopted for the tremolite in this study. Because the separation between the M4 and M4' sites (~0.32 Å) is far shorter than the spatial resolution of the diffraction data collected on our crystal, the individual cation site occupancies of the M4 and M4' sites were not refined; Ca and Na were assigned to the M4 site and Fe to the M4' site. The constraint of full occupancy of M4 + M4' was applied, and the M4' site was refined with an isotropic displacement parameter. Unit-cell dimensions and final refinement statistics are presented in Table 2. Atomic positional coordinates and isotropic displacement parameters are listed in Table 3 and anisotropic displacement factors in Table 4.<sup>1</sup> Selected interatomic distances are given in Table 5.

## RESULTS AND DISCUSSION

### The split M4 site

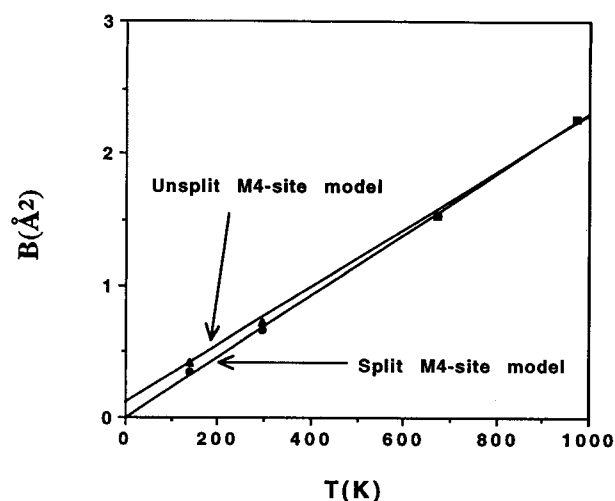
The basic features of the tremolite structure at 295 K determined in this study are very comparable to those reported by Papike et al. (1969). However, we observed, in addition, the split M4 site in a nearly end-member

<sup>1</sup> A copy of Table 4 may be ordered as Document AM-96-625 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

**TABLE 5.** Selected interatomic distances (Å) for tremolite at 140 and 295 K

|            | 140 K    | 295 K    |
|------------|----------|----------|
| T1-O1      | 1.602(1) | 1.600(1) |
| T1-O5      | 1.633(1) | 1.633(1) |
| T1-O6      | 1.631(1) | 1.630(1) |
| T1-O7      | 1.620(1) | 1.619(1) |
| Avg.       | 1.622    | 1.620    |
| T2-O2      | 1.612(1) | 1.612(1) |
| T2-O4      | 1.588(1) | 1.587(1) |
| T2-O5      | 1.658(1) | 1.656(1) |
| T2-O6      | 1.677(1) | 1.676(1) |
| Avg.       | 1.634    | 1.633    |
| M1-O1 × 2  | 2.065(1) | 2.067(1) |
| M1-O2 × 2  | 2.078(1) | 2.081(1) |
| M1-O3 × 2  | 2.084(1) | 2.087(1) |
| Avg.       | 2.076    | 2.078    |
| M2-O1 × 2  | 2.130(1) | 2.134(1) |
| M2-O2 × 2  | 2.087(1) | 2.088(1) |
| M2-O4 × 2  | 2.015(1) | 2.019(1) |
| Avg.       | 2.077    | 2.080    |
| M3-O1 × 4  | 2.069(1) | 2.073(1) |
| M3-O3 × 2  | 2.062(2) | 2.062(2) |
| Avg.       | 2.067    | 2.069    |
| M4-O2 × 2  | 2.402(1) | 2.405(1) |
| M4-O4 × 2  | 2.326(1) | 2.327(1) |
| M4-O6 × 2  | 2.537(1) | 2.535(1) |
| M4-O5 × 2  | 2.748(1) | 2.766(1) |
| Avg.       | 2.503    | 2.508    |
| M4'-O2 × 2 | 2.13(2)  | 2.17(3)  |
| M4'-O4 × 2 | 2.281(2) | 2.285(3) |
| M4'-O6 × 2 | 2.80(2)  | 2.77(3)  |
| M4'-O5 × 2 | 2.96(2)  | 2.95(3)  |
| Avg.       | 2.54     | 2.55     |
| M4-M4'     | 0.35(3)  | 0.31(4)  |
| O3-H       | 0.92(4)  | 0.91(3)  |

tremolite with, according to the microprobe analysis (Table 1), only 0.7% site occupancy of M(Fe + Mg) in the M4 site. Splitting at the M4 site has been found in numerous calcic and sodic-calcic amphiboles containing significant amounts of Mn, Fe, and Mg in the M4 site (e.g., Ungaretti et al. 1981; Ghose et al. 1986; Oberti et al. 1993; Oberti and Ghose 1993; Yang and Evans, unpublished data) and in the M2 site of calcic clinopyroxenes (e.g., Bruno et al. 1982; Rossi et al. 1987; Tribaudino et al. 1989; Benna et al. 1990). The study by Rossi et al. (1987) using single-crystal X-ray diffraction and transmission electron microscopy showed that the split M2 site is a real feature of the clinopyroxene structure and is closely related to the chemical composition of the M2 site. Because of the split M4 site, Fe in the M4' site assumes a coordination environment that is considerably more suitable for it than the standard M4 site. In fact, the M4' cation has a 4 + 4 coordination: four O atoms (two O2 and two O4) at an average distance of 2.21 Å and four (two O5 and two O6) at 2.88 Å (Table 5). The coordination of the M4' site in calcic-sodic amphiboles has been compared to that of the M4 site in Fe- and Mn-bearing magnesio-cummingtonite (Ungaretti et al. 1981; Oberti et al. 1993; Oberti and Ghose 1993). Our results show that the coordination of the M4' site in tremolite is very comparable to that of the M2' site in diopside containing a certain amount of Mg in the M2' site (Bruno et al. 1982; Rossi et al. 1987; Tribaudino et al. 1989; Benna

**FIGURE 1.** Isotropic displacement factors for the M4 site of tremolite as a function of temperature. Circles = split M4-site model, triangles = unsplit M4-site model, and squares = tremolite of Sueno et al. (1973).

et al. 1990). On the other hand, Ca + Na in tremolite retains a coordination similar to that obtained from the nonsplit M4-site model, the differences being within experimental error.

In Figure 1, the isotropic displacement factors of the M4 cation are plotted against temperature. To define better the relationship between the isotropic displacement parameter and temperature, the isotropic displacement factors for the tremolite M4 cation at 673 and 973 K reported by Sueno et al. (1973) were added to Figure 1. It can be seen that for the nonsplit M4-site model, when the trend of *B* factors of the M4 cation is extrapolated to 0 K, the value of *B* is significantly above 0 (0.14 Å²), which is consistent with the presence of positional disorder in the M4 site. On the other hand, when the *B* factors of the M4 cation for the split M4-site model are extrapolated to 0 K, the trend passes close to the origin (0.03 Å²). These results agree fully with those obtained for Ca<sub>0.8</sub>Mg<sub>1.2</sub>Si<sub>2</sub>O<sub>6</sub> clinopyroxene by Benna et al. (1990).

#### Crystal chemistry of the split M4 site

The existence of site splitting has been found in several minerals, including amphiboles, clinopyroxenes, and feldspars (e.g., Ungaretti et al. 1981; Tribaudino et al. 1989; Rossi et al. 1989). It is generally agreed that two factors are important for the development of site splitting, providing that the site symmetry allows at least one variable positional coordinate: a large cavity and two or more cation species having considerably different sizes and bonding characteristics. According to Megaw (1968a, 1968b), the minimal energy of a structure can be achieved when two cations of different sizes occupy a polyhedron with the smaller one displaced from the polyhedral center. In the case of tremolite, the size and bonding characteristics of the small cation (Fe or Mg) differ markedly

from those of the large cations Ca and Na, and hence the small cations energetically prefer a configuration that is different from that of Ca and Na in the M4 cavity. In other words, the standard M4 site, which is occupied by Ca and Na, is oversized for Fe and Mg. As a result, the smaller cation tends to move toward the underbonded O2 and O4 atoms so that the charge balance of O2 and O4 can be improved and the potential energy of the structure minimized.

There are many strong similarities between the crystal structures of tremolite and diopside, the pyroxene analog of tremolite (Sueno et al. 1973; Hawthorne 1983). Unlike tremolite, though, pure end-member diopside can be easily synthesized experimentally using various methods (see Cameron and Papike 1981, and references therein). Therefore, a comparison of the structure of tremolite, particularly the configuration of the M4 site, with that of diopside will help us gain insight into the "pure" tremolite problem. It can be seen from Table 6 that, although the M4 site in tremolite is always slightly depleted in Ca, its average M4-O bond length and polyhedral volume are slightly larger than those of the M2 site in diopside, which is completely filled by Ca. The M4 polyhedron in tremolite is also more distorted than the M2 polyhedron in diopside. The degree of distortion of the M4 polyhedron ( $D^{M4}$ ) in tremolite was calculated from the definition introduced by Bruno et al. (1982) for the M2 polyhedron ( $D^{M2}$ ) in calcic clinopyroxene. The  $D^{M2}$  parameter is defined as the difference between the longest M2-O3' bond length and the average of the three shortest ones (M2-O1, M2-O2, and M2-O3). By analogy,  $D^{M4}$  is defined as the difference between the M4-O5 bond length and the average of the M4-O2, M4-O4, and M4-O6 bond distances. The great similarities between tremolite and diopside suggest that, relative to the M2 polyhedron in diopside, the large distortion and volume of the M4 polyhedron in tremolite must at least be considered as potential factors responsible for the deviation of the Ca/M ratios in natural and synthetic tremolite samples from the ideal ratio of 2/5. The relatively large degree of distortion and volume of the M4 polyhedron in tremolite can create some strain effects around the M4 site; these strain effects can be reduced by substitution of the smaller cations (Fe and Mg) for the larger ones (Ca and Na), resulting in the slight depletion of Ca in the M4 site. Another parameter that is helpful in understanding the nature of the nonideal Ca/ $\Sigma$  M ratio in tremolite is the bond valence. On the basis of the scheme of Brown and Wu (1976), we calculated the bond valence of Ca in both tremolite and diopside using the data of Bruno et al. (1982) and this study. The bond valence of Ca in the M4 site in tremolite is  $\sim 1.96$ , indicating that the M4 cation is slightly underbonded, whereas Ca in diopside has a perfect bond valence of 2.00. This difference suggests that, to improve its bonding situation, the M4 site in tremolite prefers to incorporate some cations with relatively small size, high charge, or both, such as  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$ . This negative contribution to the enthalpy of solution of cum-

**TABLE 6.** Comparison of the configuration of the M4 polyhedron in tremolite with that of the M2 polyhedron in diopside

| Tremolite<br>(295 K, this study) |       | Diopside<br>(Bruno et al. 1982) |       |
|----------------------------------|-------|---------------------------------|-------|
| M4-O2 ( $\text{\AA}$ )           | 2.405 | M2-O1                           | 2.361 |
| M4-O4                            | 2.327 | M2-O2                           | 2.337 |
| M4-O6                            | 2.535 | M2-O3                           | 2.566 |
| M4-O5                            | 2.766 | M2-O3'                          | 2.724 |
| Avg.                             | 2.508 |                                 | 2.497 |
| $V (\text{\AA}^3)$               | 26.20 |                                 | 25.73 |
| $D (\text{\AA})^*$               | 0.346 |                                 | 0.303 |
| Bond valence                     | 1.964 |                                 | 2.002 |

\* See text for the definition.

mingtonite in tremolite is clearly relevant to the issue of its nonideal Ca/ $\Sigma$  M ratio.

### Cell dimensions of tremolite

The fine grain size of synthetic tremolite has generally meant that its composition could be determined only by mass balance among reaction products and by X-ray diffraction. The latter method requires the existence of a reliable reference standard, preferably a tremolite sample with the ideal composition. Unfortunately, certain tremolite samples that have been characterized by X-ray diffraction and have come to be regarded as standard material are off-composition. The data reported by Borg and Smith [1969; cell volume  $904.2(6) \text{\AA}^3$ ] are from sample G-21 from Gouverneur, New York (Ross et al. 1968, 1969; Papike et al. 1969). G-21 contains significant amounts of Al, Mn, Na, and F and has about 2–3 mol% cummingtonite (some of this is exsolved), although our reanalysis of this sample indicates 4–6 mol% cummingtonite. A cell volume of  $905.6(2) \text{\AA}^3$  reported by Hewitt (1975) for tremolite from Richville was adopted for standard-state tremolite by Berman (1988), and the same value is listed in Holland and Powell (1990). This tremolite contains 1.5 wt% F, 1.62 wt%  $\text{Na}_2\text{O}$ , and 1.84 wt%  $\text{Al}_2\text{O}_3$ . Tremolite from Saint Gotthard, Switzerland (Slaughter et al. 1975; Eggert and Kerrick 1981; Skippen and McKinsty 1985), seems to be extremely pure and would appear to contain no cummingtonite component (atomic proportions of Ca/ $\Sigma$  M = 0.435 and Si + Al = 7.93 pfu should be confirmed by reanalysis). Krupka et al. (1985) measured the volume of this tremolite to be  $906.21 \text{\AA}^3$ , although Skippen and McKinsty (1985) gave  $902.22(19) \text{\AA}^3$  for the same sample.

The sample we studied, CG-1, is from a paragenesis (tremolite + calcite + quartz) representing a much lower temperature than ordinarily used in the synthesis of tremolite, and it is among the purest, nearest end-member tremolite samples available (Graham et al. 1989; Welch and Pawley 1991). Until even purer material becomes available, we believe it is the best choice for a reference tremolite. It contains in solid solution  $\sim 1$  mol% magnesio-cummingtonite,  $\sim 0.6$  mol% ferroactinolite, and  $\leq 1$  mol% fluortremolite (Table 1). We obtained unit-cell volumes of 906.4, 906.4, and  $906.8(2) \text{\AA}^3$  on three single

crystals of this material. Using powder X-ray diffraction, David Bish (personal communication, 1995) determined a unit-cell volume of  $906.64(8) \text{ \AA}^3$  for CG-1, corrected for preferred orientation using GSAS (Larson and Von Dreele 1988). These results suggest that the volume of  $904.8 \text{ \AA}^3$  reported for this sample by Welch and Pawley (1991) is 0.2% too low. For a best estimate of the cell volume of pure ( $\text{Ca/Mg} = 0.4$ ) tremolite, we applied minor corrections for the minimal amounts of cummingtonite (Hirschmann et al. 1994), ferroactinolite (Ernst 1966), and fluortremolite (Raudsepp et al. 1991) impurities in CG-1 and suggest a value of  $907.0 \text{ \AA}^3$ .

Synthetic tremolite synthesized from stoichiometric starting materials has cell volumes reported to range from  $902.0$  to  $907.8 \text{ \AA}^3$  (Colville et al. 1966; Oba 1980; Troll and Gilbert 1972; Wones and Dodge 1977; Skippen and McKinstrey 1985; Jenkins 1987; Pawley et al. 1993; Smelik et al. 1994; Maresch et al. 1994; Hoschek 1995; Zimmermann et al. 1996). It is clear that the X-ray cell data for tremolite in the literature vary considerably in quality, and probably little insight would be gained by examining them for small systematic differences in cell volumes that might relate to composition, particularly in the case of synthetic tremolite, which tends to have broad reflections. The cell volumes of  $904.0$ – $904.4(4) \text{ \AA}^3$  of high-temperature tremolite starting material prepared by Jenkins (1987), Pawley et al. (1993), and Smelik et al. (1994; one of two), assuming linearity with composition, are certainly consistent with 8–10 mol% magnesio-cummingtonite in solution, as claimed by these authors.

An alternative measure of the cummingtonite content of tremolite is provided by the  $\beta$  angle. Sample CG-1 has a  $\beta$  angle of  $104.75$ – $104.78(1)^\circ$  (this study), whereas the synthetic tremolite of Jenkins (1987), Pawley et al. (1993), and Smelik et al. (1994) has  $\beta = 104.53$ – $104.58^\circ$ . Pure magnesio-cummingtonite has  $\beta = 102.1(1)^\circ$  (Hirschmann et al. 1994). Tremolite from calc-silicate parageneses has values averaging  $104.75^\circ$  (Zussman 1959; Papike et al. 1969; Hewitt 1975; Krupka et al. 1985; Skogby 1987; Comodi et al. 1991). On the basis of the  $\beta$  angle, the synthetic tremolite of Jenkins (1987), Welch and Pawley (1991), and Smelik et al. (1994) has about 9 mol% cummingtonite component. The tremolite synthesized by Maresch et al. (1994) has on average slightly larger  $\beta$  angles, perhaps reflecting the lower temperatures of synthesis (see below).

Maresch et al. (1994) correctly noted that the presence of chain-multiplicity faults in synthetic tremolite can seriously bias the estimate of composition toward more Mg-rich values when a mass-balance method is used. The newer X-ray data now available suggest that accurate cell-volume and  $\beta$ -angle measurements can in principle be used to show that synthetic tremolite is typically enriched in the cummingtonite component. However, recent syntheses of calcic amphibole with the aid of a saline aqueous fluid of appropriate composition and ionic strength have yielded crystals large enough for chemical analysis by electron microprobe (Gottschalk 1994, 1995; Knop et

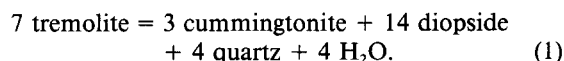
al. 1993; Zimmermann et al. 1996), and so the indirect analytical methods may no longer be so important.

### Thermodynamic considerations

The use of aqueous calcium chlorides and bromides in the synthesis of tremolite overcomes certain kinetic barriers in that crystal sizes are much larger and chain-multiplicity faults are minimal (Gottschalk 1995; Zimmermann et al. 1996). Zimmermann et al. (1996) found  $\text{Ca/Mg}$  ratios ranging from 0.33 to 0.40 in tremolite grown at  $800^\circ\text{C}$  and 2 kbar, with an average of 0.368 ( $\text{Cum}_6\text{Tr}_{94}$ ). The fact that the off-composition nature of synthetic tremolite mirrors that of natural tremolite suggests to us, as it has to others, that a more fundamental issue of energetics, rather than kinetics, governs its composition in both cases.

Site splitting on the M4 site eases the problem of structural mismatch between Ca and Mg, and so provides some enthalpic stabilization to tremolite-cummingtonite solutions. However, the presence of a broad solvus between cummingtonite and tremolite implies, in the usual way, a large positive enthalpy of solution resulting from the structural mismatch of unlike atoms. Both sources of solution enthalpy are proportional to composition along the join, and both tend to zero as pure tremolite is approached. Thus, we cannot account for the off-composition character of tremolite simply in terms of the enthalpic consequence of site splitting. On the other hand, a configurational entropy drive encouraging solution exists whether we consider Ca and Mg to reside on one type of M4 site or a split site.

An explanation for off-composition tremolite can be found by considering appropriate heterogeneous equilibria involving tremolite. At high temperatures (roughly  $970^\circ\text{C}$  at 2 kbar, according to data in Berman 1988 and Ghiorso et al. 1995) there is a metastable equilibrium among the following five phases:

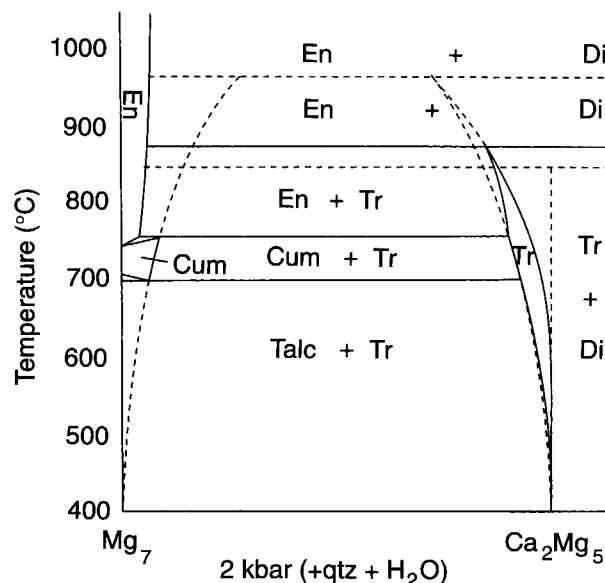


The isobarically invariant composition of tremolite in this equilibrium is of course that of the tremolite-cummingtonite (or anthophyllite) solvus, which we can infer by extrapolation from natural parageneses to be roughly  $\text{Tr}_{75}\text{Cum}_{25}$  (Fig. 2). At progressively lower temperatures, the compositional width of the tremolite field must first expand from this metastable invariant point and cover less magnesian compositions because it is constrained on the Mg-rich side by the solvus. Adopting the reasonable crystal-chemical assumption that no Ca is possible on the M1, M2, and M3 sites, the  $\text{Ca/Mg}$  ratio of tremolite approaches, but does not exceed, the theoretical ideal at low temperature. The Mg-rich limit to the stable field of tremolite is, for the most part, less magnesian than that of the solvus (Fig. 2). Our Figure 2 is an expansion of the same  $T$ - $X$  section by Jenkins (1987, Fig. 6) and Graham et al. (1989, Fig. 9). Its qualitative form may be derived from free energy-composition relations drawn at different tem-

peratures, using the method of tangents, and assuming that there is a solvus. Figure 2 is consistent with the observation that nearly all analyzed natural tremolite in metamorphic rocks (ultramafics, calc-silicates, and impure marbles) is enriched in cummingtonite relative to ideal tremolite (Jenkins 1987) and with the rare occurrence of near-end-member tremolite in metacarbonate rocks (Graham et al. 1989). Jenkins (1987) showed that high-temperature (795 and 882 °C), hydrothermal, quartz-saturated treatment of natural high-Ca/Mg tremolite yields a residue (<2 vol%) of clinopyroxene. Figure 2 is also consistent with the presence of cummingtonite exsolution lamellae in actinolite in metamorphic parageneses containing calcic pyroxene (e.g., sample 11 in Klein 1966). It is also consistent with the fact that secondary fibrous (uralitic) tremolite and actinolite, formed by replacement of clinopyroxene, has  $\text{Ca}/\Sigma \text{M}$  close to, but still slightly less than 0.4.

Thus, the general failure to obtain 100% yields of tremolite in syntheses at 700–880 °C from starting materials of pure tremolite composition ( $\text{Ca}/\text{Mg} = 0.4$ ) reflects the instability of end-member tremolite at these temperatures with respect to cummingtonite-enriched tremolite + diopside + quartz +  $\text{H}_2\text{O}$ . In this regard, the results of synthesis, the compositions of natural tremolite, and theoretical prediction are mutually consistent. The cummingtonite-bearing character of calcic amphibole is evidently not limited to tremolite and the actinolite series but is a general feature, having been shown to exist along the synthetic joins connecting tremolite to tschermakite (Ellis and Thompson 1986; Cao et al. 1986; Jenkins 1988, 1994; Cho and Ernst 1991; Smelik et al. 1994; Hoschek 1995; Gottschalk 1995), to richterite (Pawley et al. 1993), and to pargasite (Oba 1980; Sharma 1993, 1996). To generalize (and perhaps state the obvious), one can expect this behavior when the components of the amphibole being synthesized, or forming in nature, are also those of other amphibole end-members, such that the free energy of the system can be minimized by forming an amphibole solid solution, plus compositionally balancing phases. Riebeckite is another example, behaving exactly like tremolite. As it approaches the temperature of its breakdown to acmite, fayalite, quartz, and  $\text{H}_2\text{O}$ , riebeckite accommodates increasing amounts of grunerite in solid solution (Owen 1988), despite the fact that acmite is nominally free of  $\text{Fe}^{2+}$ . The phase diagram for riebeckite is topologically the same as Figure 2, with components Na,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  substituting for Ca and Mg.

According to Figure 2, the upper temperature stability limit of end-member tremolite is hundreds of degrees Celsius lower than that of tremolite in the stable breakdown assemblage of tremolite + enstatite + diopside + quartz +  $\text{H}_2\text{O}$ . Not surprisingly, this enormous difference did not show up in a comparison of bracketing experiments on natural end-member tremolite (CG-1) and synthetic tremolite (Welch and Pawley 1991; Jenkins et al. 1991). Welch and Pawley (1991) studied the metastable breakdown of end-member tremolite. High-temperature



**FIGURE 2.** Schematic diagram of phase relations along the pseudobinary join  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ – $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , showing the envelopes of stable (solid lines) and metastable (dashed lines) tremolite compositions. Magnesio-cummingtonite is depicted rather than the slightly more stable anthophyllite; this has little effect on the tremolite field.

experiments documenting progress in the reaction of end-member tremolite to Mg-enriched tremolite + diopside + quartz +  $\text{H}_2\text{O}$  (Fig. 2) would clearly be enlightening. When the objective is to synthesize tremolite with ideal composition, temperature should be kept as low as possible.

A paper by Hawthorne (1995) on end-member monoclinic amphiboles appeared as the revised version of this paper was being finalized. Hawthorne ascribes the occurrence of off-composition and site- and stacking-disordered “end-members” to the additional stabilization provided by configurational entropy. In the case of tremolite, we are in agreement. We believe that our approach to the problem is more complete because we go beyond the intrinsic properties of tremolite and view the problem in terms of minimizing the free energy of the appropriate heterogeneous system, albeit qualitatively at this stage. In addition, the energy balance (Eq. 1), taken as a four-phase system (with amphibole solid solution), allows some predictions to be made with regard to the maximum Ca/Mg ratio of tremolite as a function of temperature, pressure, and activities of  $\text{SiO}_2$  and  $\text{H}_2\text{O}$ .

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