Biopyribole evolution during tremolite synthesis from dolomite and quartz in CO2-H2O fluid

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ABSTRACT

A series of experiments with and without sample retreatment was performed on a starting mixture of dolomite plus quartz at 0.5 GPa and 600 °C in a CO2-H2O fluid with a mole fraction of CO2 of 0.2 for durations up to 582 h. The initial reaction of dolomite and quartz led to rapid formation of talc and calcite instead of tremolite and calcite by the intended reaction: 5 dolomite + 8 quartz + H2O = tremolite + 3 calcite + 7 CO2. With continued treatment, the talc + calcite + quartz assemblage gradually reacts to form increasing amounts of tremolite and diopside with the eventual loss of quartz and nearly complete loss of talc.

The detailed structure of the amphibole and the nature of the Mg enrichment were revealed using AEM analysis of individual amphibole crystals. The most abundant defects are triple-chain chain multiplicity faults (CMFs), which appear as isolated lamellae with single periodicity in short-duration experiments and increasingly as groups of lamellae with variable multiplicity and periodicity in longer duration experiments and especially in a long-duration experiment without retreatment. In this latter experiment, a calcian clinopyrothompsonite domain extending 15 unit cells along the b axis was observed. The sample after 582 h and five retreatments shows, on average, 3.5% true solid solution with Mg expressed as the Mg-cummingtonite (MC) component after correction for the presence of CMFs. This sample is thought to most closely approach the equilibrium composition for the amphibole. The sample after 250 h with three retreatments has about 10%, whereas that after 582 h without retreatment has 0.6% MC component, the latter having a relatively high density of CMFs. This study affirms the importance that precursor non-amphibole biopyriboles play in the formation of tremolitic amphibole.

Keywords: Tremolite, HRTEM, analytical electron microscopy, mineral growth, calcian clinopyrothompsonite

INTRODUCTION

Synthetic tremolite is known to form with about 3–7 mol% Mg, or 0.06–0.14 atoms per formula unit (apfu), appearing to replace Ca in the M4 site and shifting it slightly from its ideal composition Ca2Mg5Si8O22(OH)2 (e.g., Jenkins 1987; Graham et al. 1989; Maresch et al. 1994; Zimmerman et al. 1996; Gottschalk et al. 1999; Bozhilov et al. 2004). The great level of interest that this relatively minor deviation from ideal composition has generated stems from the far-reaching implications that it has on such things as: (1) the role that chain multiplicity faults (CMFs) vs. solid solution plays in controlling the bulk mineral composition (Ahn et al. 1991; Maresch et al. 1994); (2) the effect that configurational entropy, arising from cation disorder, can have on stabilizing non-ideal mineral compositions (Hawthorne 1995); (3) the influence that the mineral-forming process (the reaction path) can have on the final mineral composition (Maresch et al. 1994; Bozhilov et al. 2004); and even (4) the relevance of experimental studies on the phase equilibria and thermodynamic properties of tremolite and perhaps other Mg-rich amphiboles. Essentially all of the tremolite synthesis studies have used starting mixtures consisting of gels or mixtures of oxides, carbonates, and hydroxides. These are, however, highly unusual starting materials compared to nature, where the precursor phases to tremolite formation, though rarely preserved, are mixtures of common minerals such as dolomite, calcite, talc, clay minerals, quartz, etc. As a companion to the earlier studies that considered tremolite formation from starting mixtures of amorphous gels or oxide mixtures (e.g., Maresch et al. 1994; Bozhilov et al. 2004), the present study deals with the formation of tremolite from dolomite + quartz in a CO2-H2O fluid; this has greater relevance to nature.

EXPERIMENTAL METHODS

Starting materials and sample treatment

Natural white dolomite (northwest Adirondacks, New York) and quartz (locality unknown) were used in this study. Microprobe analysis (procedure described below) of the dolomite indicated that it was unzoned and had a uniform composition of Ca0.99(10)Mg0.00(10)Fe0.00(10)(CO3)2(OH)2, where the number in parenthesis is the uncertainty in the last digit. Dolomite and quartz were ground (but unsized) and mixed in the weight proportions of dolomite to quartz of 65.7 to 34.3 wt%, respectively,
which is in the molar ratio of dolomite:quartz of 5:8 necessary to form tremolite according to the reaction:

$$5\text{Ca}\text{Mg}(\text{CO}_3)_2 + 8\text{SiO}_2 + \text{H}_2\text{O} = \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 3\text{CaCO}_3 + 7\text{CO}_2$$  (1)
dolomite quartz tremolite calcite

This reaction is shown by the solid crossing tie lines in Figure 1a. Mixed-volatile CO$_2$-H$_2$O fluids were made using mixtures of water and oxalic acid dihydrate (Holloway et al. 1968). All treatments were made in sealed Pt capsules with a fluid: solid ratio of 1:3 by mass in internally heated gas vessels using argon as the pressure medium. Temperatures were measured with two grounded K-type chromel-alumel thermocouples placed at each end of the capsule. The thermocouples were calibrated using the freezing points of NaCl (800.5 °C) and LiCl (605 °C), and are accurate to ±2 °C. Uncertainties in temperature largely result from the thermal gradient along the sample between the thermocouples, rather than the uncertainties in the accuracy or temperature fluctuations during the treatment. Pressures were measured with both a bourdon-tube gauge and a factory-calibrated Harwood Engineering manganin cell, and are considered accurate to ±0.005 GPa.

The following procedure was used in this study. Experiments were done by combining and arc-welding the dolomite-quartz starting mixture, oxalic acid dihydrate, and distilled water in a Pt capsule. Weight measurements were taken before and after the welding process to check for fluid loss. Special care was taken during the welding process to minimize the loss of fluid by wrapping the capsule in a moist tissue and welding the capsule in short intervals to decrease the heat uptake by the capsule. Loss of mass during the welding process was assumed to be primarily the loss of platinum from the capsule during welding. This assumption was checked in a test experiment where only oxalic acid dihydrate and water were sealed in a Pt capsule that was then heated to 600 °C at 0.5 GPa. The mass of the fluid before the welding process and after the experiment was quenched were nearly identical, indicating that the loss of mass during welding was due to the loss of platinum. The soundness of the capsule was ensured by measuring the weight of the capsule before and after the experiment.

Throughout each set of experiments, the reaction progress was monitored by stopping the experiment at regular intervals, analyzing the charge, and subsequently retreating the material with an additional amount of fluid—still in the fluid:solid ratio of 1:3 by mass. Throughout this study, these steps will be referred to as the retreatment process. Care was taken to disturb the sample as little as possible upon removal from the capsule to maintain reaction textures. To achieve this, the charge was broken up with a teasing needle rather than by re-grinding. Measuring the loss of CO$_2$ from the sample after each quench provided an additional means of monitoring the reaction progress. This was done through a simple puncture-and-weigh technique with a precision of ±0.1 mg. Total water loss, or gain, by the solids was measured by drying the opened capsule at 110 °C for at least 1 h.

**Analytical techniques**

All samples were routinely analyzed by powder X-ray diffraction (XRD) using a Philips PW3046-MPD X-ray diffractometer located at Binghamton University. Operating conditions were 40 kV and 20 mA using CuKα radiation and a graphite diffracted-beam monochromator over the range of 8–40 °2θ.

Proportions of phases present were determined from Rietveld refinements of the powder XRD patterns using the program DBWS 9411 (Young et al. 1995). Due to the simple crystal chemistry of the phases present, the Rietveld refinements can be used for accurate evaluation of the amount of the phases in the run products even under non-ideal XRD pattern acquisition conditions. Refinements were made using reference structural data for quartz (Lager et al. 1982), talc (Rayner and Brown 1973), calcite (Markgraf and Reeder 1985), tremolite (Hawthorne and Grundy 1976), diopside, (Levien and Prewitt 1981), and dolomite (Reeder and Wenk 1983). Because samples were rather small, particularly toward the end of the series, it was not always possible to keep the sample fully immersed in the X-ray beam at low angles. Consequently, the Rietveld refinements were limited to the range of 12–40 °2θ and only a relatively small number of parameters were included in the refinement. These included the zero-point of 2θ, the background modeled by either a 5- or 6-term polynomial, the scale factors of all phases, and the cell dimensions of the major phases (though only the c parameter of talc that displayed strong 00l preferred orientation).

Individual amphibole grains from selected samples were chemically analyzed using a JEOL 8900 electron microprobe at Binghamton University, operated at 15 kV and 10–30 nA. Powdered samples were dispersed on polished graphite stubs with ethanol and analyzed by energy-dispersive spectroscopy using live counting times of 30 seconds and the beam diameter in the spot mode (~1 μm). Diopside was the standard for Si, Mg, and Ca, and hematite was the standard for Fe. Matrix corrections were made with the ZAF scheme. Because of the small grain sizes, the analytical totals were often well below the expected ideal value of 97 wt% because the excitation volume exceeded the volume of the grain. A lower limit of 65 wt% for the analytical total was adopted (Giblin et al. 1993).

**Figure 1.** (a) Ternary diagram of the system CaO-MgO-SiO$_2$-CO$_2$-H$_2$O projected from CO$_2$ and H$_2$O showing the chemographic relationships among the phases encountered in this study. Solid crossing tie lines illustrate reaction 1 in the text. The dotted lines illustrate the dominant assemblage at the initial stages of reaction whereas the dashed lines illustrate the dominant assemblage at the final stages of reaction. (b) Modal mineralogy as a function of time for the DQ1-6 series listed in Table 3. Errors are the size of the symbol if not shown explicitly. Lines simply connect points of the same phase and have no theoretical basis. Abbreviations are Bulk = bulk composition of the starting mixture; Cal = calcite; Di = diopside; Dol = dolomite; Mg-Cal = magnesium-calcite; Qtz = quartz; and Tr = tremolite.
Transmission electron microscopy

All specimens were studied at an accelerating voltage of 300 kV using a FEI-Philips CM300 transmission electron microscope (TEM), located at the University of California at Riverside, [objective twin-lens with spherical ($C_s$) and chromatic ($C_c$) aberration coefficients of 2.0 mm, LaB$_6$ cathode, double-tilt and rotational low-background specimen holders]. The fine-grained synthesis run products were suspended in distilled water without grinding, and after 5 min agitation with an ultrasonic cleaner were deposited onto holey carbon films supported by copper mesh grids. Selected area electron diffraction (SAED) patterns and high-resolution (HRTEM) images were obtained from about 25 crystals from each sample to study their structure and defects. The HRTEM images were obtained with a 50 μm diameter condenser aperture, effective objective aperture radius of 0.86 nm$^{-1}$, and beam convergence angle of 0.9 mrad. Images were recorded digitally using Gatan 794 Multiscribe CCD camera and GMS version 1.4 software running on a Windows 2000 PC. HRTEM image interpretation is based on comparison with published data and image simulation, which was performed using the MacTemps software version 2.1 for MacOSX.

To study the CMF type, abundance, and structure, the selected crystals were imaged with the electron beam perpendicular to the $b$ axis. The CMF abundance was characterized using the $A'(i)$ value as introduced by Ahn et al. (1991) following Maresch and Czank (1988), where $A'(i)$ is the ratio of the chains with a particular multiplicity ($i$) expressed as the number of SiO$_4$-tetrahedral chains sharing common corners parallel to the $b$ axis vs. the total number of tetrahedral chains in the crystal.

Compositions were determined quantitatively by analytical electron microscopy (AEM) using energy dispersive X-ray spectroscopy (EDS) in the CM300 TEM operated in Nano-probe mode. Analyses were done with an EDAX Phoenix energy dispersive spectrometer with Si(Li) detector and super-ultrathin window, which allows detection and quantification of light elements such as oxygen. The spectra were acquired with an effective spot size diameter of 20 to 100 nm for 60 to 100 s depending on the crystal thickness. It was discovered that analyzing with an effective spot size of less than 10 nm causes appreciable Mg diffusion away from the beam, which can alter the Ca/Mg ratio by up to 20%. To determine the composition of the thin slabs of intergrown biopyrophytes, the slightly defocused electron beam was distorted to elliptical shape with the condenser stigmators so that the signal was collected only from the area of interest. This minimized the contribution of characteristic X-rays from the surrounding matrix while still keeping the beam in a slightly defocused state to minimize rapid beam damage to the specimen and prevent atomic diffusion. The EDS analyses were performed as a rule after HRTEM imaging on areas adjacent to, but not overlapping with, the imaged areas so that any potential beam damage and diffusion artifacts could be avoided. The beam current was not measured directly but beam intensity was kept consistent between analyses by using the auto exposure function of the CM300 to measure the beam intensity.

Chemical analyses with the TEM were performed by applying a modified version of the ionetric approach of Van Cappellen and Doukhan (1994). The traditional ionic approach assumes that all elements in the sample are measured and that there is charge balance, from which absorption corrections are calculated through determination of the sample thickness by iterations of thickness values until the best fit to the stoichiometric formula is achieved. In analyses of amphiboles, this approach is not strictly applicable since the H concentration cannot be measured and assuming charge balance by omitting H leads to underestimates of the sample thickness and consequently incorrect absorption corrections. Our approach was to use two-stage calculations. For the first stage, the sample thickness was determined by assuming ideal stoichiometric oxygen content (61.56 at%) in a perfect tremolite formula and calculating elemental concentrations by subsequent thickness iterations until the expected oxygen concentration is produced. The thickness determined in this manner was subsequently used to reckon the absorption corrections for the constituent cations and calculate their concentrations in terms of oxides without directly calculating oxygen concentrations. The parameterless method (Horita et al. 1989; Van Cappellen 1990) was used to determine experimental $k$-factors for O, Mg, Si, Ca, and Fe using natural mineral standards. The accuracy and precision of the $k$-factor values and the applied quantification procedure were verified by analyses of crushed grains of natural tremolite from St. Gothard, Switzerland, with known composition determined by microprobe analysis (Evans et al. 2000).

For the purpose of comparison with the AEM analyses, the composition of the St. Gothard tremolite was normalized to 100% after omitting hydrogen and elements with concentrations less than 0.1 wt% (Table 1). The statistical variation in the observed concentrations of the major elements in the reference tremolite is less than 5% relative and is in the same range as the statistical uncertainty in X-ray intensity measurement.

RESULTS

Synthesis results

A series of experiments (DQ1-6 series) using the retreatment process was done in this study by treating a starting mixture of dolomite plus quartz at about 0.5 GPa and 600 °C in a fluid with mol fraction of CO$_2$ ($X_{CO_2}$) of 0.2. These conditions are well above the dolomite + quartz reaction boundary and are well inside the tremolite + calcite stability field according to the work of Slaughter et al. (1975). The specific temperatures, pressures, initial fluid compositions, and changes in fluid composition are listed in Table 2. Changes in the modal mineralogy of these samples based on Rietveld analysis of powder XRD patterns are listed in Table 3 and shown in Figure 1b.

Several things should be noted from this time series. At 600 °C, 0.5 GPa, and $X_{CO_2} = 0.2$, dolomite and quartz react very strongly within the first 91 h to form an initial assemblage that is dominated by calcite and talc with the remainder being quartz and a trace of diopside. With continued treatment, the talc + calcite + quartz assemblage gradually reacted to form increasing amounts of tremolite and diopside with the eventual loss of quartz and nearly complete loss of talc (Fig. 1b). This changeover in phase assemblage with time is also shown in the ternary plot of Figure 1a where the dotted lines indicate the initial talc-calcite-quartz-dominant assemblage and the dashed lines indicate the final tremolite-calcite-diopside assemblage. The presence of diopside is expected for the bulk composition used in this study so long as calcite or tremolite (or both) incorporate additional Mg. The unit-cell volumes derived for calcite in this study suggest about 4 mol% MgCO$_3$ component based on the volume-composition relationships for Mg-calcites reported by Mackenzie et al. (1983) and shown as Mg-calc on Figure 1a. Magnesium enrichment in tremolite, either by true solid solution or as apparent enrichment from wide-chain CMFs is discussed at length below. Tremolite was only present in trace amounts (less than ~1 wt%) in the initial stages of the reaction; it was not detectable on the powder XRD patterns but was, instead, visible as occasional needles with the petrographic microscope. The presence of only trace amounts of tremolite early in the reaction history of dolomite + quartz is analogous to the trace amounts of tremolite observed by Bozhilov et al. (2004) early in the formation of tremolite from oxides. In the study of Bozhilov et al. (2004), the dominant phases formed initially were pyroxenes and quartz (rather than talc + calcite) suggesting that a very small percentage of tremolite forms by direct precipitation from the ambient hydrothermal solution.

The crystallization products of experiments DQ1-6b (250 h total run time with retreatment), DQ1-6d (582 h, with retreatment), and DQ1-6L (582 h, no retreatment) were studied by TEM, which yielded the following observations about the grain sizes and habits. The product crystals are generally in the micrometer size range (Table 4). After 250 h of treatment, talc forms nearly equant platy crystals with an average diameter of ~3 μm. The thickness of these platelets is estimated to be about one tenth or less of their lateral dimensions. With reaction progress, the amount of talc decreases, its crystal size decreases to about 0.7 μm in diameter, and aggregates of fine talc crystals (50–100 nm in diameter) become readily noticeable. Calcite, quartz, and diopside form equant crystals with significant variation in
A noticeable difference is that the single-treatment experiment has which resemble closely the short duration experiments. The only without interruption (DQ1-6L) exhibits crystal morphologies, of about 10 and an average width about 0.8

The reaction progress was an initial increase in CO₂ after the samples except DQ1-6L, which is a single treatment without intermittent sampling or renewal of the ambient fluid. The only

Notes:

DQ1-6L 0.500 582 1 6.4(2) 0 67(2) 0 0 0 0
DQ1-6d 0.510 582 1 6.0(2) 0 72(2) 18.6(3) 3.3(3) 0
DQ1-6c 0.500 582 1 6.0(2) 0 72(2) 18.6(3) 3.3(3) 0
DQ1-6b 250 3 6.0(2) 0 72(2) 18.6(3) 3.3(3) 0
DQ1-6c 416 4 0 0 13(2) 18.6(3) 54(3) 14.7(7)
DQ1-6d 582 5 0 0 21(1) 17.3(7) 65(5) 18.1(9)
DQ1-6L 582 1 6.4(2) 0 63(1) 25.5(3) 4.9(4) 0

Notes: The reference analysis was normalized to 100 wt% omitting minor cations and hydrogen. The mean difference was determined as the average of the absolute value of the differences between the reference concentration compared to the 32 individual measurements for each element. The standard deviation in the accuracy is the 1st standard deviation of the mean difference. The standard deviation of the precision is the 1st standard deviation of the average analysis of each element, while the variance is

\[ \sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1} \], where \( x_i \) is each individual measurement, \( \bar{x} \) is the average, and \( n \) is the number of measurements.

An interesting observation is that the long-run experiment without interruption (DQ1-6L) exhibits crystal morphologies, which resemble closely the short duration experiments. The only noticeable difference is that the single-treatment experiment has slightly larger crystal sizes on average (Table 4).

The most noticeable pattern regarding changes in CO₂ with reaction progress was an initial increase in CO₂ after the first treatment (Tables 2 and 3). This is consistent with the observed strong reaction of dolomite and quartz to form calcite and talc. One can use the amount of CO₂ that is produced, particularly in the first treatment, as an additional check on the reaction that is occurring during treatment. According to reaction 1, 0.217 mg CO₂ is produced per milligram of solid starting mixture. For experiment DQ1-6 in Table 2, this would amount to a CO₂ production of 5.8 mg, which is much more than the observed CO₂ production of 3.1 mg. The smaller CO₂ change is closer to what one would expect for the reaction:

\[
3\text{CaMg(CO}_3\text{)}_2 + 4\text{SiO}_2 + \text{H}_2\text{O} = \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{CaCO}_3 + 3\text{CO}_2
\]
dolomite quartz talc calcite tremolite diopside

which produces only 3.8 mg of CO₂ for experiment DQ1-6 when calculated relative to the observed amount of calcite (39 wt%, Table 3). The observed lower value of CO₂ supports the suggestion that reaction 2 is kinetically favorable over reaction 1 at the initial stages of dolomite-quartz reaction. In most cases, smaller
changes in CO₂ were observed after subsequent treatments compared to the initial treatment, indicating that much less reaction involving carbonate minerals was occurring during the retreatments.

**Chemical composition of tremolitic amphibole**

Electron microprobe analyses are listed in Table 5. Due to the small grain size relatively few reliable analyses could be obtained even with a cutoff-minimum analytical total of 65 wt%. For those analyses that were acceptable, the microprobe results show that the Mg contents are higher than the ideal composition for tremolite, with an apparent excess of about 0.1–0.3 Mg atoms per formula unit (apfu) assigned to the M4 site, or an equivalent of 5–15 mol% of the magnesio-cummingtonite [Mg₇Si₈O₂₂(OH)₂ = MC] component.

Average compositions of the amphiboles determined using AEM are listed in Table 5. All analyses are normalized to 100 wt%. There is general agreement between the microprobe and the AEM analyses, particularly for the Ca/Mg ratios, pointing toward significant Mg enrichment in amphibole. Given the better imaging, better fine-grain analytical capabilities, and larger statistical basis for the AEM analyses, we will use these in subsequent discussions in this study. A minor Fe component was observed in all experimental runs, which was not measured by the microprobe analysis.

The issue that must be addressed is the extent to which the Mg enrichment is actually attributed to solid solution of Mg for Ca compared to an apparent enrichment attributed to wide-chain chain multiplicity faults (CMFs), which is discussed below.

**CMF abundances**

The detailed structure of the amphibole and the nature of the Mg enrichment were revealed using HRTEM and EDS analysis of individual amphibole crystals from different treatments. The CMF abundances are summarized in Table 6 where the $A'(i)$ values are listed. The most abundant defects are triple-chain CMFs, which appear mostly as isolated lamellae with single periodicity in the short run DQ1-6b (Fig. 2) and increasingly as groups of lamellae with variable multiplicity in the long-duration experiments (Figs. 3a and 3b) and especially in the run without retreatment (Figs. 4a and 4b). Also wider-than-triple CMFs were more abundant in the long single treatment sample DQ1-6L (Table 6, Figs. 4a and 4b). As a rule, the CMF lamellae cross the entire length of a crystal parallel to $c^*$. The presence of single and quintuple CMFs is noteworthy in the experiments with retreatments (DQ1-6b and DQ1-6d), and their abundance decrease in the run without retreatment (DQ1-6L). In contrast quadruple, sextuple, and octuple CMFs increase their presence in the DQ1-6L run (Fig. 5). Septuple and wider-than-octuple CMFs were not observed.

One of the interesting questions that has arisen in the study of synthetic tremolite is the extent to which the presence of CMFs affects the bulk composition of an amphibole-CMF composite (e.g., Ahn et al. 1991; Maresch et al. 1994). In this study we have sufficient analytical and structural data for the three samples studied here to address this question. The Ca/Mg ratio of a defect tremolite crystal with known $A'(i)$ values and assuming the addition of only Mg-bearing mica modules beyond the initial Ca-bearing pyroxene module (Thompson 1981) is given by:

$$\frac{\text{Ca}}{\text{Mg}} = \frac{2}{\sum_{i} A'(i)(3i - 1)}$$ (3)
Table 6 shows the calculated Ca/Mg molar ratio for the amphiboles in each sample analyzed. In view of the uncertainties in these values, the calculated and observed Ca/Mg values (from Table 5) are statistically identical. The average observed Ca/Mg ratios are, however, systematically lower than the calculated ratios. In all cases, the Ca/Mg ratios are less than 0.400 and one can equate this Mg enrichment to the presence of a certain amount of the MC component (= M4Mg/2). For any given Ca/Mg ratio, the percentage of the MC component is given by:

\[
\text{MC\%} = \left[1 - 2.5\frac{[\text{Ca}]}{[\text{Mg}]}\right] \times 100
\]

(4)

Table 6 lists the MC\% attributed to the CMF concentration in each sample based on the calculated Ca/Mg ratio. Also shown in Table 6 are MC\% values for each sample based on the observed Ca/Mg ratio and the true MC\% values, which are simply the difference between the observed and CMF MC\% values. It appears that the first two samples have significant solid solution with Mg, whereas the last sample (DQ1-6L) does not. These calculations assume that all wide-chain defects have Ca-end-member composition, an assumption justified by direct measurement of an individual triple-chain slab (see below).

From Table 6 it is evident that the CMF values observed in the samples with retreatment (Figs. 2 and 3) are statistically similar to the values from the run without retreatment (Fig. 4), although the spread of CMF density is significantly higher for the latter.

In the short duration experiment, Mg enrichment due to the MC component is relatively high and shows the largest statistical spread. The run with no retreatment (DQ1-6L) shows a very low MC component and a much narrower range of compositions compared to the short runs.

An interesting observation is the presence of diopside crystals with acicular habit and aspect ratio of more than 8. These crystals were observed mainly in the experiments with run interruption. Some of them have developed CMF lamellae, which cross the entire length of the crystals along their c* axis. The main types of defects in such diopside crystals are double-chain amphibole lamellae intergrown occasionally with triple-chain CMFs as seen in Figure 6.

Table 5. Electron microprobe and AEM EDS analysis of selected amphibole grains from the treatments listed in Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>DQ1-6b</th>
<th>DQ1-6d</th>
<th>DQ1-6L</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>55.9(28)</td>
<td>46.1(66)</td>
<td>42.5(27)</td>
</tr>
<tr>
<td>MgO</td>
<td>24.9(17)</td>
<td>21.2(34)</td>
<td>18.2(14)</td>
</tr>
<tr>
<td>CaO</td>
<td>11.5(10)</td>
<td>10.7(16)</td>
<td>9.7(8)</td>
</tr>
<tr>
<td>Total</td>
<td>92.3(50)</td>
<td>78.0(11)</td>
<td>70.4(47)</td>
</tr>
</tbody>
</table>

Table 6. CMF abundance and calculated MC component of selected treatments listed in Table 2 determined by HRTEM and EDS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>DQ1-6b</th>
<th>DQ1-6d</th>
<th>DQ1-6L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Mg</td>
<td>0.39(1)</td>
<td>0.39(2)</td>
<td>0.37(2)</td>
</tr>
<tr>
<td>Ca/Mg</td>
<td>0.34(5)</td>
<td>0.38(1)</td>
<td>0.37(1)</td>
</tr>
</tbody>
</table>

Notes: Values shown are the averages of n analyses with standard deviations in the last digit given in parentheses. Cations per 23 O atoms.

Notes: The calculated Ca/Mg ratio is derived from Equation 3 in the text and is based on the CMF concentrations reported in this table, while the observed Ca/Mg values are from Table 5. The CMF MC\% value is the MC\% associated with the pyrobole chains derived from the calculated Ca/Mg ratio using Equation 4 in the text. The observed MC\% value is the MC\% calculated from the observed Ca/Mg ratio, while the True MC\% is the difference between the observed and the CMF MC\% values.
Direct analysis of a triple-chain lamella in DQ1-6L

Although triple-chain CMFs are the most abundant defects in amphiboles, reliable chemical analysis of triple-chain lamellae has not been possible due to their narrow widths. In the experiment DQ1-6L, run for 582 h, large polysomes of triple-chain structures were formed, which are coherently intergrown with tremolite (Fig. 4a). Defect domains were observed with sizes ranging from 3- to 5-member triple-chain lamellae up to polysomes more than 100 nm in size parallel to the b axis with minor intercalation of double- and quadruple-chain lamellae.

An extended triple-chain pyribole slab was found consisting of a 30-member, triple-chain structure with ideal order corresponding to 15 unit cells with the clinojimthompsonite structure (Figs. 4a and 4b). Careful EDS analyses of this slab were performed using a rotational low-background specimen holder, which allows one to rotate the crystal of interest so that the c* axis of the lamella is oriented parallel to the horizontal projection of the line connecting the detector and the intersection of the incoming electron beam with the specimen. After tilting the specimen by 25° toward the detector, an optimal configuration is achieved that guarantees that the signal coming from the surrounding

FIGURE 3. HRTEM micrographs of amphibole crystals from the DQ1-6d experiment after 582 h of treatment with five retreatments. (a) Relatively low magnification view of a tremolite crystal with isolated CMF lamellae. (b) Higher magnification of a portion of another crystal. Multiplicities of the CMF lamellae are marked on the images.

FIGURE 4. HRTEM micrographs of a crystal from the DQ1-6L experiment after 582 h of treatment without interruption. Numerous CMFs are observed that intersect the entire crystal along its length parallel to the c* axis. (a) Low magnification view of part of the crystal is shown where the entire width of the crystal parallel to the b axis is visible. An extended slab consisting of a perfect triple-chain structure is marked. (b) A magnified view of the triple-chain slab in Figure 4a. The pyribole chains with multiplicity different from three are marked on the image.
matrix is minimized. Further improvement of the signal was obtained by distorting the spot with the condenser stigmators so that an elliptical spot is obtained with elongation parallel to $c^*$ of the lamella. The analyses show almost perfect Ca-end-member triple-chain pyribole (Table 7). There is a slight excess of Ca from the ideal value of 2 apfu that may be due to partial contribution from the double-chain matrix. By analysis of its electron diffraction pattern, the intergrown triple-chain slab has been determined to be monoclinic so that it can be regarded as a calcian analog of clinojimthompsonite.

**DISCUSSION**

**Reaction products and reaction path**

In the present study, the initial reaction of dolomite and quartz leads to the rapid formation of talc and calcite according to reaction 2 instead of the expected reaction 1. It is the strong partitioning of Ca into calcite and Mg into talc, rather than reaction duration, that inhibits the formation of appreciable amphibole in the initial stages of reaction. This is evident from the experiment without retreatment (DQ1-6L) where, after 582 h talc and calcite are still the dominant phases and amphibole is present in minor amounts (Tables 2 and 3). The talc and calcite formed in experiment DQ1-6L clearly represent non-equilibrium because: (1) with successive retreatment the amounts of talc and calcite decrease while amphibole and diopside increase (Fig. 1b) in response to the disruption of the system (see below); and (2) the temperature and fluid composition conditions used here are well outside of the talc + calcite stability field at 5 kbar (Slaughter et al. 1975). The calcite and talc eventually react to form tremolite by the reaction:

$$5 \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6 \text{CaCO}_3 + 4 \text{SiO}_2 = 3 \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 + 2 \text{H}_2\text{O} + 6 \text{CO}_2$$

and diopside by the reaction:

$$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3 \text{CaCO}_3 + 2 \text{SiO}_2 + \text{Ca}_3\text{Mg}_2\text{Si}_5\text{O}_{10} + \text{H}_2\text{O} + 3 \text{CO}_2$$

which can account for the increase in tremolite and diopside after 250 h (Table 3). As mentioned above, the final assemblage of diopside, tremolite, and calcite for the bulk composition studied here is attributed to the Mg enrichment of the tremolite and calcite (Fig. 1a). A possible reaction leading to the formation of the triple-chain silicate with clinojimthompsonite structure would be:

$$8 \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6 \text{CaCO}_3 + 4 \text{SiO}_2 = 3 \text{Ca}_2\text{Mg}_8\text{Si}_{12}\text{O}_{32}(\text{OH})_4 + 2 \text{H}_2\text{O} + 6 \text{CO}_2$$

In the DQ1-6L experiment, reaction 2 has reached a metastable steady state and without mechanical disturbance it would probably not proceed further in any reasonable laboratory time frame. The retreatment process disturbs the system enough to disrupt whatever steady state processes have been established in
the system and allows the reaction to proceed. A more detailed discussion of how the retreatment process could affect the reaction progress will be the subject of another study. We do stress the system and allows the reaction to proceed. A more detailed discussion of how the retreatment process could affect the reaction progress will be the subject of another study. We do stress the system and allows the reaction to proceed.

Nucleation and growth

Previous attempts at synthesizing tremolite using oxides or gels (e.g., Jenkins 1987; Ahn et al. 1991; Pawley et al. 1993; Maresch et al. 1994; Bozhilov et al. 2004) or even seeded mixtures (Boyd 1959; Slaughter et al. 1975; Yin and Greenwood; 1983; Jenkins 1983; Skippen and McKinstry 1985; Welch 1987) often yield large amounts of metastable phases, such as talc, pyroxene, and/or non-classical pyroboles. Previous attempts to form tremolite from unseeded mixtures of dolomite and quartz (Christophe-Michel-Levy 1957; Jordan et al. 1992) also led to difficulties. A common explanation for the inability to obtain 100% yields has been that the early developed metastable phases (talc, diopside) become armored by the newly formed amphibole that physically blocks the reaction progress by restricting the exchange of fluids and components between the solution and the reactants. Our observations in the current system, as well as those in earlier studies (Maresch et al. 1994; Bozhilov et al. 2004), do not provide support for this explanation. Direct replacement of precursor phases is a relatively rare process because of the lack of broad reaction fronts where, for example, talc is converting to amphibole. Instead, it appears that multi-stage dissolution and regrowth events are more common.

The formation of amphibole requires the nucleation and combination of both a pyroxene-type (P) and mica-type (M) building modules in a 1:1 ratio (Thompson 1978, 1981). We hypothesize that this nucleation process requires a narrower range of pressure-temperature-composition \((P-T-X)\) conditions than the conditions under which amphibole can grow. At the \(P-T-X\) conditions necessary for nucleating P- and M-modules, it is statistically possible that these modules are combined in random proportions such as 2:1, 1:2, 3:1, 1:3, etc. Depending on their free energy and configurational entropy, some nuclei will be more stable than others and will continue to grow. In this context amphibole nucleation with a 1:1 ratio of P- and M-modules may well occur at an invariant point or at least a very narrow field in \(P-T-X\) space. As a consequence of this, slight shifts in the synthesis conditions may favor M-module nucleation, resulting in the predominant nucleation of mica-type (e.g., talc) phases, or P-module formation, resulting in the preferential growth of pyroxene. This hypothesis is clearly supported by the experimental work to date, where syntheses done above 750 °C, but inside the tremolite stability field, yield pyroxene as a precursor to tremolite (Maresch et al. 1994; Gottschalk et al. 1999; Bozhilov et al. 2004), whereas experiments below 650 °C yield talc as the dominant precursor phase (Maresch et al. 1994; this study).

Chain multiplicity defects (CMFs) vs. solid solution

This study confirms the long-standing observation (e.g., Maresch and Czank 1988; Ahn et al. 1991) that CMFs can have a significant effect on the bulk composition of synthetic amphibole as shown in Table 6. What this study also emphasizes is the role that kinetics plays in controlling the composition of the amphibole that is formed. Crystallizing tremolite from oxides or gels outside of the stability field of talc appears to cause appreciable Mg enrichment (up to 10% MC component) due to genuine solid solution (Gottschalk et al. 1999; Bozhilov et al. 2004). In this study, the situation is more complex. In the initial 250 h (DQ1-6b) of synthesis, tremolite formed inside the stability field of tremolite but at conditions where talc grows metastably from dolomite and quartz. This tremolite represents a true solid solution of about 10% MC component, plus an additional apparent MC component of about 1.5% caused by CMFs (Table 6). On the other hand, tremolite from the long-duration experiment without retreatment (DQ1-6L) shows a very different composition. It has very low true MC component (0.6%, Table 6) and relatively high CMF density. This result is similar to that obtained by Maresch et al. (1994), especially in their synthesis region I at temperatures below 750 °C in the talc stability field. The long-duration experiment with multiple retreatments (DQ1-6d) in the present study shows relatively low true MC component (about 3.5%, Table 6) and a significant contribution from CMFs to the Mg enrichment.

The question of the thermodynamically stable amount of Mg incorporation in tremolite is still a controversial issue. This study provides evidence that kinetics is a very strong factor controlling amphibole nucleation and growth and that subsequent equilibration of the metastable compositions and phases is a sluggish process. It can be inferred from previous studies that tremolite has 3 to 7% MC component (for tremolite coexisting with pyroxene and quartz) in true solid solution at typical synthesis temperatures of 700–850 °C, with the amount of the MC component increasing with increasing temperature (e.g., Gottschalk et al. 1999; Evans et al. 2000). This MC content is supported in the present study by the experiment with the most retreatments (DQ1-6d), which has 3.5% MC after correcting for the effect of CMFs. Considering the relatively low temperatures at which these syntheses were done (–600 °C), an MC content of 3.5% is quite consistent with earlier studies. The single-treatment sample (DQ1-6L) with relatively high CMF concentrations and low (0.6%) MC content, and the sample after the third treatment

### Table 7.
The average composition of triple-chain slab based on 8 AEM analyses

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>62.05(14)</td>
</tr>
<tr>
<td>MgO</td>
<td>27.67(20)</td>
</tr>
<tr>
<td>CaO</td>
<td>10.18(65)</td>
</tr>
<tr>
<td>FeO</td>
<td>0.10(66)</td>
</tr>
</tbody>
</table>

Notes: Formula units are calculated assuming 34 and 23 oxygen apfu. Absorption corrections were determined assuming perfect triple-chain oxygen stoichiometry, which corresponds to 36 O atoms per formula unit or 62.07 at% O.
(DQ1-6b) with low CMF concentrations and high (10%) MC content, are considered far from equilibrium because the former has high CMF concentrations and the latter may have nucleated at a Mg-rich (spinodal) composition.

**Ca-clinojimthompsonite in synthetic tremolite**

The only reports of Ca-rich, triple-chain pyroxoboles in natural samples are as coherent lamellae in metasomatically altered pyroxenes from metamorphosed limestone (skarn) from Akatani, Japan (Akai, 1982), in pyroxene and amphibole formed during low-grade metamorphism of sediments from the Salton Sea geothermal field, California (Yau et al. 1986), or in tremolite from serpentinitized ultramafic rocks of the Oeyama ophiolite, Japan (Konishi et al. 1993). For the first two localities, the lamellae were too narrow for direct chemical analysis. The third locality yielded samples with lamellae wide enough to analyze with an electron microprobe. Konishi et al. (1993) were able to confirm that the lamellae in tremolite from the Oeyama ophiolite were Ca analogs of clinojimthompsonite.

To date, occurrences of triple-chain lamellae in synthetic amphiboles have been too narrow (only 5 to 6 unit cells wide parallel to b) to analyze chemically. Without direct analysis, one can not really assess what effects these lamellae have on the bulk composition of the amphibole. In the long-duration experiment without retreatment (DQ1-6L), large slabs with almost perfect triple-chain structure are present giving a nearly ideal triple-chain stoichiometry of $\text{Ca}_2.1\alpha\text{Fe}_{0.62}\text{Mg}_{0.38}\text{Si}_{1.96}\text{O}_{4.06}\cdot 2\text{H}_2\text{O}$ on the basis of 34 O atoms (Table 7). This result confirms that Ca-clinojimthompsonite is indeed forming in synthetic tremolitic amphibole. Note that calculating the composition of this wide lamella on the basis of 23 O atoms gives a stoichiometry that is a poor fit for amphibole (Table 7).

**Role of the starting material**

What is clear from the present study is that, in the absence of tremolite nuclei, dolomite and quartz react strongly to form talc and calcite in the presence of a fluid of $X_{\text{H}_2\text{O}} = 0.2$ with only a small percentage of (relatively defect-rich) tremolitic amphibole crystals forming initially. It appears that, regardless of how geologically relevant the starting materials are, the formation of tremolite by direct precipitation from a saturated solution is not the dominant mechanism and that other pyrobibole phases nucleate more readily. The textures observed with HRTEM imaging here and in the earlier study by Bozhilov et al. (2004) suggest that these precursor phases eventually convert to amphibole by a dissolution and re-precipitation process, rather than by solid-state conversion, and that the direct precipitation of amphibole is not kinetically favorable. The repeated appearance of precursor non-amphibole pyroxoboles from a wide variety of starting materials in experimental studies suggests that this is a general phenomenon and that the textures of tremolite-bearing metamorphic assemblages in nature may need to be interpreted in light of this stepwise formation process.

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