A Rietveld and infrared study of synthetic amphiboles along the potassium-richterite–tremolite join

FRANK C. HAWTHORNE,1 GIANCARLO DELLA VENTURA,2 JEAN-LOUIS ROBERT,3 MARK D. WELCH,4 MATI RAUSDSEPP,5 AND DAVID M. JENKINS6

1Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada
2Dipartimento di Scienze Geologiche, Terza Universita di Roma, Viale Ostiense 169, I-00154, Rome, Italy
3Centre de Recherche sur la Synthese et Chimie des Mine Áraux, CNRS, 1A, rue de la Férolerie, 45071 Orleans Cedex 2, France
4Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.
5Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, B.C. V6T 1Z4, Canada
6Department of Geological and Environmental Sciences, State University of New York at Binghamton, Binghamton, New York 13901, U.S.A.

ABSTRACT

Amphiboles were synthesized at 750°C, 1 kbar (H2O) for compositions at 20% intervals along the join potassium-richterite–tremolite. Structural variations, site occupancies, and modal analyses of the experimental products (amphibole + minor diopside, quartz, and enstatite) were characterized by Rietveld structure refinement, with final R_Bragg indices in the range 4–6%, and by infrared spectroscopy in the principal OH-stretching region. Amphibole compositions were determined by (1) site-scattering refinement for the A and M4 sites that are occupied by (K, Mg) (Mg = vacancy) and (Na,Ca), respectively; and (2) mass-balance calculations involving the modal analysis and the nominal experimental product composition. These measurements agree within 1% absolute and show close agreement with electron-microprobe compositions for the two samples that we could analyze. Deviations from nominal amphibole composition are up to 19% absolute. The resulting relations between cell dimension and composition are linear. The major change in cell dimensions is a decrease of 0.25 Å in a with increasing tremolite component.

The infrared spectra show two principal peaks at 3735 and 3675 cm⁻¹, corresponding to the local arrangements MgMgMg-OH-→K (the Kr band) and MgMgMg-OH-→CaMgSiO₄(OH)₂ (the Tr band), respectively. The relative variation in peak intensity as a function of amphibole composition shows that the molar absorptivities of the two bands are significantly different. The ratio of the molar absorptivities for the two bands is 2.2.

INTRODUCTION

A long-standing problem of amphibole synthesis is the adequate characterization of the product amphiboles. Critical examination of the products of amphibole synthesis (Hawthorne 1983a) showed that compositions frequently depart from their nominal values. Furthermore, spectroscopic examination showed that unexpected ordering patterns could be encountered (e.g., Raudsepp et al. 1987a), raising the question of whether some synthetic amphiboles are good analogues of their natural counterparts. These problems received an increasing amount of attention recently. Raudsepp et al. (1987a, 1987b, 1991), Robert et al. (1993), Della Ventura et al. (1993a, 1993b, 1995, 1997a), and Jenkins and Hawthorne (1995) have examined synthetic amphiboles by Rietveld structure refinement, a very powerful technique for the characterization of composition and ordering in amphiboles that have significant differences in X-ray scattering power of the components involved in the disorder. Della Ventura (1992), Della Ventura and Robert (1990), Della Ventura et al. (1991, 1993a, 1993b, 1995, 1997a), and Robert et al. (1989) showed how infrared spectroscopy in the principal OH-stretching region can give critical information on site occupancies when combined with careful and systematic synthesis of amphiboles. Maresch and Czank (1983a, 1983b) pioneered the use of high-resolution transmission electron microscopy (HRTEM) in the study of synthetic amphiboles, and the use of HRTEM characterization of synthetic amphiboles is now common (Maresch and Czank 1988; Maresch et al. 1994; Ahn et al. 1991; Pawley et al. 1993; Smelik et al. 1994). These methods, together with the more extensive use of scanning electron microscopy (SEM) and electron-microprobe analysis, have led to a resurgence of work on amphibole synthesis and phase relations.

Pawley et al. (1993) synthesized amphiboles along the join richterite–tremolite, ideally NaCaNaMg₅Si₈O₂₂(OH)₂→CaMgSiO₄(OH)₂, and showed the resulting amphiboles to be essentially defect-free (except for compositions close to tremolite) by HRTEM and close to ideal composition by electron-microprobe analysis and hydro-
gen-line extraction, and measured enthalpies of drop solution. We have synthesized amphiboles along the join potassium-richterite–tremolite, and here we report their characterization by Rietveld structure refinement, infrared spectroscopy in the principal OH-stretching region, HRTEM, and electron-microprobe analysis.

**Experimental details**

Details of synthesis procedures are given by Della Ventura et al. (1991). Compositions were prepared along the binary join potassium-richterite–tremolite at intervals of 20 mol% at 750 °C, 1 kbar $P_{\text{H}_2O}$ in externally heated Tuttle-type cold-seal vessels. The bulk composition of the experimental product (i.e., the nominal composition of the amphibole) is denoted by the amount of potassium-richterite component, Kr, where $x$ varies from 100 for end-member potassium-richterite to zero for tremolite. This name also is the sample number. The composition of the amphibole synthesized is represented by the symbol $X_K$, where $K$ designates the method of analysis: for electron-microprobe analysis $K = \text{EMP}$; for Rietveld site-scattering refinement, $K = \text{RSS}$; for Rietveld modal analysis, $K = \text{RMA}$.

The powdered experimental products were mounted on carbon tape on a brass substrate to avoid extraneous AlKα X-rays. Quantitative image-analysis work was not possible, since the gray-level contrast range from topography in the backscattered-electron image of the grains is generally larger than that from atomic contrast for these samples. Quantitative electron-microprobe analyses were attempted according to the procedure described by Della Ventura et al. (1997b).

HRTEM observations were made using a JEOL 200CX transmission electron microscope operated at 200 kV. Crystals were dispersed in dry alcohol and sedimented onto a 3 mm holey-carbon, copper grid (Agar products). All samples were very beam-sensitive and a 70 μm condenser-aperture was used to minimize beam damage. High-resolution images were formed from diffracted beams that passed through a 40 μm (0.45 Å$^{-1}$) objective aperture.

Samples were prepared for FTIR spectroscopy as KBr pellets using the procedure of Robert et al. (1989). Spectra were recorded in the range 4000–3000 cm$^{-1}$ with a Perkin-Elmer 1760 spectrometer equipped with a DTGS detector and a KBr beam splitter, and operating at a nominal resolution of 1 cm$^{-1}$. Digitized spectra (average of 64 scans) were fitted to component bands by visual optimization followed by least-squares refinement using the PEAKFIT system of programs by Jandel Corporation. The background was linear and all peaks were modeled as symmetrical Gaussians. The experimental spectra are simple two-peak envelopes with only very minor asymmetry, and no constraints were used in the fitting process.

X-ray powder diffraction data for Kr$_{100}$–Kr$_0$ were collected on a Philips PW1710 automated diffractometer system, as described by Della Ventura et al. (1993b), using a step interval of 0.10° 2θ and an integration time-step of 5 s; data for Kr$_x$ were collected on a Scintag XDS-2000. Information pertinent to structure refinement is given in Table 1. The structures of the synthetic amphiboles were refined by the Rietveld method using the program DBW 3.2 (Wiles and Young 1981). Initial structural parameters were taken from Della Ventura et al. (1993b). Anisotropic displacement factors were fixed at average values for the specific sites in the amphibole structure (according to the nomenclature of Hawthorne 1983b), and the occupancy of K at the A site was constrained to be the same as the occupancy of Na at the M4 site (note that this is an electroneutrality constraint). The A cation was set to occupy the Am site on the mirror plane, as found for previous Rietveld refinements of the potassium-richterite structure (Della Ventura et al. 1993b). In most of the experimental products there are other phases present in addition to amphibole: diopside, quartz, enstatite. These additional phases were incorporated into the Rietveld refinement with fixed compositions, fixed atomic positions, variable cell-dimensions, and variable scale factors. From the refined scale factors, quantitative amounts of all phases were determined using the method of Hill (1991).

**Experimental results**

Amphibole crystals are prismatic along $c$, up to 15 μm long, and 3 μm in diameter, but the majority of the crystals are < 3 μm long and 1 μm in diameter (Fig. 1).
amphibole yield was ~95%, and in addition to amphibole, there was also minor diopside, enstatite, and quartz. Examination by HRTEM (Fig. 2) shows that these synthetic amphiboles are essentially free of chain-multiplicity and chain-arrangement faults. An inherent problem with using HRTEM to evaluate the microstructural purity of powder samples is the sampling bias introduced by the need to look at crystals that are transparent to electrons. This usually means that the smaller populations are over-represented. Where possible, broken edges of larger grains were examined to redress this bias. It was found that, in general, the smaller amphibole crystals are more acicular and defective, as previously noted by Maresch and Czank (1983a, 1983b). Hence, HRTEM tends to overestimate the defectiveness of synthetic amphiboles. Representative high-resolution structure images are shown in Figure 2. All samples except Kr$_{20}$ are essentially free of polysomatic defects or chain-multiplicity faults (CMFs). A typical example is shown in Figure 2a, in which the microstructure consists of a monotonous uninterrupted sequence of double chains defined by the characteristic 9 Å (020) lattice fringes. Figure 2b shows one of the more defective crystallites from Kr$_{20}$; this contains many CMFs with multiplicities of 1, 3, and 4, with double chains making up only 50% of the crystal. Again, examination of broken edges of larger grains suggests that these are less defective than the more accessible fine-grained population. Overall, HRTEM indicates that the potassium-richterite–tremolite amphiboles have well-ordered microstructures.

The grain-size made electron-microprobe analysis quite difficult, and for some samples adequate results could not be obtained. Compositions for two samples were determined (Table 2), and even for these samples the analytical totals are low; however, the stoichiometry agrees closely with that expected for amphibole, even when the HRTEM results (Fig. 2b) indicate a relatively high density of chain-width errors.
Table 2. Electron-microprobe analyses of synthetic potassium-richterite–tremolite

<table>
<thead>
<tr>
<th></th>
<th>Kf90*</th>
<th>Kf95*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>57.47</td>
<td>55.29</td>
</tr>
<tr>
<td>MgO</td>
<td>24.07</td>
<td>23.22</td>
</tr>
<tr>
<td>CaO</td>
<td>7.53</td>
<td>10.01</td>
</tr>
<tr>
<td>Na2O</td>
<td>3.09</td>
<td>1.44</td>
</tr>
<tr>
<td>K2O</td>
<td>4.46</td>
<td>2.02</td>
</tr>
<tr>
<td>Total</td>
<td>96.62</td>
<td>91.98</td>
</tr>
<tr>
<td>Si</td>
<td>8.02</td>
<td>8.01</td>
</tr>
<tr>
<td>Mg</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Mg</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Ca</td>
<td>1.18</td>
<td>1.58</td>
</tr>
<tr>
<td>Na</td>
<td>0.81</td>
<td>0.40</td>
</tr>
<tr>
<td>K</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Na</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>K</td>
<td>0.79</td>
<td>0.37</td>
</tr>
<tr>
<td>ΣK</td>
<td>0.82</td>
<td>0.38</td>
</tr>
</tbody>
</table>

* Mean of two determinations.
† The totals are low because of problems associated with the analysis of very small particles.

Table 3. Cell dimensions for synthetic amphiboles along the join potassium-richterite–tremolite

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr90</td>
<td>10.059(8)</td>
<td>17.997(1)</td>
<td>5.2746(4)</td>
<td>104.832(5)</td>
<td>922.7(1)</td>
</tr>
<tr>
<td>Kr95</td>
<td>10.029(6)</td>
<td>18.001(1)</td>
<td>5.2730(4)</td>
<td>104.786(4)</td>
<td>919.7(1)</td>
</tr>
<tr>
<td>Kr97</td>
<td>9.988(8)</td>
<td>18.016(1)</td>
<td>5.2730(5)</td>
<td>104.746(5)</td>
<td>917.7(1)</td>
</tr>
<tr>
<td>Kr98</td>
<td>9.9548(9)</td>
<td>18.021(1)</td>
<td>5.2735(6)</td>
<td>104.724(7)</td>
<td>915.0(1)</td>
</tr>
<tr>
<td>Kr99</td>
<td>9.9241(1)</td>
<td>18.030(2)</td>
<td>5.2749(8)</td>
<td>104.671(1)</td>
<td>913.1(2)</td>
</tr>
<tr>
<td>Kr90*</td>
<td>9.873(1)</td>
<td>18.044(3)</td>
<td>5.271(1)</td>
<td>104.571(1)</td>
<td>908.8(3)</td>
</tr>
<tr>
<td>Kr95*</td>
<td>9.807(2)</td>
<td>18.054(3)</td>
<td>5.276(1)</td>
<td>104.561(1)</td>
<td>904.2(4)</td>
</tr>
</tbody>
</table>

* The structure of this sample was not refined.
† Data from Smelik et al. (1994).

Figure 3. Observed (solid line), calculated (dots), and difference (bottom line) X-ray powder-diffraction pattern for synthetic potassium-richterite of composition K0.82(Ca1.18Na0.82)Mg5Si8O22(OH)2.

Discussion

Amphibole composition

The compositions of the intermediate amphiboles can be derived directly from the Rietveld results by means of the refined site-scattering values at the A and M4 sites (Table 6). They may also be derived from the modal compositions of the experimental products derived from multiphase Rietveld refinement (Table 6). Neither set of compositions agrees with the nominal compositions of the experimental products derived from multiphase Rietveld refinement, are given in Table 6.

Infrared spectra are shown in Figure 4, and the band positions, widths, and intensities are listed in Table 7. The band at ~3672 cm⁻¹ is dominant in the tremolite end-member and is designated the Tr (tremolite) band. The band at ~3736 cm⁻¹ is dominant in the potassium-richterite end-member and is designated the Kr (potassium-richterite) band.

The Kr band

The infrared spectrum of nominal end-member synthetic potassium-richterite consists of two peaks: an intense peak (Kr) at 3734 cm⁻¹ and a weak peak (Tr) at 3672 cm⁻¹. The Kr peak is due to OH at O(3) locally associated with Mg at the adjacent two M1 and one M3 sites and K at the A site; this is written as MgMgMg-OH-K. The Tr peak is due to OH at O3 locally associated with Mg at the adjacent two M1 and one M3 sites and A (a vacancy) at the A site; this is written as MgMgMg-OH-A. The presence of the Tr peak in the spectrum of nominal end-member synthetic potassium-richterite indicates that the latter does not have a completely occupied A site. The Kr peak in potassium-richterite is much broader than the Tr peak in tremolite and is broader than the Tr peak in amphiboles of intermediate composition as well (Table 7). This may be explained by considering the local arrangement in a A cavity in potassium-richterite (Fig. 5a). The A cavity contains K,
FIGURE 4. Infrared spectra in the OH-stretching region for synthetic amphiboles along the join potassium-richterite–tremolite; compositions are indicated as Kr(x) where x denotes the nominal amount of potassium-richterite component.

TABLE 7. Refined values of the positions (cm$^{-1}$), widths (cm$^{-1}$), and relative intensities of the bands in the principal OH-stretching region of the infrared spectra of synthetic amphiboles along the join potassium-richterite–tremolite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position</th>
<th>Width</th>
<th>Intensity*</th>
<th>Sample</th>
<th>Position</th>
<th>Width</th>
<th>Intensity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr$_{100}$</td>
<td>3734</td>
<td>15.0</td>
<td>0.95</td>
<td>Kr$_{100}$</td>
<td>3672</td>
<td>10.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Kr$_{80}$</td>
<td>3734</td>
<td>15.8</td>
<td>0.70</td>
<td>Kr$_{80}$</td>
<td>3671</td>
<td>10.5</td>
<td>0.30</td>
</tr>
<tr>
<td>Kr$_{60}$</td>
<td>3738</td>
<td>15.9</td>
<td>0.50</td>
<td>Kr$_{60}$</td>
<td>3672</td>
<td>10.4</td>
<td>0.50</td>
</tr>
<tr>
<td>Kr$_{40}$</td>
<td>3736</td>
<td>15.9</td>
<td>0.36</td>
<td>Kr$_{40}$</td>
<td>3672</td>
<td>10.2</td>
<td>0.64</td>
</tr>
<tr>
<td>Kr$_{20}$</td>
<td>3736</td>
<td>15.8</td>
<td>0.23</td>
<td>Kr$_{20}$</td>
<td>3672</td>
<td>10.0</td>
<td>0.77</td>
</tr>
<tr>
<td>Kr$_{15}$</td>
<td>3738</td>
<td>15.7</td>
<td>0.09</td>
<td>Tr$_{23-5}$</td>
<td>3674</td>
<td>9.2</td>
<td>0.91†</td>
</tr>
<tr>
<td>Tr$_{33-8}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Tr$_{33-8}$</td>
<td>3675</td>
<td>3.8</td>
<td>1.00‡</td>
</tr>
</tbody>
</table>

* Normalized such that $P^+ + P^- = 1.0$. † Asymmetric envelope. The position determined at half-width. ‡ Omitting the cummingtonite component.

The spectrum of nominal end-member synthetic tremolite consists of a single narrow band at 3675 cm$^{-1}$ and a second minor band to the lower frequency side, centered at 3670 cm$^{-1}$ (Fig. 4). The position (3670 cm$^{-1}$) and relative intensity (~10%) of the minor band suggest that it results from the minor cummingtonite component that normally occurs in both natural and synthetic tremolite (Jenkins 1987; Graham et al. 1989; Ahn et al. 1991; Pawley et al. 1993; Maresch et al. 1994). This is in accord with the fact that the particular tremolite sample used here was prepared from a nominal composition containing 10% cummingtonite [ideally $\square$Mg$_2$Mg$_3$Si$_8$O$_{22}$(OH)$_2$] in solid solution (Smelik et al. 1994).

FIGURE 5. The local arrangements around the A site in potassium-richterite: (a) The H atom is close to K at an occupied Am site; (b) The H atom is far from K at an occupied Am site.

which occupies the Am site (Hawthorne and Grundy 1972; Hawthorne 1983b). Each OH group in a single cavity has a different local environment; one will be close to the occupied Am site and the other will be much further away (Fig. 5b). Since each occupied A cavity has a pair of OH groups, each in a different local environment, there will be an equal number of absorptions from each type of OH group, and hence the resultant two bands should be of equal intensity (allowing for any difference caused by different transition moments for the two configurations). These bands are of similar energy and can couple through K at the Am site, thus giving rise to a single broad band rather than to two sharp bands.

The Tr band

The spectrum of nominal end-member synthetic tremolite consists of a single narrow band at 3675 cm$^{-1}$ and a second minor band to the lower frequency side, centered at 3670 cm$^{-1}$ (Fig. 4). The position (3670 cm$^{-1}$) and relative intensity (~10%) of the minor band suggest that it results from the minor cummingtonite component that normally occurs in both natural and synthetic tremolite (Jenkins 1987; Graham et al. 1989; Ahn et al. 1991; Pawley et al. 1993; Maresch et al. 1994). This is in accord with the fact that the particular tremolite sample used here was prepared from a nominal composition containing 10% cummingtonite [ideally $\square$Mg$_2$Mg$_3$Si$_8$O$_{22}$(OH)$_2$] in solid solution (Smelik et al. 1994).
The infrared spectra of selected synthetic amphiboles along the join potassium richterite—tremolite in the OH-stretching region (3650–3700 cm⁻¹). Note the increasing band asymmetry with increasing tremolite component.

Inspection of Figure 4 shows that the Tr band is narrow for the nominal end-member composition (Kr₀) but is much broader for intermediate compositions (Table 7). In Kr₀, all OH groups have the same short-range environment (omitting consideration of the cummingtonite component) and a sharp absorption in the principal OH-stretching region. In amphiboles of intermediate composition along the Kr-Tr join, OH groups in the Tr configuration have different next-nearest-neighbor configurations. They can be associated with either a tremolite or a richterite configuration at the O3 site adjacent either along the O3-O3 edge or along the O3-M3-O3 trimer. Because the energies of these different local arrangements are very similar and they are spatially associated, the absorptions couple and a single broad band results instead of two or more sharp single bands. Consider the end-member potassium richterite arrangement; replacement of one $^A$K produces two tremolite-like configurations (associated with $^\Box$) and two configurations that involve next-nearest-neighbor arrangements not found in either end-member structure. Thus an equal number of tremolite-like and adjacent arrangements are produced, and the resultant bands are of equal intensity (allowing for differences in transition moment). At compositions closer to end-member tremolite, replacement of $^A$K by $^\Box$ still produces two tremolite-like configurations; however, adjacent configurations now also tend to be tremolite-like as $^A$K $\approx$ $^\Box$. Hence the relative intensity of the band attributed to the tremolite-like configuration should become larger than the relative intensity of the band for the intermediate configuration. Figure 6 shows the spectral envelope for members of the tremolite end of the solid solution. For Krᵣᵐ, the envelope is fairly symmetrical, as predicted from the above argument. As the potassium-richterite component decreases, the width of the band decreases and the band becomes asymmetric; in this region, it is apparent that the band has two components: an intense higher-frequency component at 3675 cm⁻¹ that coincides with the intense sharp band in the end-member tremolite spectrum and a weaker lower frequency component at 3670 cm⁻¹ (the correspondence with the 3670 cm⁻¹ band in end-member tremolite is accidental). The gradual decrease in intensity of this lower frequency component as the potassium richterite component in the solid-solution decreases is also in accord with the above argument.

Variation in band intensity in the OH-stretching spectrum

In previous work concerned with the derivation of site populations from infrared spectra of amphiboles (see surveys by Strens 1974; Hawthorne 1981, 1983b), it was implicitly assumed that the molar absorptivity of all fun-
damental OH-stretching bands is the same. However, Skogby and Rossman (1991) showed that this is not the case for polarized single-crystal absorption spectra of amphiboles, and Groat et al. (1995) showed the same for vesuvianite over a broad range of absorption frequencies (~4500 cm⁻¹). Burns and Hawthorne (1994a, 1994b) showed that the same feature is exhibited by powder infrared spectra of borate minerals. The molar absorptivity of OH-stretching bands can increase strongly with decreasing absorption frequency. Della Ventura et al. (1997b) measured the powder infrared spectra of (magnesium, nickel)- and (magnesium, cobalt)-potassium-richterite solid solutions and showed that the molar absorptivities of the four OH-stretching bands are the same in a single powder sample. Thus the situation regarding variation in molar absorptivity as a function of band frequency in amphiboles is currently unclear. However, it is clear that we must consider possible variations in molar absorptivity in relating band intensities to structural and chemical features.

In the spectra of Figure 4, let the band intensities vary from zero to \( I_\text{Tr} \) (for the Tr band) and \( I_\text{Kr} \) (for the Kr band). At a composition \( x \) (= proportion of tremolite component in the amphibole)

\[
I_\text{Tr} = x \cdot I_\text{Tr}^\text{pred}
\]

\[
I_\text{Kr} = (1 - x) \cdot I_\text{Kr}^\text{pred}.
\]  

Let there be a difference in molar absorptivity of the bands such that

\[
I_\text{Tr} = k \cdot I_\text{Kr}.
\]

The relative intensity ratio, \( R \), giving the amount of tremolite component in the amphibole is

\[
R = \frac{I_\text{Tr}}{I_\text{Tr} + I_\text{Kr}}.
\]

Substitution of equations 1 and 2 into equation 3 reduces to

\[
x = R[k + R(1 - k)].
\]  

According to the curve of Skogby and Rossman (1991), \( k \) is in the range 3–4 and hence this effect may
be quite large. In fact, we can measure $k$ by comparing intensities of the infrared bands with the compositions of the M1,3 sites derived by Rietveld structure refinement. A little algebra produces the following expression from Equation 4:

$$R/(1 - R) = k \cdot [x/(1 - x)].$$

(5)

Figure 7 shows that the data do indeed define a linear relation as predicted by Equation 5, and $k$ is determined from the slope of the relation to be 2.2.

The situation is somewhat complicated in the present case as neither amphibole is of nominal end-member composition. For tremolite, the absorption from a "cummingtonite" component more-or-less overlaps with that of tremolite, and hence this is not a problem; the cummingtonite component is included in the tremolite band intensity. For nominal end-member potassium richterite, the actual composition has an unknown amount of tremolite component (<5%), but this is not sufficient to affect materially the value of $k$ derived in Figure 7.

Cell dimensions

The variation in cell dimensions along the series is shown in Figure 8. All cell dimensions vary linearly as a function of amphibole composition, supporting the compositions derived from Rietveld structure refinement. The cell volume decreases regularly from potassium richterite to tremolite in response to the decreasing amount of K at the A site and to the decreasing size of the constituent cations at the M4 site. The $a$ dimension shows by far the greatest variation across the series, decreasing as the amount of tremolite component increases in the amphibole. This observation is in accord with the idea that K at the A site holds the back-to-back double chains apart, and removal of K allows the chains to relax toward each other. Relaxation in the $b$ and $c$ directions is much less (Fig. 8), as is expected from this particular substitution.

Site occupancies and mean bond lengths

The refined site occupancies of the synthesized amphiboles are listed in Table 8. The Rietveld method provides quite accurate site occupancies and bulk compositions if reasonable values for isotropic displacement factors are used (Raudsepp et al. 1990). There is no change in occupancy of the M1,2,3 and T1,2 sites across this series, and thus, the refined structures show no significant change in the grand mean bond lengths at these sites. Change is significant at the M4 and A sites across this series, and thus, the re­fined structures show no significant change in the grand mean bond lengths at these sites.

**REFERENCES CITED**


**ACKNOWLEDGMENTS**

We thank Anton Beran and Ronald Miletich for their comments that greatly improved the clarity of this manuscript. Part of this work was done during the stay of G.D.V. at the Department of Geological Sciences, University of Manitoba, Winnipeg, supported by an International Council for Canadian Studies grant. Financial assistance was provided by a C.N.R. grant no. 92.00774.CT05 to G.D.V. and by the Natural Sciences and Engineering Research Council of Canada through Operating, Infrastructure and Major Equipment grants to F.C.H.


Raudsepp, M., Turnock, A.C., and Hawthorne, F.C. (1987a) Characterization of synthetic eckermannitic amphiboles (NaNa₂Mg₄Al₃Si₉O₂₄(OH)), M³⁺ = Al, Cr³⁺, Ga, Sc, In) and scandium-fluor-nyboite (NaNa₂Mg₆Sc₂Si₂Al₂O₂₄F₂) by infrared spectroscopy and Rietveld structure refinement. American Mineralogist, 72, 959–964.

Raudsepp, M., Turnock, A.C., Hawthorne, F.C., Sheriff, B.L., and Hartman, J.S. (1987b) Characterization of synthetic pargasitic amphiboles (NaCa₂Mg₅Al₃Si₉O₂₄(OH,F)) and synthetic Ti-rich potassium richterite (NaNa₂Mg₅Al₃Si₇Al₂O₂₂F₂; M³⁺ = Al, Cr³⁺, Ga, Fe³⁺, Sc, In) by infrared spectroscopy, Rietveld structure refinement and ⁶⁰⁰₂ and ⁶¹⁰₂ MAS NMR spectroscopy. American Mineralogist, 72, 580–593.


MANUSCRIPT ACCEPTED MARCH 17, 1997

MANUSCRIPT ACCEPTED MAY 14, 1996