

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 RAUDSEPP,⁵ AND DAVID M. JENKINS⁶

¹Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

²Dipartimento di Scienze Geologiche, Terza Università di Roma, Viale Ostiense 169, I-00154, Rome, Italy

³Centre de Recherche sur la Synthèse et Chimie des Minéraux, CNRS, 1A, rue de la Férollerie, 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, □) (□ = 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-⁺□ (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-□Ca₂Mg₅Si₈O₂₂(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-

TABLE 1. Rietveld structure-refinement details for synthetic amphiboles along the join potassium-richterite-tremolite

	Kr ₁₀₀	Kr ₈₀	Kr ₆₀	Kr ₄₀	Kr ₂₀	Kr ₀
2θ scan range (°)	9–130	9–100	9–100	9–100	9–100	13–100
No. of unique reflections*	856	523	523	523	523	510
No. of structural parameters	36	41	41	48	48	36
No. of experimental parameters	13	14	14	16	14	11
No. of ref. phases	1	2	2	4	4	2
N – P†	1162	856	856	847	847	864
R _p (%)	9.17	7.63	8.51	8.56	8.91	14.95
R _{wp} (%)	12.08	10.37	10.91	11.18	11.70	19.85
R _{exp} (%)	7.28	6.61	6.68	6.78	6.77	16.40
R _{Bragg} (%)	6.10	5.41	4.97	4.29	4.99	8.36
Durbin-Watson <i>d</i> statistic	1.36	1.30	1.25	1.34	1.14	1.57

* Refers to the amphibole phase only, space group *C2/m*.

† N – P = number of observations – number of parameters in least-squares refinement.

gen-line extraction, and measured enthalpies of drop solution. We have synthesized amphiboles along the join potassium-richterite (Kr)-tremolite (Tr), 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_{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_{*x*}, 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_A^K, where A designates the method of analysis: for electron-microprobe analysis A = EMP; for Rietveld site-scattering refinement, A = RSS; for Rietveld modal analysis, A = RMA.

The powdered experimental products were mounted on carbon tape on a brass substrate to avoid extraneous AlK α 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. Crystallites 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 μ m condenser-aperture was used to minimize beam damage. High-resolution images were formed from diffracted beams that passed through a 40 μ m (0.45 Å⁻¹) objective aperture.

Samples were prepared for FTIR spectroscopy as KBr pellets using the procedure of Robert et al. (1989). Spec-

tra 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 Kr₁₀₀-Kr₂₀ 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 Kr₀ 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). Isotropic 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 μ m long, and 3 μ m in diameter, but the majority of the crystals are < 3 μ m long and 1 μ m in diameter (Fig. 1). The

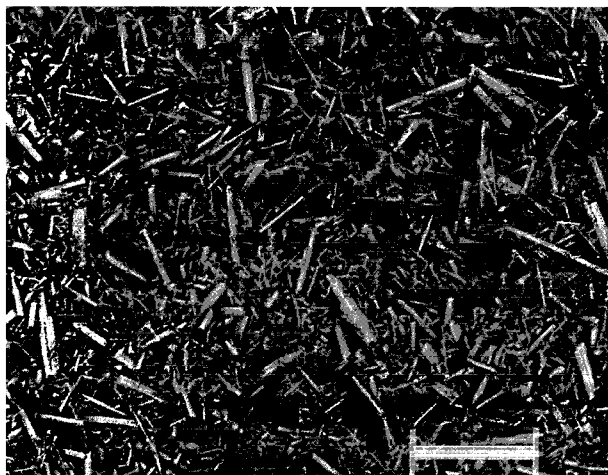


FIGURE 1. SEM image of synthetic potassium-rich richterite-tremolite solid solution; the scale bar is 20 μm .

amphibole yield was $\sim 95\%$, 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 \AA (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-rich 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.

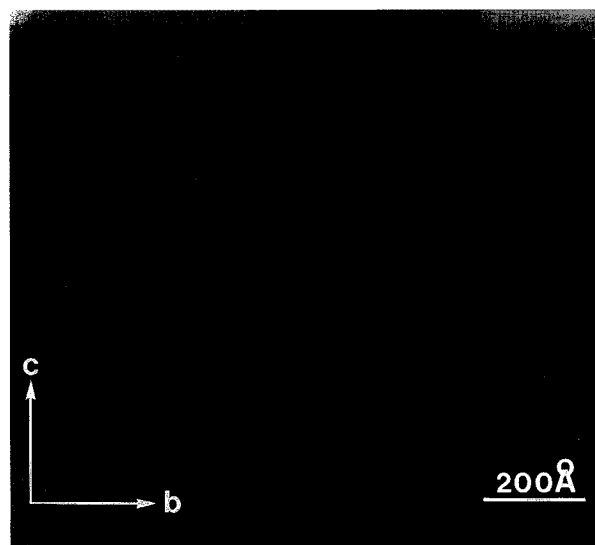
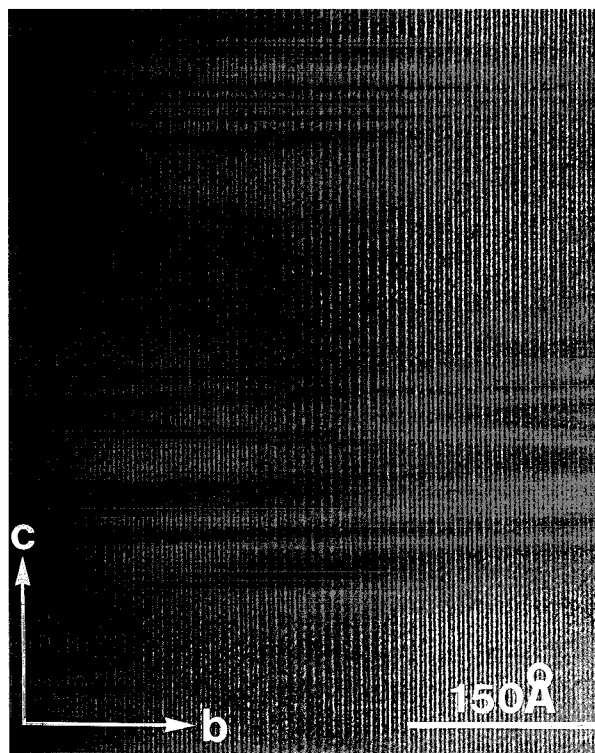


FIGURE 2. HRTEM images showing the typical structure of the synthetic amphiboles; (a) Kr_{60} ; (b) Kr_{20} .

Unit-cell dimensions are given in Table 3. Final atomic positions are listed in Table 4¹, and selected interatomic

¹ For a copy of Tables 4 and 5, order Document AM-97-641 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street, Suite 601, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche. Deposit items may also be available on the *American Mineralogist* web site, refer to the inside back cover of a current issue for web address.

TABLE 2. Electron-microprobe analyses of synthetic potassium-richterite-tremolite

	Kr ₈₀ *	Kr ₂₀ *
SiO ₂	57.47	55.29
MgO	24.07	23.22
CaO	7.53	10.01
Na ₂ O	3.09	1.44
K ₂ O	4.46	2.02
Total†	96.62	91.98
Si	8.02	8.01
Mg	5.00	5.00
Mg	0.01	0.02
Ca	1.18	1.58
Na	0.81	0.40
ΣB	2.00	2.00
Na	0.03	0.01
K	0.79	0.37
ΣA	0.82	0.38

* Mean of two determinations.

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

distances and angles are given in Table 5.¹ Typical observed, calculated, and difference X-ray powder-diffraction patterns for an amphibole of intermediate composition are shown in Figure 3. The modal amounts of all phases in 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.

DISCUSSION

Amphibole composition

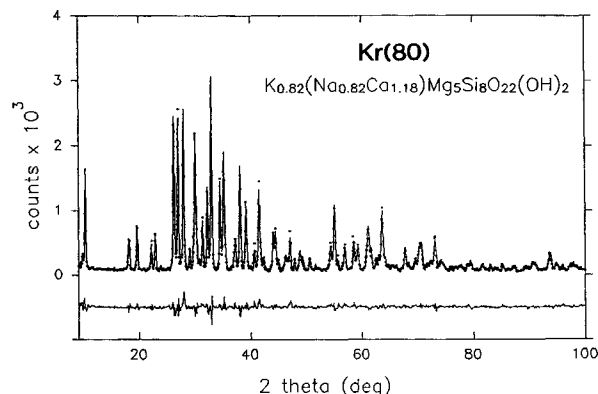
The compositions of the intermediate amphiboles can be derived directly from the Rietveld results by means of the refined site-scattering values at the A and M4 sites (Table 6). They may also be derived from the modal compositions of the experimental products derived from multiphase Rietveld refinement (Table 6). Neither set of compositions agrees with the nominal compositions of the amphibole (Table 8), in accord with the presence of additional phases in the intermediate-composition experi-

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

Sample	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
Kr ₁₀₀	10.0547(8)	17.997(1)	5.2746(4)	104.832(5)	922.7(1)
Kr ₈₀	10.0209(6)	18.001(1)	5.2730(4)	104.786(4)	919.7(1)
Kr ₆₀	9.9884(8)	18.016(1)	5.2730(5)	104.746(5)	917.7(1)
Kr ₄₀	9.9548(9)	18.021(1)	5.2735(6)	104.724(7)	915.0(1)
Kr ₂₀	9.924(1)	18.030(2)	5.2749(8)	104.67(1)	913.1(2)
Kr ₀ *	9.873(1)	18.044(3)	5.271(1)	104.57(1)	908.8(3)
Kr ₀ †	9.807(2)	18.054(3)	5.276(1)	104.56(1)	904.2(4)

* 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 K_{0.82}(Ca_{1.18}Na_{0.82})Mg₅Si₈O₂₂(OH)₂.

mental products (Table 6). However, there is almost exact correspondence between the Rietveld site populations and the amphibole composition derived from the modal-analysis results. Although both these values are derived from Rietveld structure refinement, the site populations and modal-analysis results are not in any way constrained to give the same result for the amphibole composition. The compositions for Kr₈₀ and Kr₂₀ so derived agree closely with those measured by electron-microprobe analysis (Table 2).

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 vacancy) at the A site; this is written as MgMgMg-OH⁻□. 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 an A cavity in potassium-richterite (Fig. 5a). The A cavity contains K,

TABLE 6. Modal analysis of experimental products derived from Rietveld structure refinement

Sample	Kr ₁₀₀	Kr ₈₀	Kr ₆₀	Kr ₄₀	Kr ₂₀	Kr ₀
Amphibole	100	95.8 (2.0)	90.0 (2.0)	75.3 (2.0)	53.0 (2.0)	100
Diopside	—	5.2 (0.4)	10.0 (0.6)	17.9 (0.7)	32.3 (1.0)	—
Quartz	—	—	—	1.5 (0.1)	3.7 (0.2)	—
Enstatite	—	—	—	5.3 (0.8)	11.1 (1.0)	—

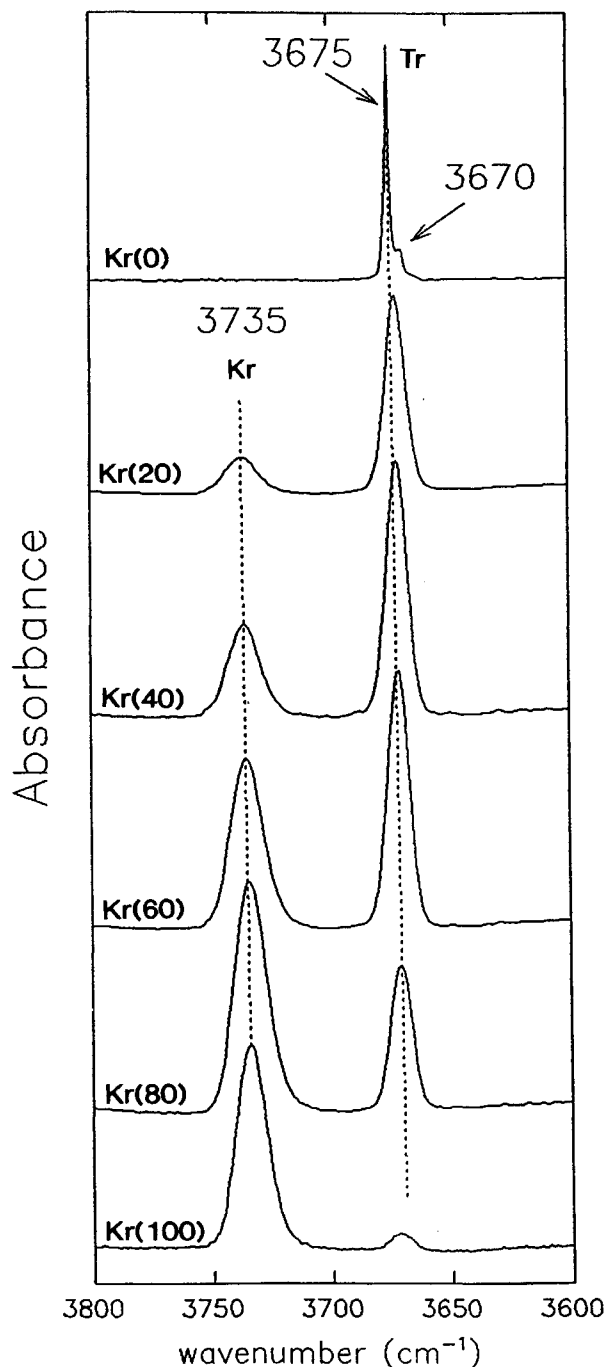


FIGURE 4. Infrared spectra in the OH-stretching region for synthetic amphiboles along the join potassium-richterite-tremolite; compositions are indicated as Kr(x) where x denotes the nominal amount of potassium-richterite component.

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

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

Sample	MgMgMg-OH-K band			MgMgMg-OH-□		
	Position	Width	Intensity*	Position	Width	Intensity*
Kr ₁₀₀	3734	15.0	0.95	3672	10.1	0.05
Kr ₈₀	3734	15.8	0.70	3671	10.5	0.30
Kr ₆₀	3738	15.9	0.50	3672	10.4	0.50
Kr ₄₀	3736	15.9	0.36	3672	10.2	0.64
Kr ₂₀	3736	15.8	0.23	3672	10.0	0.77
Kr ₁₅	3738	15.7	0.09	3674	9.2	0.91†
Tr ₂₃₋₅	—	—	—	3675	3.8	1.00‡

* Normalized such that $K + T = 1.0$.

† Asymmetric envelope. The position determined at half-width.

‡ Omitting the cummingtonite component.

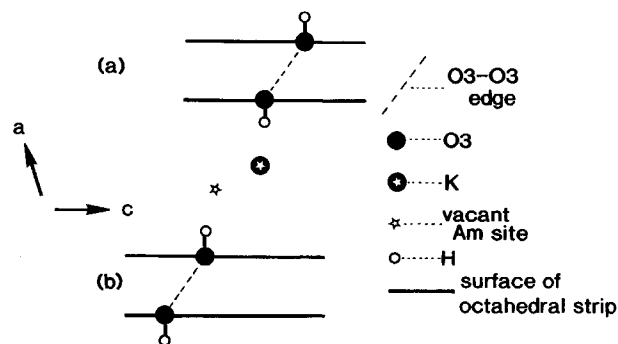


FIGURE 5. The local arrangements around the A site in potassium-richterite: (a) The H atom is close to K at an occupied Am site; (b) The H atom is far from K at an occupied Am site.

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 ($\sim 10\%$) 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 $\square\text{Mg}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$] in solid solution (Smelik et al. 1994).

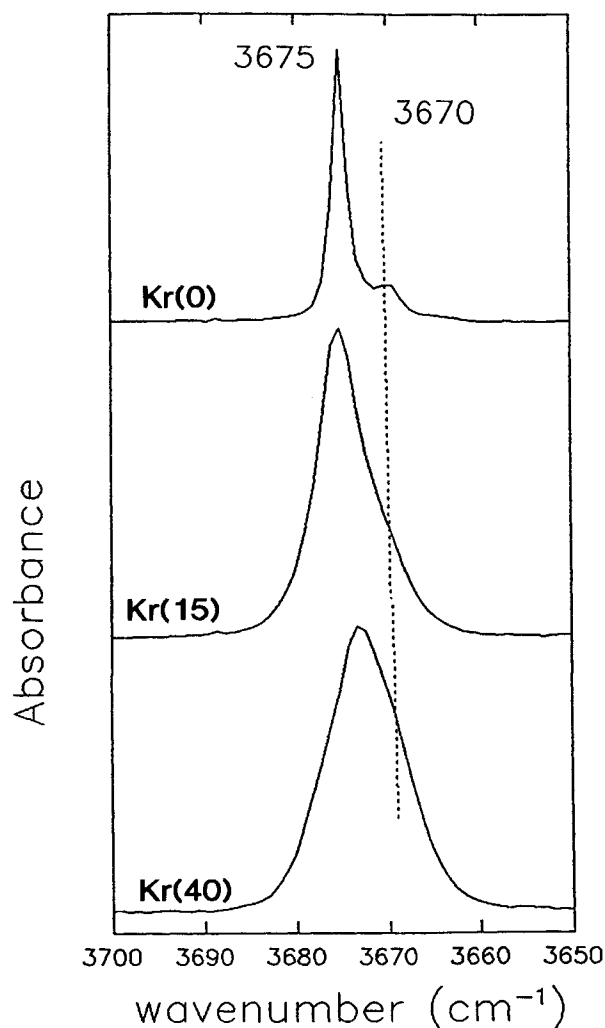


FIGURE 6. The infrared spectra of selected synthetic amphiboles along the join potassium-richertite-tremolite in the OH-stretching region ($3650\text{--}3700\text{ cm}^{-1}$). Note the increasing band asymmetry with increasing tremolite component.

Inspection of Figure 4 shows that the Tr band is narrow for the nominal end-member composition (Kr_0) but is much broader for intermediate compositions (Table 7). In Kr_0 , 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-richertite arrangement; replacement of

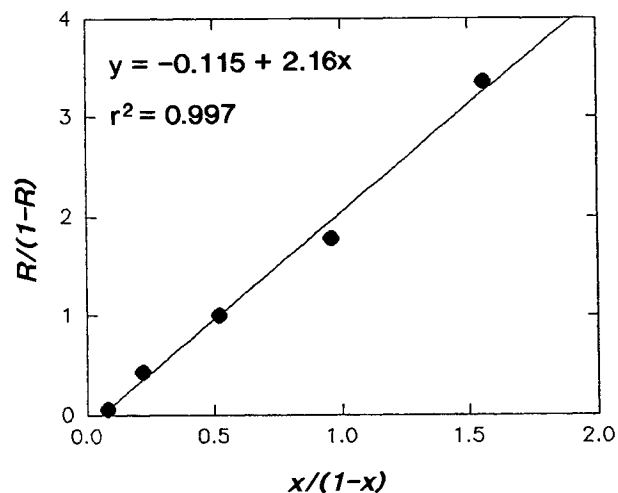


FIGURE 7. The variation in $R/(1-R)$ as a function of $x/(1-x)$ for synthetic amphiboles along the join potassium-richertite-tremolite; the slope of the trend determines the value of k .

one ${}^A\text{K}$ produces two tremolite-like configurations (associated with ${}^A\Box$) 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 ${}^A\text{K}$ by ${}^A\Box$ still produces two tremolite-like configurations; however, adjacent configurations now also tend to be tremolite-like as ${}^A\text{K} \ll {}^A\Box$. 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 Kr_{60} , the envelope is fairly symmetrical, as predicted from the above argument. As the potassium-richertite 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 $\sim 3670\text{ cm}^{-1}$ (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-richertite 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-

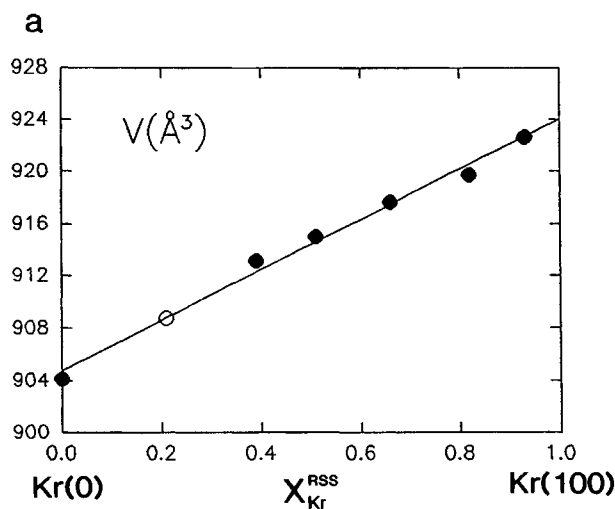


FIGURE 8. Variation in cell dimensions for the synthetic amphiboles along the potassium-richertite-tremolite join: (a) cell volume; (b) a , b , c , and β . The hollow circle is for Kr_{15} , for which no precise modal-analysis data are available. Standard deviations are smaller than the symbols.

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 ($\sim 4500\text{ cm}^{-1}$). 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-richertite 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.

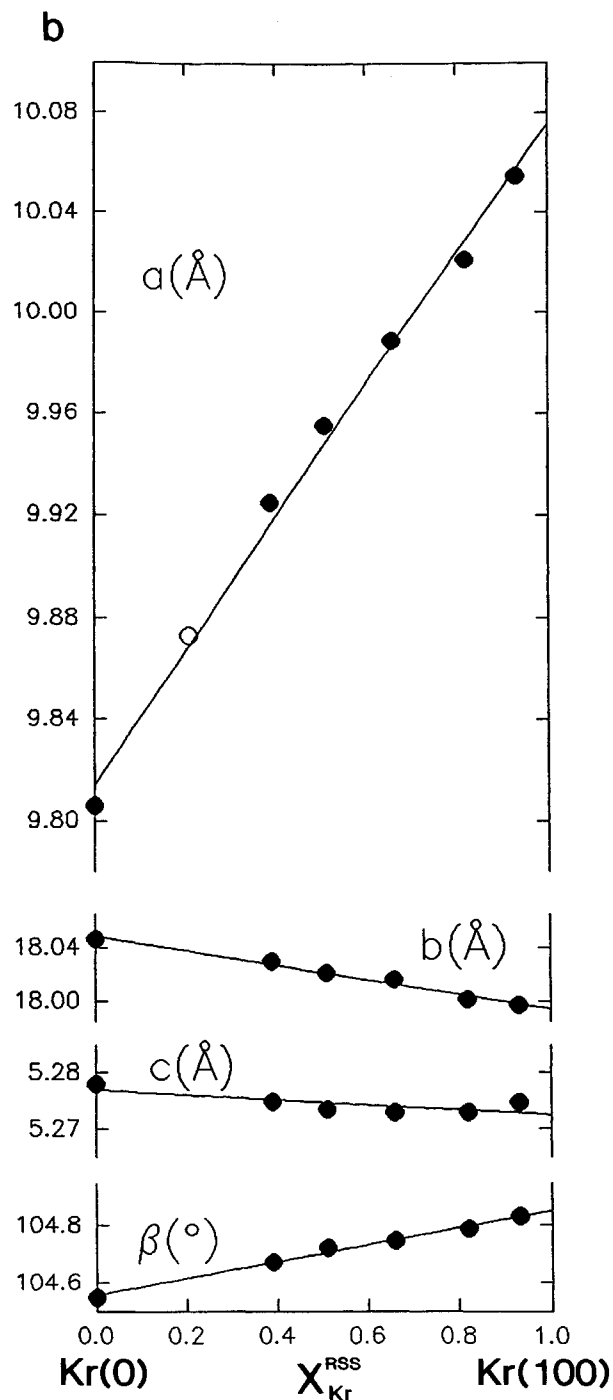
In the spectra of Figure 4, let the band intensities vary from zero to I_x^T (for the Tr band) and I_{1-x}^K (for the Kr band). At a composition x (= proportion of tremolite component in the amphibole)

$$\begin{aligned} I_x^T &= x \cdot I_1^T \\ I_{1-x}^K &= (1 - x) \cdot I_1^K. \end{aligned} \quad (1)$$

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

$$I_x^T = k \cdot I_{1-x}^K. \quad (2)$$

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



$$R = I_x^T / (I_x^T + I_{1-x}^K). \quad (3)$$

Substitution of equations 1 and 2 into equation 3 reduces to

$$x = R / [k + R(1 - k)]. \quad (4)$$

According to the curve of Skogby and Rossman (1991), k is in the range 3–4 and hence this effect may

TABLE 8. Comparison of nominal M4 and A site populations with Rietveld, modal analysis, and electron-microprobe site populations for synthetic amphiboles along the join potassium-richterite-tremolite

		Kr ₁₀₀	Kr ₈₀	Kr ₆₀	Kr ₄₀	Kr ₂₀	Kr ₀
Nominal							
M4	Ca	1.00	1.20	1.40	1.60	1.80	1.80*
	Na	1.00	0.80	0.60	0.40	0.20	0.0
A	□	0.00	0.20	0.40	0.60	0.80	1.0
	K	1.00	0.80	0.60	0.40	0.20	0.0
Rietveld							
M4	Ca	1.07(2)	1.18(2)	1.34(2)	1.49(3)	1.61(4)	1.8(1)*
	Na	0.93(2)	0.82(2)	0.66(2)	0.51(3)	0.39(4)	—
A	□	0.07(2)	0.18(2)	0.34(2)	0.49(3)	0.61(4)	—
	K	0.93(2)	0.82(2)	0.66(2)	0.51(3)	0.39(4)	—
Modal analysis							
M4	Ca	—	1.16	1.34	1.47	1.61	—
	Na	—	0.84	0.66	0.53	0.39	—
A	□	—	0.16	0.34	0.47	0.61	—
	K	—	0.84	0.66	0.53	0.39	—
Electron microprobe							
M4	Ca†	—	1.19	—	—	1.60	—
	Na	—	0.81	—	—	0.40	—
A	□	—	0.18	—	—	0.62	—
	K‡	—	0.82	—	—	0.38	—

* Nominal M4 = 1.80Ca + 0.20Mg; Rietveld-refined value = 1.8(1)Ca + 0.2(1)Mg.
 † Includes 0.01–0.02 Mg apfu.
 ‡ Includes 0.01–0.03 Na apfu.

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:

$$R/(1 - R) = k \cdot [x/(1 - x)]. \quad (5)$$

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

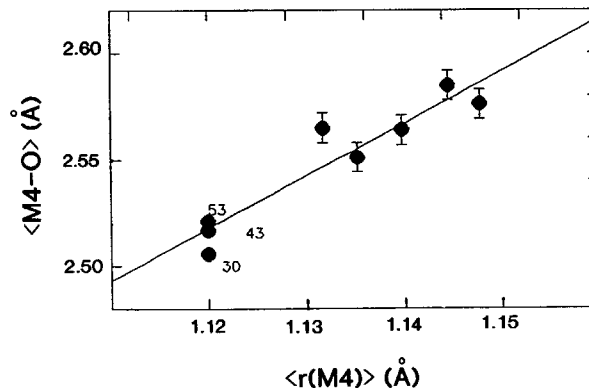


FIGURE 9. Variation in mean M4-O bond-length as a function of constituent-cation radius for synthetic amphiboles of the series potassium-richterite-tremolite. The numbered data points are from single-crystal structure-refinements of tremolite given in Hawthorne (1983b).

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 the series. Figure 9 shows the variation in ⟨M4-O⟩ as a function of the aggregate constituent-cation radius (Shannon 1976). There is a linear increase in mean bond-length with increasing cation size (i.e., increasing Na content), and the variation is in accord with ⟨M4-O⟩ bond lengths derived from single-crystal structure refinement of compositionally similar amphiboles (Fig. 9).

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.

REFERENCES CITED

- Ahn, J.H., Cho, M., Jenkins, D.M., and Buseck, P.R. (1991) Structural defects in synthetic tremolitic amphiboles. *American Mineralogist*, 76, 1811–1823.

- Burns, P.C. and Hawthorne, F.C. (1994a) Structure and hydrogen bonding in preobrazhenskite, a complex heteropolyhedral borate. *Canadian Mineralogist*, 32, 387–396.
- (1994b) Kaliborite, an example of a crystallographically symmetrical hydrogen bond. *Canadian Mineralogist*, 32, 885–894.
- Della Ventura, G. (1992) Recent developments in the synthesis and characterization of amphiboles. *Synthesis and crystal-chemistry of richterites*. *Trends in Mineralogy*, 1, 153–192.
- Della Ventura, G. and Robert, J.-L. (1990) Synthesis, XRD and FTIR studies of strontium richterites. *European Journal of Mineralogy*, 2, 171–175.
- Della Ventura, G., Robert, J.-L., and Bény, J.-M. (1991) Tetrahedrally coordinated Ti^{4+} in synthetic Ti-rich potassic richterite: Evidence from XRD, FTIR and Raman studies. *American Mineralogist*, 76, 1134–1140.
- Della Ventura, G., Robert, J.-L., Bény, J.-M., Raudsepp, M., and Hawthorne, F.C. (1993a) The OH-F substitution in Ti-rich potassium-richterites: Rietveld structure refinement and FTIR and micro-Raman spectroscopic studies of synthetic amphiboles in the system $K_2O-Na_2O-CaO-MgO-SiO_2-TiO_2-H_2O-HF$. *American Mineralogist*, 78, 980–987.
- Della Ventura, G., Robert, J.-L., Raudsepp, M., and Hawthorne, F.C. (1993b) Site occupancies in monoclinic amphiboles: Rietveld structure refinement of synthetic nickel magnesium cobalt potassium richterite. *American Mineralogist*, 78, 633–640.
- Della Ventura, G., Robert, J.-L., and Hawthorne, F.C. (1995) Short-range disorder of Si and Ti in the tetrahedral double-chain unit of synthetic Ti-bearing potassium-richterite. *American Mineralogist*, 81, 56–60.
- Della Ventura, G., Robert, J.-L., Hawthorne, F.C., and Raudsepp, M. (1997a) Contrasting ^{69}Al ordering in synthetic Mg- and Co-pargasite. *European Journal of Mineralogy*, in press.
- Della Ventura, G., Robert, J.-L., Raudsepp, M., Hawthorne, F.C., and Welch, M.D. (1997b) Site occupancies in synthetic monoclinic amphiboles: Rietveld structure-refinement and infrared spectroscopy of (nickel, magnesium, cobalt)-richterite. *American Mineralogist*, 82, 291–301.
- Graham, C.M., Maresch, W.V., Welch, M.D., and Pawley, A.R. (1989) Experimental studies on amphiboles: a review with thermodynamic perspectives. *European Journal of Mineralogy*, 1, 535–555.
- Groat, L.A., Hawthorne, F.C., Rossman, G.R., and Ercit, T.S. (1995) The infrared spectroscopy of vesuvianite in the OH region. *Canadian Mineralogist*, 33, 609–626.
- Hawthorne, F.C. (1981) Amphibole spectroscopy. In *Mineralogical Society of America Reviews in Mineralogy*, 9A, 103–139.
- (1983a) Characterization of the average structure of natural and synthetic amphiboles. *Periodico di Mineralogia*, 52, 543–581.
- (1983b) The crystal chemistry of the amphiboles. *Canadian Mineralogist*, 21, 173–480.
- Hawthorne, F.C. and Grundy, H.D. (1972) Positional disorder in the A-site of clino-amphiboles. *Nature*, 235, 72–73.
- Hill, R.J. (1991) Expanded use of the Rietveld method in studies of phase abundance in multiphase mixtures. *Powder Diffraction*, 6, 74–77.
- Jenkins, D.M. (1987) Synthesis and characterization of tremolite in the system $H_2O-CaO-MgO-SiO_2$. *American Mineralogist*, 72, 707–715.
- Jenkins, D.M. and Hawthorne, F.C. (1995) Synthesis and Rietveld refinement of amphiboles along the join $Ca_2Mg_5Si_8O_{22}F_2-NaCa_2Mg_4Ga_3Si_6O_{22}F_2$. *Canadian Mineralogist*, 33, 13–24.
- Maresch, W.V. and Czank, M. (1983a) Phase characterization of amphibole on the join $Mn_xMg_{7-x}Si_8O_{22}(OH)_2$. *American Mineralogist*, 68, 744–753.
- (1983b) Problems of compositional and structural uncertainty in synthetic hydroxyl-amphiboles: with an annotated atlas of the Realbau. *Periodico di Mineralogia*, 52, 463–542.
- (1988) Crystal chemistry, growth kinetics and phase relationships of structurally disordered (Mn^{2+}, Mg) -amphiboles. *Fortschritte der Mineralogie*, 66, 69–121.
- Maresch, W.V., Czank, M., and Schreyer, W. (1994) Growth mechanisms, structural defects and composition of synthetic tremolite: what are the effects on macroscopic properties? *Contributions to Mineralogy and Petrology*, 118, 297–313.
- Pawley, A.R., Graham, C.M., and Navrotsky, A. (1993) Tremolite-richterite amphiboles: Synthesis, compositional and structural characterization, and thermochemistry. *American Mineralogist*, 78, 23–25.
- Raudsepp, M., Turnock, A.C., and Hawthorne, F.C. (1987a) Characterization of synthetic eckermannitic amphiboles ($NaNa_2Mg_4M^{3+}Si_8O_{22}(OH,F)_2$; $M^{3+} = Al, Cr^{3+}, Ga, Sc, In$) and scandium-fluor-nyboite ($NaNa_2Mg_4Sc_2Si_8AlO_{22}F_2$) 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 ($NaCa_2Mg_4M^{3+}Si_8Al_2O_{22}(OH,F)_2$; $M^{3+} = Al, Cr^{3+}, Ga, Fe^{3+}, Sc, In$) by infrared spectroscopy, Rietveld structure refinement and ^{29}Si MAS NMR spectroscopy. *American Mineralogist*, 72, 580–593.
- Raudsepp, M., Hawthorne, F.C., and Turnock, A.C. (1990) Crystal-chemistry of synthetic pyroxenes on the join $CaNiSi_3O_6-CaMgSi_2O_6$ (diopside): a Rietveld structure refinement study. *American Mineralogist*, 75, 1274–1281.
- Raudsepp, M., Turnock, A.C., and Hawthorne, F.C. (1991) Amphibole synthesis at low pressure: what grows and what doesn't. *European Journal of Mineralogy*, 3, 983–1004.
- Robert, J.-L., Della Ventura, G., and Thauvin, J.-L. (1989) The infrared OH-stretching region of synthetic richterites in the system $Na_2O-K_2O-CaO-MgO-SiO_2-H_2O-HF$. *European Journal of Mineralogy*, 1, 203–211.
- Robert, J.-L., Della Ventura, G., Raudsepp, M., and Hawthorne, F.C. (1993) Rietveld structure refinement of synthetic strontium-rich potassium-richterites. *European Journal of Mineralogy*, 5, 199–206.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Skogby, H. and Rossman, G.R. (1991) The intensity of amphibole OH bands in the infrared absorption spectrum. *Physics and Chemistry of Minerals*, 18, 64–68.
- Smelik, E.A., Jenkins, D.M., and Navrotsky, A. (1994) A calorimetric study of synthetic amphiboles along the tremolite-tschemmakite join and the heats of formation of magnesiohornblende and tschemmakite. *American Mineralogist*, 79, 1110–1122.
- Strens, R.G.J. (1974) The common chain, ribbon, and ring silicates. In V.C. Farmer, Ed., *The Infrared Spectra of Minerals*, Mineralogical Society, London.
- Wiles, D.B. and Young, P.A. (1981) A new computer program for Rietveld analysis of X-ray powder diffraction patterns. *Journal of Applied Crystallography*, 14, 149–151.

MANUSCRIPT RECEIVED MAY 14, 1996

MANUSCRIPT ACCEPTED MARCH 17, 1997