American Mineralogist, Volume 81, pages 56–60, 1996

Short-range disorder of Si and Ti in the tetrahedral double-chain unit of synthetic Ti-bearing potassium-richterite

GIANCARLO DELLA VENTURA,[1] JEAN-LOUIS ROBERT,[2] FRANK C. HAWTHORNE,[3] AND RENÉ PROST[4]

[1]Dipartimento di Scienze Geologiche, Terza Università di Roma, Via Ostiense 169, I-00154 Rome, Italy
[2]Centre de Recherche sur la Synthèse et Chimie des Mineraux, CNRS, 1A, Rue de la Férollerie, F-45071 Orléans Cedex 2, France
[3]Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada
[4]INRA, Station de Science du sol, Route de Saint-Cyr, F-78026 Versaille, France

ABSTRACT

Ti-rich potassium-richterite samples were synthesized at 900 °C and 1 kbar P_{H_2O} and characterized by Fourier-transform infrared spectroscopy (FTIR) and Rietveld structure refinement. The infrared spectrum of end-member Ti-free potassium-richterite shows a main band at 3734 cm^{-1} assigned to an OH anion bonded to three octahedral Mg cations and directed toward K at the A site facing a tetrahedral ring of composition Si_6. When Ti is introduced into the structure, two new overlapping components appear in the infrared spectrum. Using a symmetric Gaussian model, they can be resolved into two single bands at 3711 and 3698 cm^{-1}. These two bands are assigned to OH groups facing rings of tetrahedra with compositions Si_5Ti and Si_4Ti_2, respectively. Their intensities are linearly related to the Rietveld-refined Ti content at T2 up to 0.8 apfu (atoms per formula unit). The analysis of relative band intensities indicates short-range disorder of Si and Ti over the T2 sites.

INTRODUCTION

In the OH-stretching region of OH-bearing minerals, the measured infrared absorptions are not usually single bands but consist of overlapping components that must be resolved for use in quantitative interpretation. In the past, there has been much infrared spectroscopy done on natural amphiboles (Strens 1966; Burns and Strens 1966; Burns and Greaves 1971), but the method fell into disuse owing to the difficulties involved. Specifically, most natural amphiboles are chemically complex, which introduces too many sources of uncertainty into the spectrum-resolution procedure. However, IR analysis of well characterized, compositionally simple, synthetic solid-solutions is more tractable and provides an ideal situation for examining the behavior of OH absorption bands in terms of multiplicity, position, shape, and intensity.

In the last few years, we have devoted much effort to this approach. By experimentally producing selected cation substitutions at single structural sites in amphiboles, bands can be associated with specific substitutions at particular crystallographic sites. These efforts have allowed us to make progress in understanding some crystal-chemical aspects of the clino-amphibole structure (Robert et al. 1989; Della Ventura and Robert 1990; Della Ventura et al. 1991, 1993a; Hawthorne et al. 1993). The evolution of IR spectra in the OH-stretching region along the Si-Ti join for potassium-richterite has been briefly considered in previous works (Della Ventura and Robert 1988; Della Ventura et al. 1991, 1993a). Here we propose a model to quantify the Si-Ti substitution from measured band intensities and to derive the short-range order associated with Si-Ti substitution at the T2 sites in the structure.

This work required development of an accurate and physically consistent model for depicting the absorption band shape and for the spectrum-fitting procedure. The situation in the present study is almost ideal: Because the samples were previously characterized by a variety of techniques, and both the location and amount of Ti present in the phase are known, the spectrum-fitting procedure can be optimized.

EXPERIMENTAL METHODS

The amphiboles studied here are those synthesized at 900 °C and 1 kbar P_{H_2O} by Della Ventura et al. (1991). Description of the synthesis conditions and characterization methods may be found in Mottana et al. (1990), Della Ventura et al. (1991), and Paris et al. (1993). Along the join between potassium-richterite and the Ti end-member of potassium-richterite, a single-phase amphibole was obtained for compositions up to 0.6 apfu of Ti in the system; for higher Ti contents, minor amounts of additional Ti-bearing phases were observed (Della Ventura et al. 1991). Only the single-phase experimental products (i.e., those with a nominal content up to 0.6 Ti apfu in the amphibole) were used for structure refinement by the Rietveld method, with final R_{Bragg} values in the range 4–6%. Full details of the XRD data collection and refinement procedures may be found in Della Ventura et al. (1993a, 1993b). Detailed discussion of the Rietveld results is beyond the scope of the present paper. We merely

0003–004X/96/0102–0056$05.00

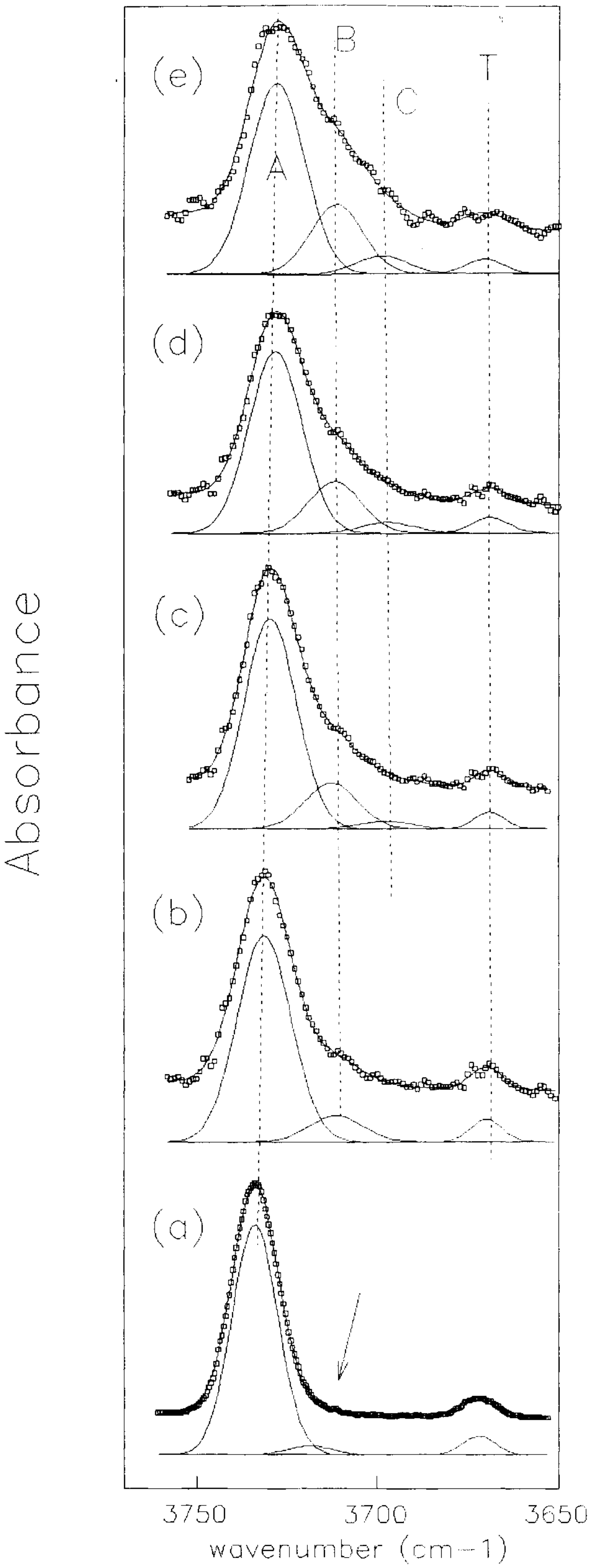
note that, for all samples, the refined tetrahedral site occupancies are coincident (within 2σ) with the nominal values.

For the FTIR data collection, samples were prepared as KBr pellets using the procedure of Robert et al. (1989). Spectra in the range 4000–3000 cm^{-1} were recorded on a Perkin-Elmer model 1760 spectrometer equipped with a DTGS detector and a KBr beamsplitter and operating at a nominal resolution of 1 cm^{-1}. Low-temperature spectra were collected on a Bruker IFS113V spectrophotometer equipped with a nitrogen-cooled cryostat.

SPECTRUM FITTING

Digitized spectra (average of 64 scans) were fitted by interactive optimization followed by least-squares refinement. The background was modeled as a linear function, and all peaks were modeled as symmetric Gaussians. The distribution of absorption as a function of energy (wavenumber) was described by the relationship: y = A exp[$-$0.5(X $-$ P/W)^2] where A is the amplitude, P is the peak centroid, and W is the full width at half maximum (FWHM).

The infrared spectrum of end-member Ti-free potassium-richterite (Fig. 1a), when fitted by symmetric Gaussian bands, shows residual intensity toward the lower wavenumber tail of the main band, indicating a slight asymmetry of the band itself. Initially, it was not clear whether the asymmetry is intrinsic to the single-band shape or results from a second weak component. The asymmetric band in the end-member could be fitted equally well by a single asymmetric Gaussian band and by two symmetric Gaussian bands. This is an important issue to resolve because it affects the fitting of more complex spectra of the solid solution. Consequently, we recorded the spectrum also at liquid-nitrogen temperature (77 K) to improve the resolution. The resulting spectrum (Fig. 2) clearly shows that there is an additional weak band on the low energy side of the main band. The origin of this band is discussed elsewhere. The intensity of this second component centered at 3720 cm^{-1} (indicated by the arrow in Fig. 1a) is not more than 4–5% of the total band intensity. Thus any possible asymmetry of the component bands was neglected, and all peaks were modeled as symmetric Gaussians. The 3720 cm^{-1} band overlaps partly with the A band (3734 cm^{-1}) and partly with the B band (3711 cm^{-1}). Because the intensity of the 3720 cm^{-1} band is approximately 5% of the total intensity, ignoring the 3720 cm^{-1} band in the refinement process introduces errors of approximately ≤2% into the intensities of the A and B bands. This amount of error is not significant in the present case.



→

FIGURE 1. FTIR spectra in the OH-stretching region for amphiboles synthesized along the join between potassium-richterite and the Ti end-member of potassium-richterite. The band nomenclature is also given. (**a**) Ti-free sample, (**b**) Ti = 0.2 apfu, (**c**) Ti = 0.4 apfu, (**d**) Ti = 0.6 apfu, and (**e**) Ti = 0.8 apfu.

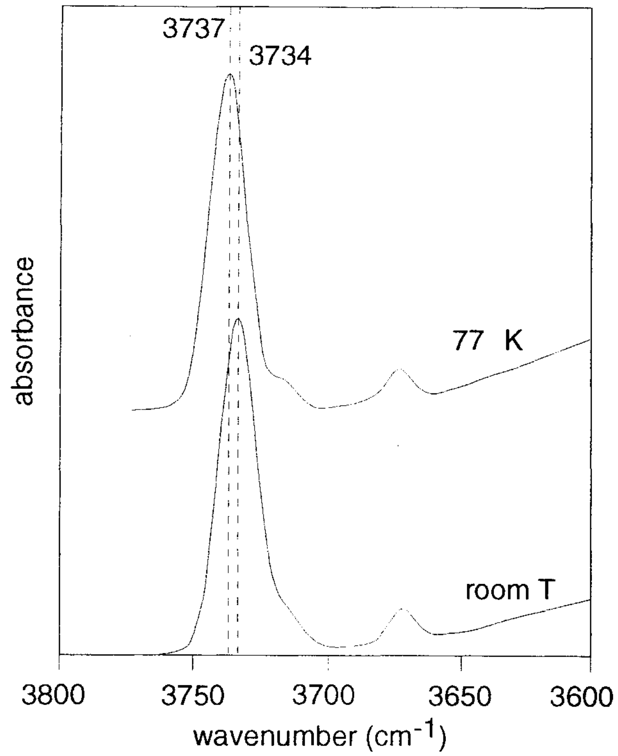


Figure 2. FTIR spectra of potassium-richterite recorded at room temperature and 77 K.

There are two ways in which one can fit a spectrum to component peaks: (1) by fitting a prior model or series of models to the spectrum, or (2) if no prior model is available, by introducing the minimum number of variables required to fit the data. Here, we have no prior model, and hence the spectra were fitted with the smallest number of peaks needed for an accurate description of the spectral profile. We can rationalize this choice because we cannot adequately fit the data with less than three peaks, and we have no statistical justification for using more than three peaks (i.e., three peaks adequately fit the data). The initial refinement was done with all parameters unconstrained. After examination of the results, and on the basis of our knowledge of the OH-stretching region of these amphiboles (Robert et al. 1989; Della Ventura et al. 1991, 1993a; Hawthorne et al. 1993), peak positions and half-widths were constrained to be equal in all spectra. During the final refinement cycles, the peak positions were allowed to vary while constraining the half-widths to be equal for all component bands.

It is well known that OD-stretching bands are much sharper than the corresponding OH-stretching bands (Ryskin 1974). In some cases, this allows better resolution of overlapping components. In addition, because of the different OD/OH reduced-mass ratio, the OD bands are shifted to a lower frequency region of the spectrum that is free of any interference with atmospheric water or sample moisture. For this reason, OD counterparts of both end-member Ti-free and Ti-rich (nominal composition Ti = 1.0 apfu) potassium-richterite were synthesized at 800 °C and 1 kbar P_{D_2O}. Powder X-ray diffraction shows that the experimental products are identical to those for the OH-containing amphiboles (i.e., a monophase product for Ti-free richterite and an assemblage of amphibole plus minor priderite + titanite + rutile for the Ti-rich composition). The IR spectrum of Ti-free OD-containing richterite (Fig. 3a) shows a main band at 2751 cm^{-1} plus a minor component at 2708 cm^{-1}. The main band is consistently sharper than the OH-stretching band (FWHM = 11 vs. 17 cm^{-1}), and the shape is identical. It can be fitted by a symmetric Gaussian with slight asymmetry toward the low-wavenumber tail, exactly as for the OH analog.

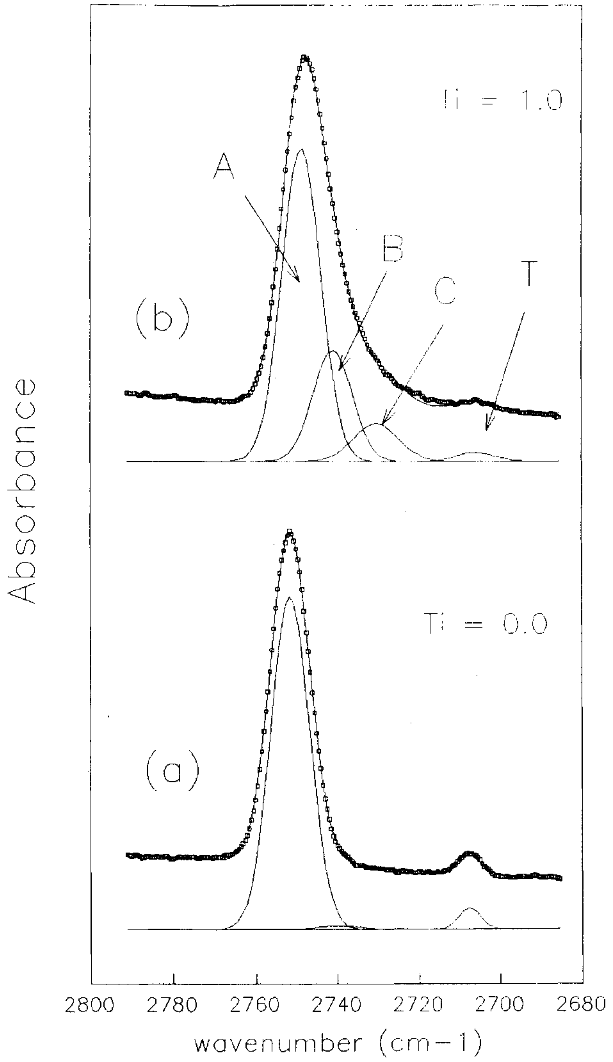


Figure 3. FTIR spectra in the OD-stretching region for (**a**) Ti-free end-member and (**b**) Ti-rich potassium-richterite. Band nomenclature as in Figure 1.

TABLE 1. Measured areas (%) under each component band for the analyzed samples

Sample Ti (apfu)	RICH30 0.2	RICH31 0.4	RICH32 0.6	RICH33 0.8	RICH34 1.0	DEUT 1.0
A	0.89	0.80	0.75	0.66	0.72	0.68
B	0.11	0.17	0.21	0.27	0.22	0.24
C	0.00	0.03	0.04	0.07	0.06	0.08

TABLE 2. Probability of occurrence of local T2-T2 configurations

T2 pair comp.	Prob. of occurrence	Band
Si-Si	$(1 - x/4)^2$	A
Si-Ti	$2(1 - x/4)(x/4)$	B
Ti-Ti	$(x/4)^2$	C

Note: x = Ti apfu.

EXPERIMENTAL RESULTS

The resolved spectra and band nomenclature are shown in Figure 1. The spectrum of end-member potassium-richterite shows an intense band centered at 3734 cm^{-1}, assigned to an MgMgMg-OH → K configuration, and a minor 3670 cm^{-1} band, possibly due to the presence of some vacant A sites in the amphibole (band T in Fig. 1). The addition of Ti^{4+} into the T2 tetrahedron of these amphiboles (Della Ventura et al. 1991, 1993a; Paris et al. 1993) correlates with the appearance of two additional bands at 3711 and 3698 cm^{-1} (bands B and C in Figs. 1b–1e). The intensities of these bands increase with increasing Ti content of the amphibole; hence, these two bands must be assigned to configurations involving $^{[4]}Ti$ because they are absent in the spectrum of Ti-free potassium-richterite (Fig. 1a). The same pattern is also observed in the spectrum of the OD-containing Ti-rich richterite (Fig. 3b), in which the A, B, and C bands are found at 2748, 2740, and 2730 cm^{-1}, respectively. The measured areas under each component band are given in Table 1. Figure 4 shows the relationship between the intensity of the B + C bands (relative to the total band intensity) and the refined Ti^{4+} occupancy at T2. The data define a linear trend up to 0.8 Ti apfu in the amphibole.

The regression line defining this trend is given by $y = 0.046 + 0.35Ti$ ($r^2 = 0.98$). Note that the regression line was calculated for the points representing samples up to 0.6 Ti apfu because only for these samples was the Ti content at T2 refined by the Rietveld method. The point representing the $Si_{7.2}Ti_{0.8}$ tetrahedral composition (diamond in Fig. 4) also plots on the same line, and we infer that the maximum solubility limit for Ti in potassium-richterite is at least 0.8 apfu under the synthesis conditions used. The same conclusion was reached by Della Ventura et al. (1991) by considering the cell-parameter variation along this join. In Figure 4, we also plot the sample with a nominal composition of 1.0 Ti apfu. Calculation of the relative (B + C)/(A + B + C) band intensities allows an estimation of 0.7 Ti apfu in this amphibole. A value of 0.8 Ti apfu is calculated for the OD-containing Ti-rich sample (Table 1, Fig. 4).

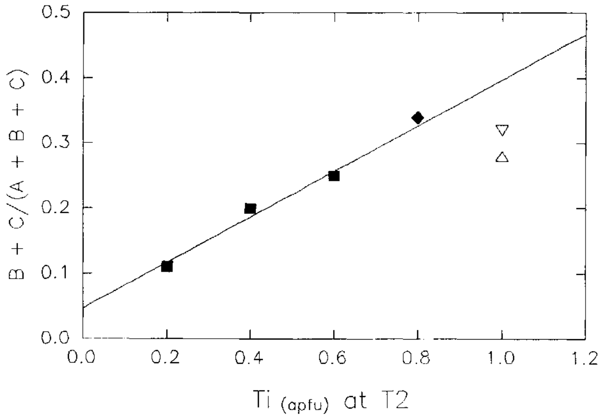


FIGURE 4. Intensity of the B + C bands (Ti bands) relative to the total band intensity (A + B + C) as a function of Ti at T2. Squares = refined samples, diamond = not refined, triangle = Ti-rich end-member, and inverted triangle = OD-containing Ti-rich end-member.

DISCUSSION

With increasing $^{[4]}Ti$, there is no continuous downward shift in the position of the main band; it remains fixed at around 3730 cm^{-1} and new bands appear at constant wavenumber (Fig. 1). This is known as a two-mode behavior and suggests the existence of distinct local tetrahedral configurations, each with its own composition and degree of distortion. The appearance of these new bands must be associated with local order-disorder of Si and Ti in the tetrahedra. It is well established that $^{[4]}Ti$ orders completely at the T2 site in potassium-richterite (Della Ventura et al. 1991, 1993a; Mottana et al. 1990; Oberti et al. 1992; Paris et al. 1993), and hence there is no long-range disorder.

There are two T2 sites in each ring of six tetrahedra, and each of these may be occupied by Si or Ti. Thus there are only three possible configurations around each OH group: Si-Si, Si-Ti, and Ti-Ti. The intensity of an OH-stretching band is proportional to the number of OH groups in each configuration. Assuming a random distribution of Si and Ti over the two T2 sites, one can calculate the probability of occurrence of each type of T2-T2 pair as a function of the bulk Ti content (Table 2). Figure 5 shows the observed relative intensities of the

TABLE 3. Ideal band intensities calculated according to the equations of Table 2

Sample	RICH30	RICH31	RICH32	RICH33
A	0.90	0.81	0.72	0.64
B	0.10	0.18	0.26	0.32
C	0.00	0.01	0.02	0.04

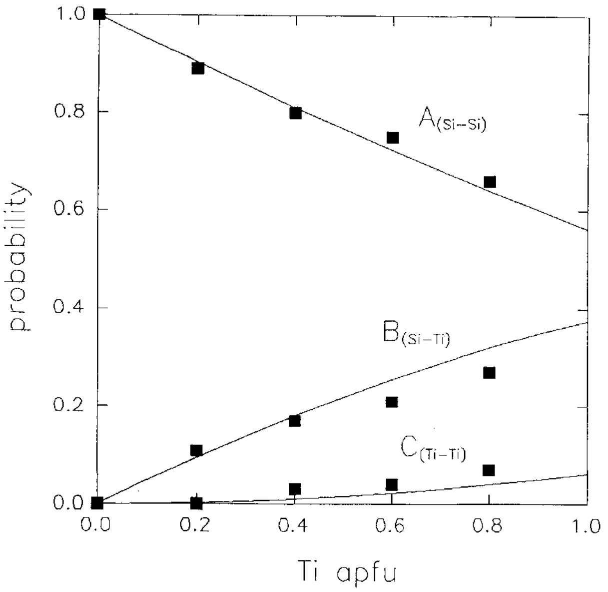


FIGURE 5. The measured A, B, and C band intensities (squares) as a function of Ti content; the lines are calculated from probability equations of Table 2 assuming a random distribution.

three resolved bands as a function of the calculated probabilities of occurrence of the three possible Si-Ti arrangements. The result of this plot leads us to assign the B band (3711 cm^{-1}) to the Si-Ti configuration and the C band (3698 cm^{-1}) to the Ti-Ti configuration. Thus, the A band (3734 cm^{-1}) is due to OH groups adjacent to a ring of composition Si_6, the B band to a Si_5Ti ring, and the C band to a Si_4Ti_2 ring. The close agreement between the calculated and observed values (Tables 1 and 3, Fig. 5) indicates that there is complete short-range disorder of Si and Ti over the T2 sites in the double-tetrahedral-chain of the potassium-richterite structure.

The Si-Ti substitution does not modify the charge balance around the OH groups. Hence the appearance of the low-wavenumber bands must be caused by the different local distortions of the tetrahedral rings resulting from the different T2 compositions. The replacement of $^{[4]}Si^{4+}$ (0.26 Å) by $^{[4]}Ti^{4+}$ (0.42 Å, Shannon 1976) must induce kinking of the double chain to preserve linkage with the octahedral strip. This kinking must shorten the distance between the proton in the OH group and the tetrahedral oxygens, inducing the appearance of new OH-stretching bands.

Finally, there is another point that deserves comment. The extrapolation of the regression line to Ti = 0.0 shows the apparent presence of a minor Ti-related component in a nominally Ti-free sample (Fig. 4). This is due to the presence of the weak low-wavenumber component of band A in the spectrum of Ti-free richterite, which, as discussed above, partly overlaps with the new (Ti-related) band B (Fig. 1).

ACKNOWLEDGMENTS

We thank David Jenkins, Charles A. Geiger, and Anton Beran for their comments, which greatly improved the clarity of the manuscript. Part of this work was done during the stay of G.D.V. at the Department of Geological Sciences, University of Manitoba, supported by an International Council for Canadian Studies grant. Financial assistance was provided by a CNR grant to G.D.V. and by Operating, Equipment and Infrastructure grants from the Natural Sciences and Engineering Research Council of Canada to F.C.H.

REFERENCES CITED

Burns, R.G., and Strens, R.G.J. (1966) Infrared study of the hydroxyl bands in clinoamphiboles. Science, 153, 890–892.

Burns, R.G., and Greaves, C.J. (1971) Correlations of infrared and Mössbauer site population measurements of actinolites. American Mineralogist, 56, 2010–2033.

Della Ventura, G., and Robert, J.-L. (1988) OH-stretching region IR study of Ti-rich synthetic richterites (abs.). Terra Cognita, 8, 60.

——— (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 richterite: 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.

Hawthorne, F.C., Della Ventura, G., and Robert, J.-L. (1993) Short-range order in amphiboles: Can we derive such data from infrared spectra in the principal OH-stretching region? (abs.). GAC-MAC Annual Meeting, Edmonton, Canada.

Mottana, A., Paris, E., Della Ventura, G., and Robert, J.-L. (1990) Spectroscopic evidence for tetrahedrally-coordinated titanium in richteritic amphiboles. Rendiconti Fisici Accademia Lincei, 1, 387–392.

Oberti, R., Ungaretti, L., Cannillo, E., and Hawthorne, F.C. (1992) The behaviour of Ti in amphiboles: I. Four- and six-coordinated Ti in richterite. European Journal of Mineralogy, 4, 425–439.

Paris, E., Mottana, A., Della Ventura, G., and Robert, J.-L. (1993) Titanium valence and coordination in synthetic richterite–Ti-richterite amphiboles: A synchrotron-radiation XAS study. European Journal of Mineralogy, 5, 455–464.

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.

Ryskin, Ya.I. (1974) The vibration of protons in minerals: Hydroxyl, water and ammonium. In R.G. Farmer, Ed., The infrared spectra of minerals, p. 137–181. Mineralogical Society, London, U.K.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Strens, R.G.J. (1966) Infrared study of cation ordering and clustering in some (Fe,Mg) amphibole solid solutions. Chemical Communications, 15, 519–520.

MANUSCRIPT RECEIVED MARCH 10, 1995
MANUSCRIPT ACCEPTED SEPTEMBER 27, 1995