

Infrared spectroscopy of synthetic (Ni,Mg,Co)-potassium-richterite

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Abstract—The two series (Mg,Ni)- and (Mg,Co)-potassium-richterite were synthesized at 750°C, 1 kbar P(H₂O) and characterized by FTIR spectroscopy. The infrared spectra of nominal end-member compositions show a single main band assigned to an OH anion bonded to three identical octahedral M²⁺ (M²⁺ = Ni, Mg or Co) cations and directed toward K at the A-site, and a minor band at lower wavenumbers assigned to an OH anion bonded to three identical octahedral cations and directed toward a □ (vacancy) at the A-site. Intermediate binary compositions show fine-structure caused by ordering of cations over the M(1) and M(3) sites in the structure; this fine structure constitutes a quartet of bands for each single band in the nominal end-member compositions. Precise band-intensities were derived by non-linear least-squares fitting of Gaussian band-shapes to the observed spectra. The relative intensities of the combinations of bands $3I_A + 2I_B + I_C$ and $I_B + 2I_C + 3I_D$ are in accord with the equations of BURNS and STRENS (1966) and seem to contradict the experimental results of SKOGBY and ROSSMAN (1991) on variation in molar absorptivity with principal-stretching frequency in amphiboles. Using the equations of HAWTHORNE *et al.* (1996) and the long-range site-populations of DELLA VENTURA *et al.* (1993) for the same series indicates that there is significant short-range order in these amphiboles involving MgMgMg and NiNiNi (or CoCoCo) clustering.

INTRODUCTION

ORDERED END-MEMBER amphiboles have a single absorption band in the principal OH-stretching region of the infrared. In intermediate amphibole compositions, this band has a prominent fine-structure that can be attributed to cation substitution effects within the structure. STRENS (1966) and BURNS and STRENS (1966) used the relative band-intensities of this fine structure to derive information on LRO (long-range order) and SRO (short-range order) of divalent cations, specifically Mg and Fe²⁺, over the M(1) and M(3) sites in amphiboles (see surveys by STRENS, 1974 and HAWTHORNE, 1981, 1983). However, work by LAW (1976), WHITTAKER (1979) and SKOGBY and ROSSMAN (1991) indicated significant problems with the models used for the quantitative interpretation of these spectra, and the method fell into disuse for such work. In contrast to natural amphiboles, infrared spectroscopy in the principal OH-stretching region has played an increasingly important role in the characterization of ordering in synthetic amphiboles (SEMET, 1973; RAUDSEPP *et al.*, 1987, 1991; ROBERT *et al.*, 1989; DELLA VENTURA and ROBERT, 1990; DELLA VENTURA, 1992; DELLA VENTURA *et al.*, 1991, 1993a). However, none of these applications has addressed the question of ordering of divalent cations over the M(1) and M(3) sites, the original problem to which the method was applied in natural amphiboles. It is apparent from all of the original work done on natural amphiboles that the fine structure of the absorption in the principal OH-stretching region contains significant information on ordering of divalent cat-

ions over the M(1) and M(3) sites. This being the case, it seems wasteful not to extract this information and characterize ordering in amphiboles. With this end in mind, here we examine the infrared spectra of the two solid-solution series (Mg, Ni)-potassium-richterite and (Mg,Co)-potassium-richterite, $K(\text{CaNa})(\text{Mg},\text{M}^{2+})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$, M²⁺ = Ni or Co. DELLA VENTURA *et al.* (1993b) described the synthesis and characterization of these amphiboles, and reported site-populations derived by Rietveld structure-refinement. We note that these latter data provide significant quantitative constraints on our interpretation of band-intensity variations in the infrared spectra of these amphiboles.

EXPERIMENTAL

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.

Digitized spectra (average of 64 scans) were fitted by interactive optimization followed by least-squares refinement. The background was modelled as linear and all peaks were modelled as symmetric Gaussians (STRENS, 1974). The distribution of absorption, y , as a function of energy (wavenumber, x) 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 height (FWHM). The spectra were fitted to the smallest number of peaks needed to get an accurate description of the spectral profile. For intermediate compositions, all parameters were well defined by the envelope of the spectrum and all peak parameters could be refined unconstrained. For compositions close to the end

members, the weak bands tended to merge with the background if all their parameters were refined unconstrained; consequently, for the weak bands, the positions were fixed at the values determined in those spectra in which the corresponding peaks are intense, and the band widths, W , were constrained to be equal to the width of the same band.

RESULTS

The raw spectra and band nomenclature are shown in Fig. 1 and the fitted spectra are shown in Fig. 2. Band positions, widths and relative intensities ($=I/I^{\text{TOTAL}}$) are given in Table 1. The spectrum of end-member potassium-richterite shows an intense band centered at 3735 cm^{-1} , assigned to an $\text{MgMgMg}-\text{OH} \rightarrow \text{K}$ configuration and designated the A band, and a minor band at 3670 cm^{-1} due to the presence of some vacant A-sites in the amphibole (band A* in Fig. 1). We have tried to synthesize both richterite and potassium-richterite under a variety of conditions in order to get rid of the A* band and produce an amphibole with a fully occupied A-site. However, the A* band is always present, even in richterites synthesized in concentrated NaCl or KCl solutions, and we conclude that a significant amount of vacancy at the A site is characteristic of the richterite structure. The spectrum of Ni(20) shows four reasonably intense bands designated A, B, C and D, and these bands are present in the spectra of all intermediate synthetic amphiboles examined here. These bands are due to the local configurations around the OH site (Table 2), as first established by STRENS (1966, 1974) and BURNS and STRENS (1966).

Examination of the spectra of the intermediate-composition amphiboles (Fig. 1) shows that the A* band is also associated with a triplet of additional bands that are most easily seen in the spectra of Ni(40), Co(40) and Co(60) (Fig. 1). These bands are designated as B*, C* and D*, and their assignment to specific local configurations is given in Table 2.

DISCUSSION

Variation in molar absorptivity with frequency

The primary interest in using infrared spectroscopy in the principal OH-stretching region to look at amphiboles is to derive information on LRO (Long-Range Order) and SRO (Short-Range Order) of cations in the amphibole structure. In the approach developed by STRENS (1966), BURNS and STRENS (1966) and LAW (1976), the relative intensities of the A, B, C and D bands are directly related to cation ordering over the M(1) and M(3) sites.

However, this approach implicitly assumed that the molar absorptivity is the same for each of these bands (*i.e.*, the transition moment is the same for all local cation configurations in the structure). In a polarized single-crystal infrared absorption study of amphiboles, SKOGBY and ROSSMAN (1991) showed that the integrated molar absorptivity for the principal OH-stretching-band increases with decreasing stretching frequency. The analogous relation was also observed in polarized single-crystal spectra of vesuvianite (GROAT *et al.*, 1995). BURNS and HAWTHORNE (1994) showed the analogous relation for normalized OH-stretching-band intensities in powder infrared spectra of borate minerals. Thus the implicit assumption of previous work on powder spectra of amphiboles, that there is no variation in molar absorptivity with frequency, seems invalid. This relation must be experimentally characterized if we wish to relate the intensities of the OH-stretching bands to the concentrations of specific local configurations in the amphibole structure.

HAWTHORNE *et al.* (1996) show that the binary site occupancies $x (= \text{Mg}/[\text{Mg} + \text{M}^{2+}])$ and $y (= \text{M}^{2+}/[\text{Mg} + \text{M}^{2+}])$ at the M(1) and M(3) sites in the amphibole structure are related to the observed relative intensities, I° , in the following way, provided that there is no variation in molar absorptivity with band frequency *within a single sample*.

$$I_A^{\circ} + I_B^{\circ} + I_C^{\circ} = x_{\text{M}(3)}$$

$$I_B^{\circ} + I_C^{\circ} + I_D^{\circ} = y_{\text{M}(3)}$$

$$2I_A^{\circ} + 2I_B^{\circ} + I_B^{\circ} + I_C^{\circ} = 2x_{\text{M}(1)}$$

$$I_B^{\circ} + 2I_C^{\circ} + I_C^{\circ} + 2I_D^{\circ} = 2y_{\text{M}(1)} \quad (1)$$

If we sum the band intensities in equation (1) relating to the occupancies of M(1) and M(3), we get the following relations:

$$\text{Mg}_{\text{M}(1,3)} = 3I_A^{\circ} + 2I_B^{\circ} + I_C^{\circ} \quad (2.1)$$

$$\text{M}_{\text{M}(1,3)}^{2+} = I_B^{\circ} + 2I_C^{\circ} + 3I_D^{\circ} \quad (2.2)$$

These are the original equations of BURNS and STRENS (1966) who used them for amphiboles in which the M(2) site is occupied by Al and Fe^{3+} , and for which the unit formulae give directly the cations occupying the M(1,3) sites. For the (Ni,Mg,Co)-potassium-richterites of this work, DELLA VENTURA *et al.* (1993b) derived the populations of the M(1), M(2) and M(3) sites by Rietveld structure-refinement, and hence the contents of Mg and M^{2+} at the M(1,3) sites are known for these amphiboles. In equation (2), the band intensities must be corrected for variation in molar absorptivity as a function of absorption fre-

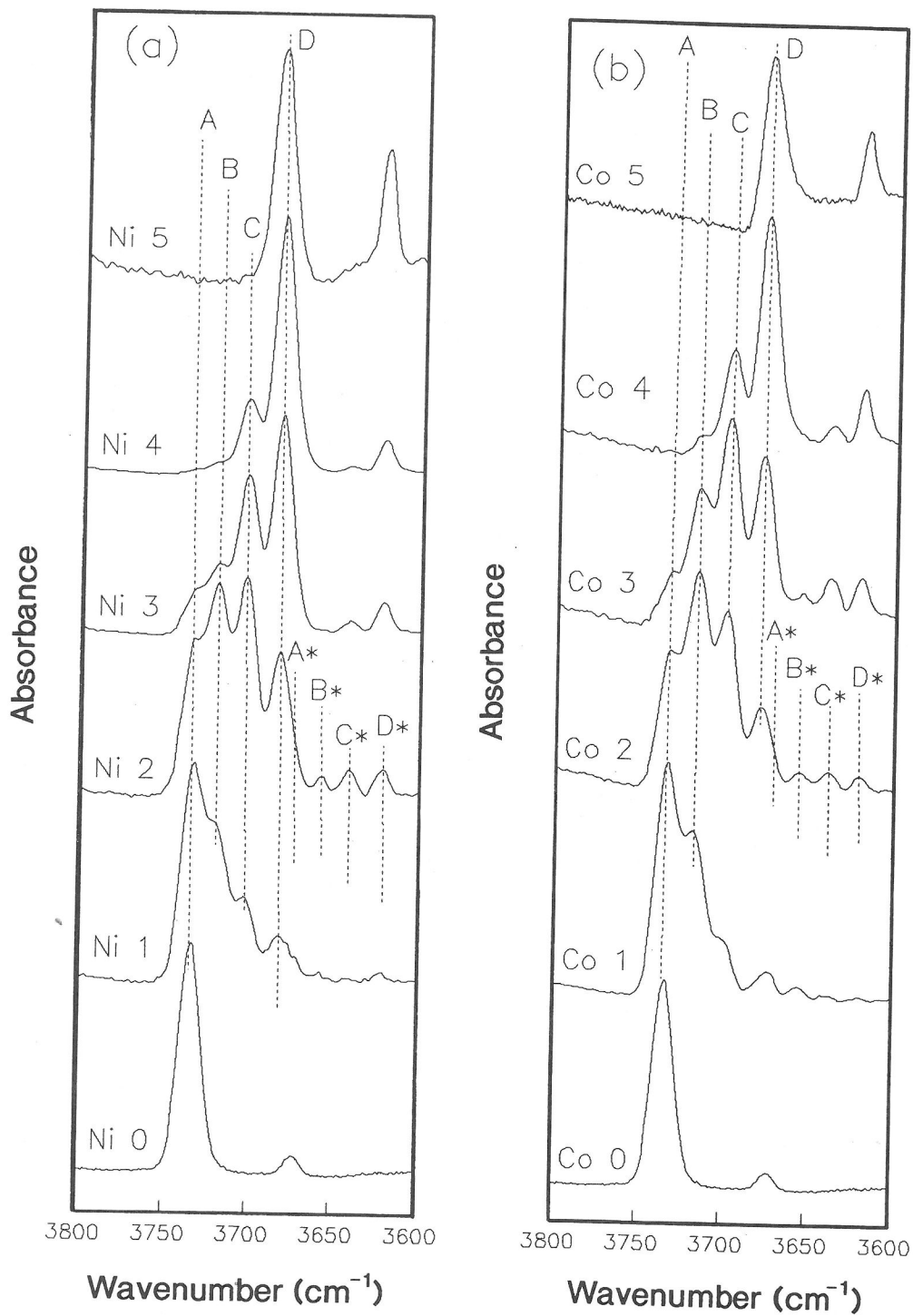


FIG. 1. FTIR spectra in the OH-stretching region for amphiboles synthesized along (a) the Ni-potassium-richterite—potassium-richterite join; (b) the potassium-richterite—Co-potassium-richterite join. The band nomenclature is also given.

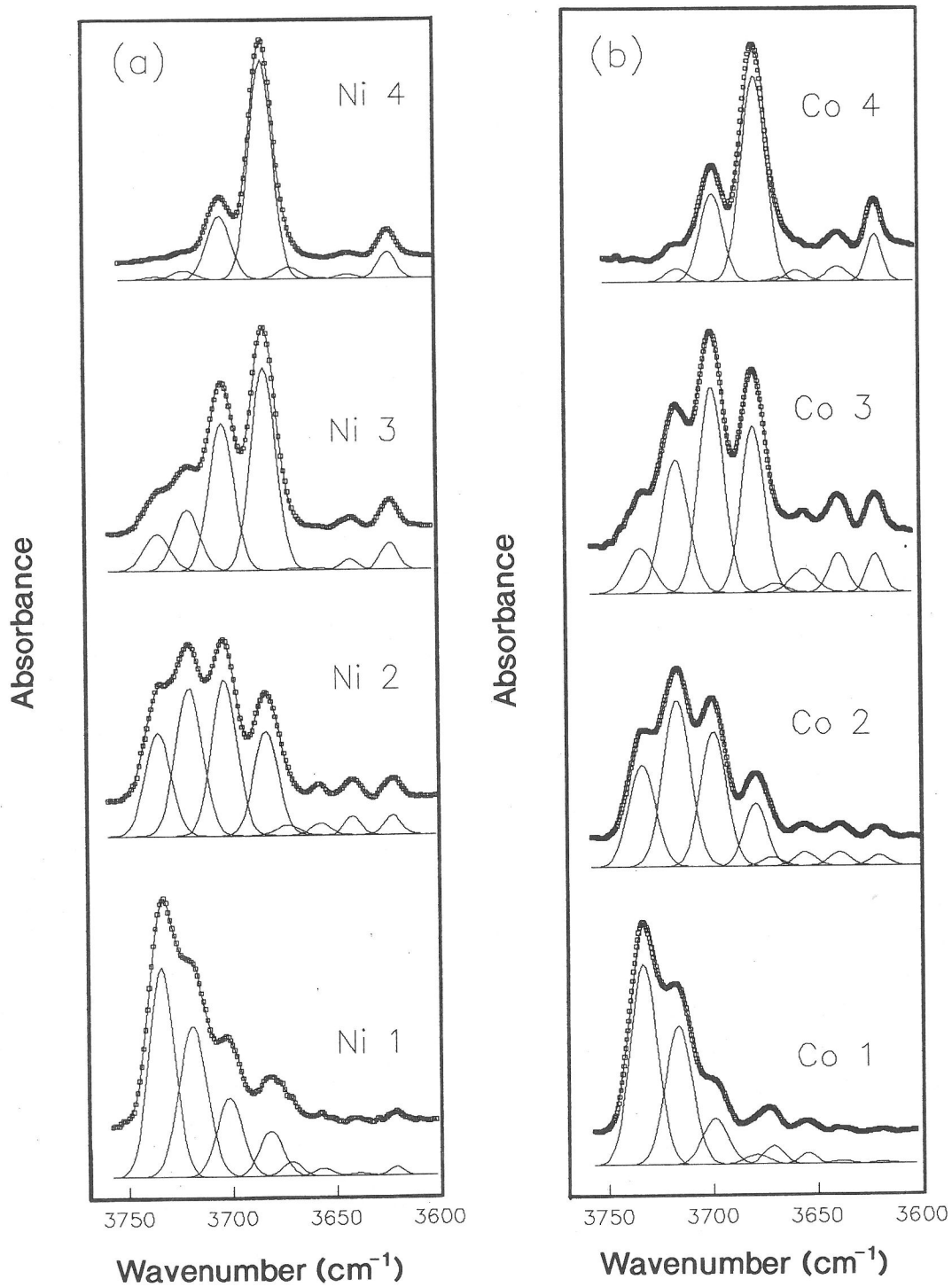


FIG. 2. Resolved spectra for the intermediate amphiboles synthesized along (a) the (Mg,Ni)-potassium-richterite join; (b) the (Mg,Co)-potassium-richterite join. Resolved bands are vertically displaced for clarity; observed intensities are shown by the hollow squares, and the line following the observed intensities is the envelope of the sum of the fitted component bands.

Table 1. Refined positions (cm^{-1}), widths (cm^{-1}) and normalized integrated intensities of fine-structure bands in the principal OH-stretching region of the infrared spectra of synthetic (Ni,Mg,Co)-potassium-richterites

		A	B	C	D	A'	B'	C'	D'
Ni(20)	Position ¹	3734.4	3719.5	3701.6	3682.1	3671.7	3656.8	3639.5	3622.0
	Width ²	14.0	16.1	14.8	12.1	10.7	10.4	11.9	10.8
	Intensity	0.390	0.324	0.155	0.075	0.026	0.011	0.006	0.013
Ni(40)	Position	3735.0	3719.9	3702.7	3682.6	3672.4	3656.6	3641.1	3621.5
	Width	14.3	15.3	14.4	13.8	12.7	10.5	9.1	9.7
	Intensity	0.181	0.282	0.280	0.179	0.016	0.016	0.022	0.024
Ni(60)	Position	3735.2	3720.1	3702.7	3682.5	3670.5	3656.5	3641.3	3621.8
	Width	13.3	16.1	13.8	14.0	11.6	9.7	8.9	9.3
	Intensity	0.067	0.149	0.303	0.425	0.004	0.003	0.013	0.036
Ni(80)	Position	3734.5	3720.7	3703.2	3682.7	3669.2	3656.8	3641.2	3621.8
	Width	11.2	13.6	13.5	13.3	12.5	11.2	10.5	10.6
	Intensity	0.005	0.026	0.192	0.663	0.034	0.003	0.012	0.065
Co(20)	Position	3733.3	3717.0	3699.2	3678.4	3671.3	3654.9	3638.5	3618.7
	Width	14.6	15.7	13.9	13.2	11.3	8.7	10.4	11.7
	Intensity	0.470	0.351	0.104	0.020	0.032	0.015	0.005	0.003
Co(40)	Position	3733.3	3716.5	3698.9	3678.8	3671.0	3655.4	3638.7	3619.7
	Width	14.8	15.4	14.6	12.5	11.8	11.8	11.6	10.3
	Intensity	0.203	0.344	0.265	0.106	0.017	0.024	0.024	0.017
Co(60)	Position	3733.4	3716.2	3698.6	3678.7	3668.3	3654.8	3638.0	3620.36
	Width	13.4	15.3	13.9	13.1	12.6	13.8	10.5	9.5
	Intensity	0.065	0.228	0.322	0.248	0.012	0.036	0.047	0.042
Co(80)	Position	3734.7	3714.8	3698.1	3677.4	3666.4	3657.4	3638.9	3619.6
	Width	12.2	11.1	12.8	13.9	10.0	11.7	9.0	8.7
	Intensity	0.005	0.030	0.231	0.583	0.009	0.028	0.031	0.083

¹ standard deviations are $\leq 0.5 \text{ cm}^{-1}$; ² standard deviations are $\leq 0.4 \text{ cm}^{-1}$.

quency. Although the relation of SKOGBY and ROSSMAN (1991) indicates a significant variation in molar absorptivity as a function of frequency, we cannot rigorously apply their relationship to our powder data as they did not measure the $E//\beta$ spectrum. However, we will quantitatively apply their relation to our data in order to evaluate qualitatively the order of magnitude of the effect. We emphasize here that we are examining this effect on the relative band intensities within a single spectrum (and hence avoid grain-size effects, etc.); we are not comparing band intensities between samples. The inclined line in Fig. 3 shows the variation in integrated molar absorptivity, ϵ , as a function of wavenumber, and the position of the four bands, A, B, C and D are marked, together with the corresponding values of integrated molar absorptivity ϵ_A , ϵ_B , ϵ_C and ϵ_D , respectively. Let us normalize the band intensities to the wavelength of the A band by multiplying the observed B, C and D band intensities by ϵ_A/ϵ_B , ϵ_A/ϵ_C and ϵ_A/ϵ_D , respectively. From Fig. 3,

$$\epsilon_A/\epsilon_B = \Delta/(\Delta + \delta) \quad (3.1)$$

$$\epsilon_A/\epsilon_C = \Delta/(\Delta + 2\delta) \quad (3.2)$$

$$\epsilon_A/\epsilon_D = \Delta/(\Delta + 3\delta) \quad (3.3)$$

where Δ is the distance (in cm^{-1}) of the A band from the projected position of zero molar absorptivity, and δ is the separation of the A, B, C and D bands. We may write the corrected band intensities, I^T , as

$$\begin{aligned} I_A^T &= I_A^0 \\ I_B^T &= I_B^0 \times \Delta/(\Delta + \delta) \\ I_C^T &= I_C^0 \times \Delta/(\Delta + 2\delta) \\ I_D^T &= I_D^0 \times \Delta/(\Delta + 3\delta) \end{aligned} \quad (4)$$

In equation (2), we need to replace the observed intensities, I^0 , by the corrected intensities, I^T , as equation (2) implicitly assumes that the integrated

Table 2. Possible local arrangements around the O(3) site in with (Mg, M²⁺) at M(1) and M(3)

	M(1)	M(1)	M(3)	Band ⁺	Band (A=Na) ⁺⁺	Band (A=□)
(1)	Mg	Mg	Mg	A	A	A*
(2)	Mg	Mg	M ²⁺	B'		
(3)	M ²⁺	Mg	Mg		B	B*
(4)	Mg	M ²⁺	Mg	B''		
(5)	M ²⁺	M ²⁺	Mg	C'		
(6)	M ²⁺	Mg	M ²⁺		C	C*
(7)	Mg	M ²⁺	M ²⁺	C''		
(8)	M ²⁺	M ²⁺	M ²⁺	D	D	D*

* ideal band-structure; (3) and (4) are symmetry equivalent and give rise to only one band: B''; similarly (5) and (6) are symmetry equivalent and give rise to only one band: C''.

** band structure usually observed; (2) and [(3)+(4)] are pseudo-symmetrically degenerate, and only one band (B) is observed experimentally; similarly, (5) and [(6)+(7)] are pseudo-symmetrically degenerate and only one band (C) is observed experimentally.

molar absorptivity is the same for all bands in the spectrum. Thus for the M²⁺ content of the M(1,3) sites, we may write

$$M_{M(1,3)}^{2+} = I_B^T + 2I_C^T + 3I_D^T \quad (5.1)$$

$$= I_B^T \times [\Delta/(\Delta + \delta)] + 2I_C^T \times [\Delta/(\Delta + 2\delta)] + 3I_D^T \times [\Delta/(\Delta + 3\delta)] \quad (5.2)$$

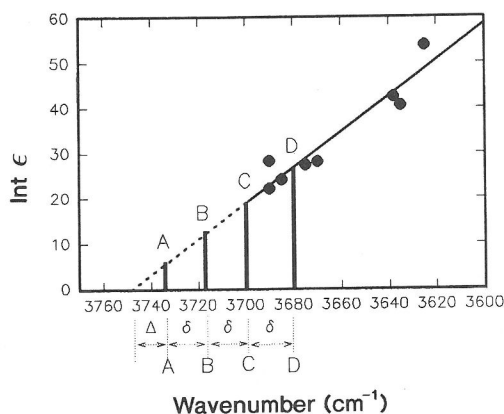


FIG. 3. The variation in integrated molar absorptivity vs. absorption frequency (data points for miscellaneous single-crystal amphibole spectra taken from SKOGBY and ROSSMAN, 1991) projected to zero absorptivity (at 3750 cm⁻¹). The band frequencies for the synthetic (Ni, Mg,Co)-potassium-rich richterites of this work are marked by the letters A, B, C, D corresponding to the band nomenclature of Table 1; the lengths of the vertical lines at the band frequencies for A, B, C and D are relative measures of the integrated molar absorptivities at the corresponding absorption frequencies.

The curve of SKOGBY and ROSSMAN (1991) intersects the wavenumber axis at 3750 cm⁻¹. For M²⁺ = Ni and Co, the A band occurs at ~3735 cm⁻¹ and the separation between the individual A, B, C and D bands is 15 cm⁻¹; thus Δ = δ = 15 cm⁻¹. Insertion of these values into equation (5.2) allows calculation of the amount of Ni and Co at the M(1,3) sites from the relative band intensities.

There is a problem in directly applying this relationship to the synthetic amphiboles of this work due to the presence of a second set of absorptions, the A*... bands. However, we may correct the band intensities for this effect using the curve of Fig. 3 and the same algebraic argument given above. Insertion of these values into equation (5), together with the values Δ = δ = 15 cm⁻¹ allows calculation of the amount of Ni or Co at the M(1,3) sites. The resultant values are shown in Fig. 4 (hollow symbols). Although there is a linear relationship between the two sets of values, there is also a complete lack of correspondence between the magnitudes of the two sets of values. For the most Ni- and Co-rich amphiboles, the predicted Ni and Co contents of the M(1,3) sites are incompatible with the bulk composition of the amphiboles.

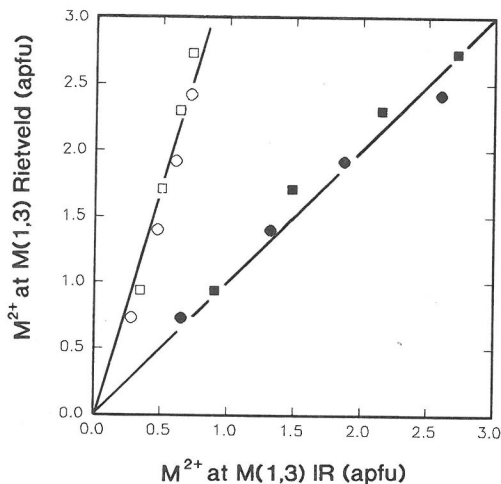


FIG. 4. Variation in Ni (squares) and Co (circles) content of the M(1,3) sites in (Ni,Mg,Co)-potassium-richterites calculated from the IR band intensities vs. the corresponding values measured by Rietveld structure-refinement; hollow symbols: calculated using the integrated molar-absorptivity curve of SKOGBY and ROSSMAN (1991); shaded symbols: calculated assuming the same relative integrated molar absorptivity (=1) for all bands in the spectrum.

If we assume that the integrated molar absorptivity does *not* vary as a function of absorption frequency, then we can sum the A... and A*... band-intensities and use the resulting values in equation (2). The predicted Ni and Co contents of the M(1,3) sites show very close agreement with the values measured by Rietveld structure-refinement (Fig. 4, shaded symbols). This provides us with somewhat of a conundrum, as this result seems totally incompatible with the results of SKOGBY and ROSSMAN (1991) and BURNS and HAWTHORNE (1994). Unfortunately, we *absolutely* cannot compare band intensities *between* samples, as SKOGBY and ROSSMAN (1991) were able to do with their single-crystal spectra, because of differential particle effects between samples, and hence we are limited to examining *relative* band intensities *within* a single spectrum. Nevertheless, the argument given above indicates that there is *not* any significant variation in integrated molar absorptivity with absorption frequency in the synthetic (Ni,Mg,Co)-potassium-richterites. Perhaps this is due to some form of coupling within a specific sample; this matter is currently being examined.

The A*, B*, C*, D* bands

Previous work on nominal end-member richterite and potassium-richterite has assigned the A* band

to an empty A-site configuration (DELLA VENTURA *et al.*, 1991, 1993a; ROBERT *et al.*, 1989). In accord with this assignment, the quartet of bands A, B, C, D are accompanied by a corresponding set of A*, B*, C*, D* bands (Fig. 1). It is of interest to compare the relative intensities of the individual corresponding bands, as there is no intrinsic reason why the two sets of bands should show the same distribution of relative intensities. Fig. 5 compares the *normalized* relative intensities of all the bands calculated as $NORM I_A^O = I_A^O / (I_A^O + I_B^O + I_C^O + I_D^O)$ and $NORM I_{A^*}^O = I_{A^*}^O / (I_{A^*}^O + I_{B^*}^O + I_{C^*}^O + I_{D^*}^O)$. There is a general correspondence of the individual bands, as they scatter about a 1:1 relationship. However, there are systematic patterns in the distribution of the intensities. The A* and D* bands tend to be relatively more intense than the A and D bands [except for the D band of Ni(80) and Co(80)], and the B* and C* bands tend to be relatively less intense than the B and C bands [except for the C* band in Co(80)]. This suggests that the ordering over M(1) and M(3) associated with a vacant A-site differs from that associated with an occupied A-site.

Short-range disorder

HAWTHORNE *et al.* (1996) show that the relative band-intensities of amphiboles involving binary solid-solution of C-group cations are dependent on both LRO and SRO. If the state of LRO is known, then the state of SRO may be derived from the

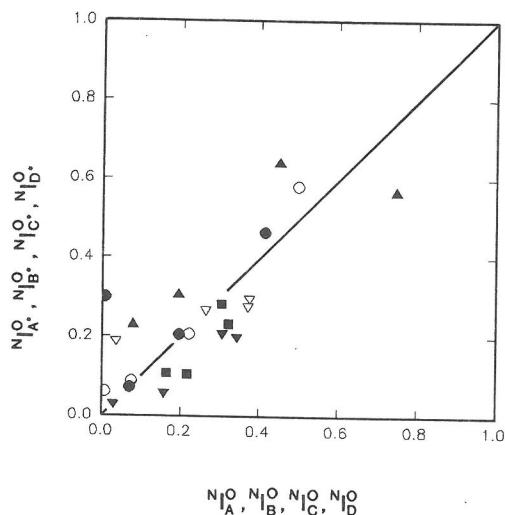


FIG. 5. The relative intensities of the A* (O), B* (∇), C* (□) and D* (Δ) bands vs. the relative intensities of the A, B, C and D bands in (Mg,Ni)-potassium-richterite (full symbols) and (Mg,Co)-potassium-richterite (hollow symbols).

observed band intensities. Referring to equation (1), although SRO can change the values of $I_A^c \dots$, the intensity sums of equation (1) are fixed by the state of LRO over the M(1) and M(3) sites. Assuming no SRO, the relative band intensities are given by the following relations (LAW, 1976; HAWTHORNE *et al.*, 1996):

$$\begin{aligned} I_A^c &= (1 - \frac{1}{2}[Y - y_{M(3)}])^2(1 - y_{M(3)}) \\ I_B^c &= (1 - \frac{1}{2}[Y - y_{M(3)}])^2 \times y_{M(3)} \\ &\quad + 2(1 - \frac{1}{2}[Y - y_{M(3)}]) \times \frac{1}{2}[Y - y_{M(3)}](1 - y_{M(3)}) \\ I_C^c &= \frac{1}{4}[Y - y_{M(3)}]^2(1 - y_{M(3)}) \\ &\quad + 2(1 - \frac{1}{2}[Y - y_{M(3)}]) \times \frac{1}{2}[Y - y_{M(3)}]y_{M(3)} \\ I_D^c &= \frac{1}{4}[Y - y_{M(3)}]^2 \times y_{M(3)} \end{aligned} \quad (6)$$

where Y is the total amount of M^{2+} cations at the M(1) and M(3) sites. HAWTHORNE *et al.* (1996)

show that specific patterns of deviation of the observed band intensities, $I_A^o \dots$, from the calculated band intensities, $I_A^c \dots$, are characteristic of particular patterns of SRO. In accord with the relation of Fig. 4 (squares and circles), we sum corresponding $A \dots$ and $A^* \dots$ band intensities to use in this calculation. Although Fig. 5 indicates that there are systematic differences in the two sets of intensities, the $A \dots$ set is sufficiently more intense than the $A^* \dots$ set that any error introduced by this summation procedure should be negligible. The observed and calculated values are shown in Fig. 6. The general pattern of values does deviate from that expected for complete short-range disorder (EEEE), following the general scheme UEDu in the nomenclature of HAWTHORNE *et al.* (1996). This corresponds to there being significant MgMgMg clustering and very slight NiNiNi (or CoCoCo) clustering.

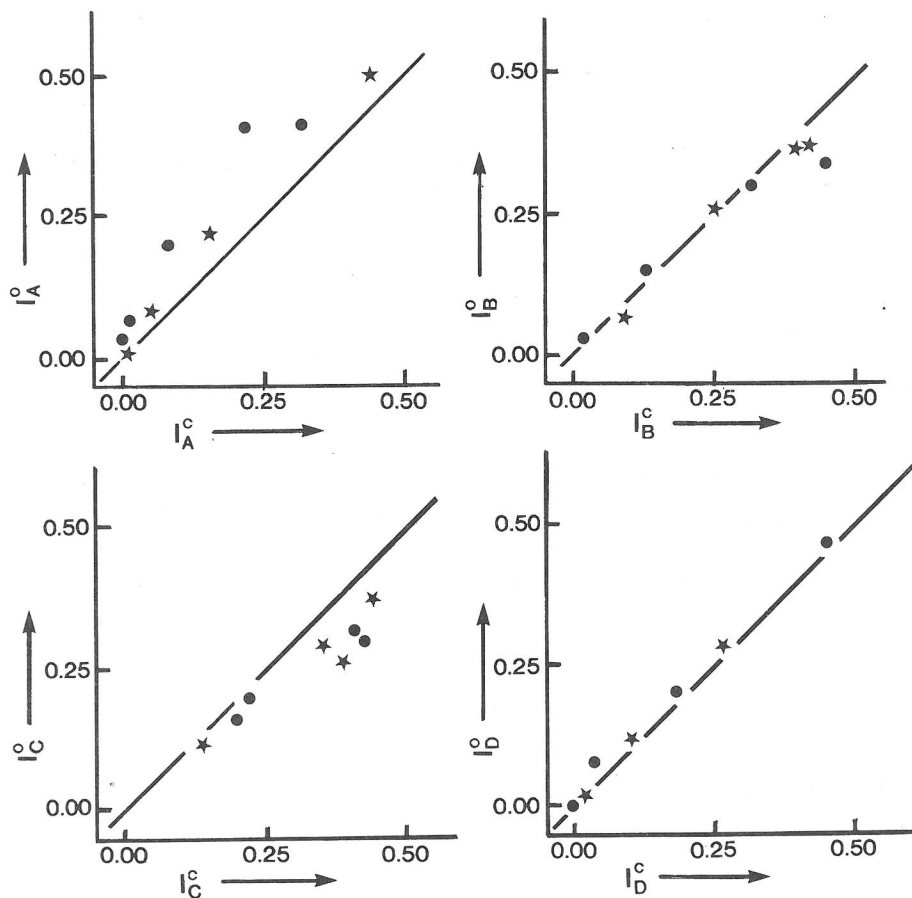


FIG. 6. The observed relative intensities of the A, B, C and D bands ($I_A^o \dots$) versus the relative intensities of these bands calculated from equation (6), assuming no SRO in the amphibole; ●: (Mg,Ni)-potassium-richertite; ○: (Mg,Co)-potassium-richertite.

Fig. 6 shows the behaviour for two separate richterite series, (Mg,Ni)-potassium-richterite and (Mg,Co)-potassium-richterite; we see the same type of behaviour for both series. This suggests that the deviation from an EEEE pattern of band-intensity differences is a real effect. This deviation cannot be due to variation in band intensity as a function of band frequency, as discussed above. Variation in molar absorptivity with band frequency as described by SKOGBY and ROSSMAN (1991) would decrease the relative intensity of I_A^0 , whereas I_A^1 is larger than I_A^2 . Thus, if the relative intensities are affected by such variations in molar absorptivity, the real deviation from an EEEE pattern of band intensities will be even greater than that currently observed.

SUMMARY

(1) There seems to be no effect of principal OH-stretching band frequency on band intensity (molar absorptivity) in these amphiboles.

(2) Satellite bands (denoted as A*. . .) show a different pattern of intensities than the corresponding A. . . bands. This indicates that (Mg,Ni) and (Mg,Co) ordering differs around an empty A-site from that around an occupied A-site.

(3) Comparison of the observed band-intensities with ideal values calculated for no SRO indicate that there is significant MgMgMg clustering and slight NiNiNi/CoCoCo clustering in these amphiboles.

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REFERENCES

- BURNS P. C. and HAWTHORNE F. C. (1994) Structure and hydrogen bonding in preobrazhenskite, a complex heteropolyhedral borate. *Can. Mineral.* **32**, 387–396.
- BURNS R. G. and STRENS R. G. J. (1966) Infrared study of the hydroxyl bonds in clinoamphiboles. *Science* **153**, 890–892.
- DELLA VENTURA G. (1992) Recent developments in the synthesis and characterization of amphiboles. Synthesis and crystal chemistry of richterites. *Trends in Mineral.* **1**, 153–192.
- DELLA VENTURA G. and ROBERT J.-L. (1990) Synthesis, XRD and FTIR studies of strontium richterites. *Eur. Jour. Mineral.* **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. *Amer. Mineral.* **76**, 1134–1140.
- DELLA VENTURA G., ROBERT J.-L., RAUDSEPP M., and HAWTHORNE F. C. (1993a) Site occupancies in monoclinic amphiboles: Rietveld structure refinement of synthetic nickel magnesium cobalt potassium richterite. *Amer. Mineral.* **78**, 633–640.
- DELLA VENTURA G., ROBERT J.-L., BÉNY J.-M., RAUDSEPP M., and HAWTHORNE F. C. (1993b) 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 $K_2O-Na_2O-CaO-MgO-SiO_2-TiO_2-H_2O-HF$. *Amer. Mineral.* **78**, 980–987.
- GROAT L. A., HAWTHORNE F. C., ROSSMAN G. R. and ERCIT, T. S. (1995) The infrared spectroscopy of vesuvianite in the OH region. *Can. Mineral.* **33**, 609–626.
- HAWTHORNE F. C. (1981) Amphibole Spectroscopy. In *Amphiboles and Other Hydrous Pyriboles—Mineralogy*. (ed. D. R. VEBLEN). *Rev. Mineral.* **9a**, pp. 103–140. Mineralogical Society of America.
- HAWTHORNE F. C. (1983) The crystal chemistry of the amphiboles. *Can. Mineral.* **21**, 173–480.
- HAWTHORNE F. C., DELLA VENTURA G. and ROBERT J.-L. (1996) Short-range order and long-range order in amphiboles: a model for the interpretation of infrared spectra in the principal OH-stretching region. *Geochim. Cosmochim. Acta* (in press).
- LAW A. D. (1976) A model for the investigation of hydroxyl spectra of amphiboles. In *The Physics and Chemistry of Minerals and Rocks*. (ed. R. G. J. STRENS), pp. 677–686. Wiley.
- RAUDSEPP M., TURNOCK A. C. and HAWTHORNE F. C. (1991) Amphiboles synthesis at low-pressure: what grows and what doesn't. *Eur. Jour. Mineral.* **3**, 983–1004.
- RAUDSEPP M., TURNOCK A. C., HAWTHORNE F. C., SHERIFF B. L. and HARTMAN J. S. (1987) Characterization of synthetic pargasitic amphiboles ($NaCa_2Mg_4M^{3+}Si_6Al_2O_{22}(OH,F)$; $M^{3+} = Al, Cr, Ga, Sc, In$) by infrared spectroscopy, Rietveld structure refinement and ^{27}Al , ^{29}Si , and ^{19}F MAS NMR spectroscopy. *Amer. Mineral.* **72**, 580–593.
- ROBERT J.-L., DELLA VENTURA G. C. and THAUVIN J.-L. (1989) The infrared OH-stretching region of synthetic richterites in the system $Na_2O-K_2O-CaO-MgO-SiO_2-H_2O-HF$. *Eur. Jour. Mineral.* **1**, 203–211.
- SEMET M. P. (1973) A crystal-chemical study of synthetic magnesiohastingsite. *Amer. Mineral.* **58**, 480–494.
- SKOGBY H. and ROSSMAN G. R. (1991) The intensity of amphibole OH bands in the infrared absorption spectrum. *Phys. Chem. Mineral.* **18**, 64–68.
- STRENS R. G. J. (1966) Infrared study of cation ordering and clustering in some (Fe,Mg) amphibole solid solutions. *Chem. Comm.* **15**, 519–520.
- WHITTAKER E. J. W. (1979) Clustering of cations in amphiboles. *Phys. Chem. Mineral.* **4**, 1–10.

