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Site occupancies in synthetic monoclinic amphiboles: Rietveld structure refinement and infrared spectroscopy of (nickel, magnesium, cobalt)-richterite

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ABSTRACT

Amphiboles were synthesized at 750 °C, 1 kbar (H2O) on the binary joins (nickel, magnesium)-richterite and (magnesium, cobalt)-richterite. Structural variations and site occupancies were characterized by Rietveld structure refinement, with final R_Bragg indices in the range 4–9%, and by powder infrared spectroscopy in the principal OH-stretching region. Site-occupancy refinement of Ni-Mg and Mg-Co distributions give the partition coefficients over M1,3 and M2 where $K_{M2} = (M2/Mg)_{M1,3}/(M2/Mg)_{M2}$, and $M2 = Ni$ or $Co$, $K_2 = 2.98 \pm 0.37$ and $K_2 = 1.34 \pm 0.31$. Both $K$ values are greater than 1.0, whereas $10^5(Ni^{2+}) < 10^5(Mg) < 10^5(Co^{2+})$; this indicates that cation size is not the primary factor affecting the ordering of Ni-Mg and Mg-Co over the octahedral sites. The infrared spectra of intermediate binary compositions show fine structure caused by ordering of Ni-Mg or Mg-Co over the M1,3 sites and by ordering of Na and (vacancy) at the A site; thus intermediate compositions show an eight-band spectrum in the principal OH-stretching region. Precise band intensities were derived by nonlinear least-squares fitting of Gaussian band shapes to the observed spectra. The relative observed intensities of the combinations of bands $3f_e + 2f_o + f_e$ and $f_e + 2f_o + 3f_e$ are in accord with the equations of Burns and Strens (1966), indicating that there is no significant variation in molar absorptivity with frequency (energy) for individual bands within a single sample (spectrum). Combined with the results of Skogby and Rossman (1991) on polarized single-crystal infrared spectra of amphiboles, this result suggests that different local configurations of M1,3 cations in amphiboles couple such that the transition probabilities of the associated OH groups are equal.

INTRODUCTION

The experimental techniques by which synthetic amphiboles are characterized have considerably increased in number during the last decade (Hawthorne 1983a; Graham et al. 1989; Raudsepp et al. 1991; Della Ventura 1992). The standard methods of powder X-ray diffraction and optical microscopy have been augmented by single-crystal X-ray diffraction (e.g., Boschmann et al. 1994; Oberti et al. 1995), infrared (Robert et al. 1989; Della Ventura 1992; Della Ventura and Robert 1990), Raman (Della Ventura et al. 1991), MAS NMR spectroscopies (Raudsepp et al. 1987a; Welch et al. 1994), EXAFS and XANES (Mottana et al. 1990; Paris et al. 1993), and HRTEM (Maresch and Czank 1983, 1988; Maresch et al. 1994; Ahn et al. 1991). The Rietveld method (Rietveld 1969; Young et al. 1977) is proving to be very useful for the characterization of cation site occupancies and bulk compositions in synthetic amphiboles (Raudsepp et al. 1987a, 1987b; Della Ventura et al. 1993a, 1993b; Robert et al. 1993; Jenkins and Hawthorne 1995). With reference to the present study, Della Ventura et al. (1993b) characterized the ordering behavior in synthetic (nickel, magnesium, cobalt)-potassium-richterite and showed that Ni-Mg and Mg-Co show ideal distributions over the M1,3 and M2 sites, with $K$ values of 4.26 and 1.92, respectively. Here, we present analogous results for the solid-solution series (nickel, magnesium) and (magnesium, cobalt)-richterites with end-member compositions richterite [Na(NaCa)Mg5 Si8 O22 (OH)2], Ni-rich richterite [Na(NaCa)Ni5 Si8 O22 (OH)2], and Co-rich richterite [Na(NaCa)Co5 Si8 O22 (OH)2] and compare the results with data for the analogous potassium-richterite series.

EXPERIMENTAL DETAILS

Details of synthesis procedures are given by Della Ventura et al. (1993b). Compositions were prepared along the binary joins (nickel, magnesium)-richterite and (magnesium, cobalt)-richterite.
were very beam sensitive, and a 70
low magnification (about 1000
thousands of grains by rastering the beam at relatively
spectrum of each run product was acquired from
than that resulting from atomic contrast. A bulk EDS
scattered-electron image of the grains is generally greater
grey-level contrast range from topography in the back-
N-P
Experimental param.
Structural param.
Unique re¯.
Integration time/step (s)
N-P
R Bragg (%)
R wp (%)
R p (%)
8
Scan range (°)
9±100
9±100
9±100
9±100
9±100
9±100
9±100
9±100
9±100
9±100
8.56
10.25
9.00
8.50
7.84
10.36
9.76
9.50
9.00
9.03
1.44
1.38
1.10
1.38
1.31
1.52
1.54
1.54
1.74
1.68
1.60
1.50
1.84
1.59
1.53
1.47
1.44
1.43
1.37
1.39
ues for the specific sites in the amphibole structure (Haw-
thorne 1983b). During initial refinement, the A cation was
fixed at the A2/m site (Hawthorne and Grundy 1972).
Refinements were then repeated, allowing the A cation to
occupy the A2 site along the twofold axis. Better agree-
ment was obtained with this second model, and all sub-
sequent refinements were made with the A cation at the
A2 site. Information pertinent to structure refinement is
given in Table 1.

For scanning electron microscopy (SEM) study, the
powdered experimental products were mounted on carbon
tape on a brass substrate (Cu,Zn) to avoid extraneous
Kα X-rays (conventional SEM stubs are Al). Quantitative
image-analysis work was not possible, because the
grey-level contrast range from topography in the back-
scattered-electron image of the grains is generally greater
than that resulting from atomic contrast. A bulk EDS
spectrum of each run product was acquired from
thousands of grains by rastering the beam at relatively
low magnification (about 1000×); this represents the bulk
composition of the product plus extraneous phases such
as capsule fragments and mortar contamination. Addi-
tional spectra for the same length of time (200 s) were
acquired from single amphibole grains with a focused
beam. Superimposing the spectra after scaling to a large
peak (Si) indicated whether the amphibole is on compo-
sition or not (taking into account the mechanical
contamination).

HRTEM observations were made using a JEOL 200CX
transmission electron microscope operated at 200 kV and
having a ±30° tilt about two orthogonal axes. All samples
were very beam sensitive, and a 70 μm condensor aper-
ture 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. Crystal-
lites were dispersed in dry alcohol and sedimented onto
a 3 mm holey-carbon copper grid (Agar products) using
a pipette.

The structures of the synthetic amphiboles were refined
by the Rietveld method using the program DBWS-
9006PC (Sakthivel and Young 1991), which is based on
the program DBW 2.9 (Wiles and Young 1981). Initial
structural parameters were taken from the single-crystal
study of synthetic fluor richterite (Cameron et al. 1983).
Isotropic displacement factors were fixed at average val-
ues for the specific sites in the amphibole structure (Haw-
thorne 1983b). During initial refinement, the A cation was
fixed at the A2/m site (Hawthorne and Grundy 1972).
Refinements were then repeated, allowing the A cation to
occupy the A2 site along the twofold axis. Better agree-
ment was obtained with this second model, and all sub-
sequent refinements were made with the A cation at the
A2 site. Information pertinent to structure refinement is
given in Table 1.

For FTIR study, the samples were prepared as KBr
pellets using the procedure of Robert et al. (1989). Spec-
tra in the range 4000–3000 cm⁻¹ were recorded on a Per-
klin 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 fol-
lowed by least-squares refinement. The background was
modeled as linear, and all peaks were modeled as sym-
metric Gaussians (Strens 1974). The distribution of ab-
sorption, y, as a function of energy (wavenumber, x) is
described by the relationship

\[ y = A \exp\left[-0.5(x - P/W)^2\right] \]

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 need-
ed 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 com-
positions close to the end-members, the weak bands tended
to merge with the background if all parameters were re-
fining unconstrained; consequently, for the weak bands,
the positions were fixed at the values determined for 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.

EXPERIMENTAL RESULTS

Single-phase experimental products of amphibole were
obtained for all starting compositions, indicating com-
plete solid solution along both joins under the experi-
mental conditions used. Additional phases were not de-
tected with the use of a binocular microscope or by X-ray
powder diffraction, but SEM examination showed the

| Table 1. Data collection and Rietveld-refinement details for synthetic amphiboles along the joins (nickel, magnesium)-
<table>
<thead>
<tr>
<th>Mg(100)</th>
<th>Ni(20)</th>
<th>Ni(40)</th>
<th>Ni(60)</th>
<th>Ni(80)</th>
<th>Ni(100)</th>
<th>Co(20)</th>
<th>Co(40)</th>
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<td>9–100</td>
<td>9–100</td>
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<td>9–100</td>
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<td>Step interval (°/h)</td>
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<td>0.10</td>
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<td>0.10</td>
<td>0.10</td>
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<td>860</td>
<td>860</td>
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<td>R B (%)</td>
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<td>7.80</td>
<td>6.75</td>
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<td>7.85</td>
<td>7.30</td>
<td>7.16</td>
<td>7.05</td>
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<td>7.84</td>
<td>10.36</td>
<td>9.76</td>
<td>9.50</td>
<td>9.00</td>
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<td>6.28</td>
<td>4.65</td>
<td>6.90</td>
<td>5.61</td>
<td>4.87</td>
<td>4.14</td>
<td>6.26</td>
<td>6.27</td>
<td>7.47</td>
<td>7.17</td>
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<tr>
<td>D-W d-statistic</td>
<td>1.44</td>
<td>1.38</td>
<td>1.10</td>
<td>1.38</td>
<td>1.31</td>
<td>1.52</td>
<td>1.54</td>
<td>1.54</td>
<td>1.74</td>
<td>1.74</td>
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<tr>
<td>Ead multid.</td>
<td>1.60</td>
<td>1.50</td>
<td>1.84</td>
<td>1.59</td>
<td>1.53</td>
<td>1.47</td>
<td>1.44</td>
<td>1.43</td>
<td>1.37</td>
<td>1.37</td>
</tr>
</tbody>
</table>
presence of variable amounts of Al2O3 (0 – <5%), which presumably originated from grinding the sample in a corundum mortar. Very minor SiO2 in some samples presumably resulted from grinding in an agate mortar. Sample Mg(100) consists of very acicular amphibole crystals averaging 1–2 × 10 μm, with a maximum size of 4 × 50 μm (Fig. 1a). Ni(100) consists of very acicular amphibole crystals varying in size from 1 × 10 μm to 4 × 20 μm (Fig. 1b). Co(100) amphibole is generally stubby to prismatic, ranging in size from 2 × 5 μm to 10 × 20 μm, again with some Al2O3 present (Fig. 1c). Intermediate compositions have similar morphology (Fig. 1d). Redox conditions were close to that of the Ni-NiO buffer. The color of the experimental product was green (Ni-Mg series) or violet-pink (Mg-Co series), with the intensity of color increasing with the content of the transition-metal present. No trace of unreacted material was detected. High-resolution TEM images of various (nickel, magnesium, cobalt)-richterite samples are shown in Figure 2. No chain-multiplicity faults, chain-arrangement faults, or additional phases were observed by TEM in any of the samples. The patchy contrast in Figure 2b is due to differential beam damage.

Unit-cell dimensions are given in Table 2. Final atomic positions, selected interatomic distances, and refined site occupancies are listed in Tables 3, 4, and 5, respectively\(^1\). Typical observed, calculated, and difference X-ray powder diffraction patterns for an amphibole of intermediate composition are shown in Figure 3.

The raw infrared spectra and band nomenclature are shown in Figure 4, and the fitted spectra are shown in Figure 5. Band positions, widths, and relative intensities (I/I\(_{\text{tot}}\)) are given in Table 6. The spectrum of end-member richterite shows an intense band centered at 3730 cm\(^{-1}\), assigned to an MgMgMg-OH → Na configuration and designated the A band, and a minor band at 3675 cm\(^{-1}\) resulting from the presence of some vacant A sites in the

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\(^1\) A copy of Tables 3 and 4 may be ordered as Document AM-97-634 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.
Table 2. Cell parameters of synthetic (nickel, magnesium, cobalt)-richterite

<table>
<thead>
<tr>
<th></th>
<th>Mg(100)</th>
<th>Ni(20)</th>
<th>Ni(40)</th>
<th>Ni(60)</th>
<th>Ni(80)</th>
<th>Ni(100)</th>
<th>Co(20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>9.9076(6)</td>
<td>9.9073(6)</td>
<td>9.9024(6)</td>
<td>9.8956(6)</td>
<td>9.8886(6)</td>
<td>9.890(1)</td>
<td>9.9180(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.988(1)</td>
<td>17.978(1)</td>
<td>17.965(1)</td>
<td>17.948(1)</td>
<td>17.933(1)</td>
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<td>17.999(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.2706(4)</td>
<td>5.2669(3)</td>
<td>5.2603(4)</td>
<td>5.2567(3)</td>
<td>5.2525(3)</td>
<td>5.2527(6)</td>
<td>5.2714(3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>104.252(4)</td>
<td>104.303(4)</td>
<td>104.361(4)</td>
<td>104.413(4)</td>
<td>104.461(4)</td>
<td>104.501(8)</td>
<td>104.246(4)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>910.41</td>
<td>905.03</td>
<td>906.55</td>
<td>904.24</td>
<td>901.93</td>
<td>901.52</td>
<td>912.08</td>
</tr>
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amphibole (band A* in Table 6). The spectra of the intermediate amphibole solid solution show four relatively intense bands designated A, B, C, and D, and these bands are due to the local Ni-Mg and Mg-Co configurations around the OH site. The spectra of the intermediate-composition amphiboles (Fig. 5) also show that the A* band is also associated with a triplet of additional bands. These bands are designated B*, C*, and D*. The assignment of bands to specific local configurations is shown in Table 7.

**Discussion**

The variation in cell dimensions is shown in Figures 6 and 7, together with the data for synthetic (nickel, magnesium, cobalt)-potassium-richterite (Della Ventura et al. 1993b) and the synthetic richterite-ferro-richterite series (Charles 1974). For (magnesium, iron)-richterite, Charles (1974) gave several sets of cell dimensions for each composition. Virgo (1972) showed by Mössbauer spectroscopy that these specific synthetic amphiboles all contain some Fe³⁺. Incorporation of Fe³⁺ into the richterite structure reduces the cell dimensions below those of ideal Fe³⁺-free richterite. Consequently, we used the cell dimensions of Charles (1974) with the largest cell volume for each nominal composition, presuming that these amphiboles will have the lowest content of Fe³⁺. In each series, the cell volume increases regularly (Fig. 6) in response to the increasing size of the constituent cations

$\frac{\alpha}{\beta}r(\text{Ni}^{2+}) = 0.690 \text{ Å, } \frac{\alpha}{\beta}r(\text{Mg}) = 0.720 \text{ Å, } \frac{\alpha}{\beta}r(\text{Co}^{2+}) = 0.745 \text{ Å, } \frac{\alpha}{\beta}r(\text{Fe}^{2+}) = 0.780 \text{ Å; Shannon 1976.}$

The one exception to this is the Ni(100) sample, which has a cell volume similar to that of the Ni(80) sample. We recollected the diffraction data on this sample and obtained the same result. We then recalculated the data on the complete (nickel, magnesium)-richterite series and obtained the same result. Next, we resynthesized the (nickel, magnesium)-richterite samples, collected the diffraction data, and obtained the same result. Thus, we conclude that Ni(100) has about the same cell volume as Ni(80).

The relative variation of individual cell dimensions differs significantly between the two series. Along the Ni-Mg join (Fig. 7), a, b, and c increase with increasing cation size, but the beta angle decreases markedly. Significantly different behavior is observed in the Mg-Co series. The a and b dimensions of the Mg-Co series increase more strongly with increasing constituent-cation radius than those of the Ni-Mg series. This is also the case in the a dimension for the Mg-Fe series, but the rate of increase is not as great as in the Mg-Co series. The c dimension shows the reverse behavior. The rate of increase of c as a function of constituent-cation radius is smaller than in the Mg-Co series relative to that in the Ni-Mg series, whereas the Mg-Fe series is colinear with the Ni-Mg series (Fig. 7). The beta angle decreases from nickel-richterite to richterite but increases slightly to cobalt-richterite, whereas it continues to decrease from richterite to ferro-richterite.

The cell volumes for the K series are greater than those of the analogous Na series (Fig. 6), in accord with the larger size of K relative to Na, but the general trends are parallel. Careful inspection of Figure 6 shows that the trends for the K and Na amphiboles are slightly nonlinear, with a break at $r(\text{Fe}^{2+}) = 0.72$ Å (Mg). Although the behaviors of the K and Na analogs are generally similar, some interesting differences are apparent. For a, the trends are virtually identical but displaced by approximately 0.14 Å. The values for b for the K and Na amphiboles are very similar (Fig. 7), in accord with the conclusion of Colville et al. (1966) that the b dimension in amphiboles is controlled primarily by the aggregate radius of the cations occupying the M2 site. The variation in the c dimension (Fig. 7) is very interesting. In the Ni-Mg series, c increases linearly with constituent-cation radius for both the K and the Na amphiboles, the displacement between the

**Table 5.** Refined site populations of synthetic (nickel, magnesium, cobalt)-richterite

<table>
<thead>
<tr>
<th></th>
<th>Mg(100)</th>
<th>Ni(20)</th>
<th>Ni(40)</th>
<th>Ni(60)</th>
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<td>904.24</td>
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<td>901.52</td>
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**Table 5.** Refined site populations of synthetic (nickel, magnesium, cobalt)-richterite
TABLE 2. Extended Co(40) Co(60) Co(80) Co(100)

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<td></td>
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</table>

trends being 0.03–0.04 Å. At the end-member Mg composition, there is a sharp discontinuity in each trend; in (magnesium, cobalt)-richterite, $c$ continues to increase but at a lower rate, whereas in (magnesium, cobalt)-potassium-richterite, $c$ actually decreases slightly with increasing Co content. In the K and Na amphiboles, there is a marked break in the variation in $c$ between the Ni-Mg series and the Mg-Co series, whereas in the Na amphiboles, the $c$ values for the Mg-Fe series are approximately colinear with those of the Ni-Mg series. The behavior of the beta values is very similar (Fig. 7), with both (magnesium, cobalt)-potassium-richterite and (magnesium, cobalt)-richterite deviating markedly from the linear (or near-linear) trends for (nickel, magnesium)-potassium-richterite, (nickel, magnesium)-richterite, and (magnesium, iron)-richterite.

The variation in cell dimensions as a function of the composition of the octahedral strip is affected by (1) the cation size and (2) the electronic configuration of the constituent cations. The almost linear increase in cell volume as a function of increasing cation size in the octahedral strip (Fig. 6) shows that cation size has its usual scalar effect, with slight nonlinearity at the Ni end of the series. However, the unusual discontinuities in individual cell dimensions and the markedly different behavior of the different transition-metal compositions indicate that electronic configuration is also a major factor, as discussed by Della Ventura et al. (1993b).

**Bulk composition**

The refined site occupancies of synthetic (nickel, magnesium, cobalt)-richterite are given in Table 5. Raudsepp et al. (1990) showed that the Rietveld method gives quite accurate site occupancies and bulk compositions if reasonable values are used for the isotropic displacement factors. Comparison of the refined and nominal Ni-Mg and Mg-Co compositions (Fig. 8) shows generally good agreement, in accord with the fact that there were no significant amounts of additional phases found by X-ray diffraction or SEM, although there is a significant difference for the most Co-rich amphiboles (Table 5).

**Site occupancies: Long-range and short-range order**

Both Ni and Co preferentially enter the OH-coordinated M1 and M3 sites for intermediate compositions (Table 5), whereas Mg prefers M2. The Ni and Co distributions over M1 and M3 are similar, with a slight preference for M3 over M1; this is not significant in terms of the assigned standard deviation but is systematic across the se-
juries. The relation between Ni and Co at M1,3 and M2 is shown in Figure 9. The data of Table 5 allow calculation of the partition coefficients for Ni and Co over the M1,3 and M2 sites, defined as
\[ K_{\text{Ni}^{2+}} = \frac{(\text{M}^{2+}/\text{Mg})_{\text{M}1,3}}{(\text{M}^{2+}/\text{Mg})_{\text{M}2}} \]
for Ni and Co.

For the (nickel, magnesium)-richterite series; \( K_{\text{Ni}^{2+}} = 2.98 \pm 0.37 \); for the (magnesium, cobalt)-richterite series; \( K_{\text{Ni}^{2+}} = 1.34 \pm 0.31 \). The corresponding values for the analogous potassium-richterite series are \( K_{\text{Ni}^{2+}} = 4.26 \pm 0.56 \) and \( K_{\text{Co}^{2+}} = 1.92 \pm 0.29 \).

The \( K \) values indicate that electronic structure has a major effect on long-range ordering (LRO) of cations in the amphibole structure. Ni\(^{2+}\) is smaller than Mg, whereas Co\(^{2+}\) is larger than Mg, and if LRO of cations were controlled solely by cation size (for a specific structure type),

**Table 6.** Refined positions (cm\(^{-1}\)), widths (cm\(^{-1}\)), and intensities of (nickel, magnesium)- and (magnesium, cobalt)-richterite

<table>
<thead>
<tr>
<th>A Position</th>
<th>Ni(0)</th>
<th>Ni(20)</th>
<th>Ni(40)</th>
<th>Ni(60)</th>
<th>Ni(80)</th>
<th>Ni(100)</th>
<th>Co(20)</th>
<th>Co(40)</th>
<th>Co(60)</th>
<th>Co(80)</th>
<th>Co(100)</th>
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<td>3730.7</td>
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</tr>
<tr>
<td>Width</td>
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<tr>
<td>Intensity</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Width</td>
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<tr>
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<tr>
<td>Width</td>
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<tr>
<td>Intensity</td>
<td>0.134</td>
<td>0.241</td>
<td>0.288</td>
<td>0.223</td>
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<td></td>
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<tr>
<td>D Position</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<td>3677.5</td>
<td>3677.7</td>
<td>3678.7</td>
<td>3678.9</td>
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<td>3671.3</td>
<td>3671.5</td>
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<td></td>
</tr>
<tr>
<td>Width</td>
<td>15.5</td>
<td>14.8</td>
<td>14.8</td>
<td>14.8</td>
<td>15.7</td>
<td>15.0</td>
<td>14.8</td>
<td>15.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intensity</td>
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<td>0.171</td>
<td>0.291</td>
<td>0.442</td>
<td>0.86</td>
<td>0.037</td>
<td>0.112</td>
<td>0.285</td>
<td>0.495</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.** Observed (top line), calculated (dots), and difference (bottom line) X-ray powder diffraction pattern for Na(NaCa)(Mg\(_3\)Co\(_2\))Si\(_8\)O\(_{22}\)(OH)\(_2\).

**Figure 4.** FTIR spectra in the OH-stretching region for amphiboles synthesized along (a) the (magnesium, nickel)-richterite join and (b) the (magnesium, cobalt)-richterite join.
then $K_i$ for Ni$^{++}$-Mg ordering should lie on one side of 1.0 and $K_i$ for Co$^{+++}$-Mg ordering should lie on the other side of 1.0. The fact that $K_i$ values for both Ni$^{++}$ and Co$^{+++}$ are $>1.0$ indicates that the primary factor controlling LRO is not cation size in this case. The other obvious factor involved is the electronic structure of the transition metal (Della Ventura et al. 1993b). In the 1960s and 1970s, there was a considerable amount of work on the effects of crystal-field stabilization energies on the ordering of transition metals in minerals. However, the arguments were qualitative or semiquantitative in nature and not very definitive in terms of explaining cation ordering. Recent results on synthetic amphiboles and pyroxenes suggest that electronic structure plays an important role in affecting both cation ordering and variation in cell dimensions in these structures, indicating that a more quantitative approach to those aspects of electronic structure of minerals is warranted.

Hawthorne et al. (1996) showed that it is possible to get information on short-range ordering (SRO) of cations over the M1 and M3 sites in amphibole from the fine structures in the principal OH-stretching spectrum. Della Ventura et al. (1996) showed that there is slight preferential SRO in synthetic (nickel, magnesium, cobalt)-potassium-richterite, with MgMgMg and possible NiNiNi (and CoCoCo) clusters being more common than expected for random mixing. In (nickel, magnesium, cobalt)-richterite, the A*-D* bands are much more relatively intense than in (nickel, magnesium, cobalt)-potassium-richterite, preventing a convincing examination of short-range order-disorder in (nickel, magnesium, cobalt)-richterite.

**Bond Lengths**

Previous work (Raudsepp et al. 1987a, 1987b) on the structural refinements of amphiboles by the Rietveld method noted the low accuracy of the resulting individual bond lengths because of pseudosymmetry in the amphibole structure. However, the grand (M-O) bond lengths are more well behaved (Della Ventura et al. 1993b). The grand (M-O) bond lengths of the (nickel, magnesium)- and (magnesium, cobalt)-richterite series (Fig. 10) do show an increase with increasing constituent-cation radius. Fitting the variation with a single straight line gives a slope of 0.89 (Fig. 10), somewhat less than the value of ~1 observed for natural amphiboles (Hawthorne 1983b). A much closer fit to the data is obtained for a bilinear model with a break at 0.72 Å (Mg) (broken line in Fig. 10), although the slope of the segment with \( r > 0.72 \) Å is significantly steeper than the analogous line for natural amphiboles. The synthetic (nickel, magnesium, cobalt)-potassium-richterite series (Della Ventura et al. 1993b) and the synthetic diopside series containing (Ni,Mg,Co, and Fe$^{++}$) (Raudsepp et al. 1990) also show this feature, whereas synthetic olivine (Raudsepp et al. 1990, Fig. 7) does not. Raudsepp et al. (1990) concluded that this nonlinearity is an intrinsic feature of the calcic pyroxene structure and results because the structure is

**Figure 5.** Resolved spectra for the intermediate amphiboles synthesized along (a) the (magnesium, nickel)-richterite join and (b) the (magnesium, cobalt)-richterite join. Resolved bands (dotted lines) are vertically displaced for clarity; observed intensities are shown by the open squares, and the line through the observed intensities is the envelope of the fitted component bands.

**Table 7.** Possible local arrangements around the O3 site in amphiboles with (Mg,Fe$^{++}$) at M1 and M3

<table>
<thead>
<tr>
<th>M1</th>
<th>M1</th>
<th>M3</th>
<th>Band*</th>
<th>Band (A = Na)**</th>
<th>Band (A = □)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg</td>
<td>Mg</td>
<td>Mg</td>
<td>A</td>
<td>A</td>
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<tr>
<td>2</td>
<td>Mg</td>
<td>Mg</td>
<td>M$^{++}$</td>
<td>B$^*$</td>
<td>B</td>
</tr>
<tr>
<td>3</td>
<td>Mg$^{++}$</td>
<td>Mg</td>
<td>Mg</td>
<td>B$^*$</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>Mg</td>
<td>M$^{++}$</td>
<td>Mg</td>
<td>C$^*$</td>
<td>C</td>
</tr>
<tr>
<td>5</td>
<td>M$^{++}$</td>
<td>M$^{++}$</td>
<td>Mg</td>
<td>C$^*$</td>
<td>C</td>
</tr>
<tr>
<td>6</td>
<td>M$^{++}$</td>
<td>Mg</td>
<td>M$^{++}$</td>
<td>D</td>
<td>D</td>
</tr>
<tr>
<td>7</td>
<td>Mg</td>
<td>M$^{++}$</td>
<td>M$^{++}$</td>
<td>D</td>
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</tr>
<tr>
<td>8</td>
<td>M$^{++}$</td>
<td>M$^{++}$</td>
<td>M$^{++}$</td>
<td>D</td>
<td>D</td>
</tr>
</tbody>
</table>

* Ideal band structure; 3 and 4 are symmetrically equivalent and produce only one band: B$^*$; similarly, 6 and 7 are symmetrically equivalent and produce only one band: C$^*$.

**Band structure usually observed; 2 and (3 + 4) are pseudosymmetrically degenerate, and only one band (B) is observed experimentally; similarly, 5 and (6 + 7) are pseudosymmetrically degenerate, and only one band (C) is observed experimentally.
nearing its lower limit of stability with regard to the incorporation of small divalent cations at the M1 site. The similarity between pyroxene and amphibole suggests that these structures might behave in a similar fashion; the results of the present work show this to be the case.

**Variation in molar absorptivity with frequency**

Strens (1966), Burns and Strens (1966), and Law (1976) showed that the relative intensities of the A, B, C, and D bands in the principal OH-stretching spectra of amphiboles are related to cation ordering over the M1 and M3 sites. This approach assumed implicitly 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 study of amphiboles, Skogby and Rossman (1991) showed that the integrated molar absorptivity of the total envelope of the principal OH-stretching bands increases with decreasing mean stretching frequency. Similar qualitative molar-absorptivity–frequency relations are also observed in polarized single-crystal spectra of vesuvianite (Groat et al. 1995). Burns and Hawthorne (1994) showed the analogous relation for normalized single OH-stretching-band intensities in powder infrared spectra of borate minerals. Thus, the implicit assumption in previous work on powder spectra of amphiboles, that there is no variation in molar absorptivity with frequency, seems invalid. We must experimentally characterize this relation if we wish to quantitatively relate the intensities of the OH-stretching bands to cation ordering in amphiboles.

Hawthorne et al. (1996) reexamined the problem of relating the binary site occupancies \( x = \frac{\text{Mg}}{\text{Mg} + \text{M}^{2+}} \) and \( y = \frac{\text{M}^{2+}}{\text{Mg} + \text{M}^{2+}} \) at the M1 and M3 sites in the amphibole structure to the observed relative intensities, \( I_\alpha \), of the component bands in the principal OH-stretching spectrum. They showed that, provided there is no variation in molar absorptivity with band frequency within a single sample, the original equations of Burns and Strens (1966),

\[
\begin{align*}
M_{\text{M1,3}} & = 3I_\alpha + 2I_\beta + I_\gamma \\
M_{\text{M1,3}}^{2+} & = I_\alpha + 2I_\beta + 3I_\gamma
\end{align*}
\]

are correct. Della Ventura et al. (1996) showed that Equation 1 correctly predicts the Mg and M\(^{2+}\) contents of the M1,3 sites in (magnesium, nickel)- and (magnesium, cobalt)-potassium richterite, i.e., when the molar absorptivity of all four bands, A—D, are assumed to be the same. Because this result apparently contradicts the work of
Skogby and Rossman (1991), and the issue is extremely important for the application of infrared spectroscopy in general to the characterization of cation ordering in minerals, we examine Equation 1 for the amphiboles of this study. The situation is complicated somewhat in the present case by the presence of the A*-D* set of bands, which also represent Mg-M2+ ordering over the M1,3 sites. There are two ways in which this problem can be handled: (1) by using the A–D set of bands only and (2) by summing the analogous bands A + A*, B + B*, etc. We get the same result in either case and hence just show the first case. Figure 11 shows the M2+ content of M1,3 sites as derived from the Rietveld site populations and from the infrared band intensities by Equation 1. There is close correspondence between the two sets of values for both (magnesium, nickel)- and (magnesium, cobalt)-richterite. This indicates that there is no significant variation in molar absorptivity with band frequency (energy) within a single powder spectrum. The latter condition is extremely important because it possibly accounts for the difference between the results of Skogby and Rossman (1991) and the results derived here and by Della Ventura et al. (1996). Skogby and Rossman (1991) measured the molar absorptivity (excluding the β component) on oriented single crystals and were able to compare measurements for different samples. Here, we measured only the relative intensities of bands within a single sample. We cannot compare absolute intensities between samples, as did Skogby and Rossman (1991), because particle effects among samples are so variable (we confirmed this experimentally). In powder samples, one can compare intensities only within a single spectrum (i.e., for a single sample in which particle effects are the same). Thus, Skogby and Rossman (1991) recorded a difference in transition probability (by molar absorptivity) with frequency in different samples, whereas we recorded no difference in transition probability (by relative band-intensity correlation with bulk composition) with frequency within a single sample. We may account for this in the following manner. In the amphibole structure, adjacent M1M1M3-OH-A configurations share two out of three cations, and it is not unreasonable to propose that there are cooperative interactions between adjacent configurations such that transitions are coupled. Such coupling could lead to equal transition probabilities for adjacent configurations, and the continuous nature of the M1M1M3-OH-A configurations throughout the amphibole structure could lead to the same transition probability for all these configurations. Such coupling would not, of course, occur between different samples, and hence different samples may show different transition probabilities (molar absorptivities) as a function of mean absorption frequency. This proposal seems to account satisfactorily for the apparently different results obtained by Skogby and Rossman (1991).
**Figure 10.** Variation of the grand (M–O) bond length for synthetic (nickel, magnesium, cobalt)-richterite as a function of the mean cation radius at M1,2,3; vertical bars represent the estimated standard deviations of (a) the linear fit to the data and (b) the bilinear fit to the data.

and by this study. Whether such coupling occurs in a specific mineral presumably depends on the details of its structure.

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

The A* band has been assigned to an empty A-site configuration (Phillips and Rowbotham 1973; Della Ventura et al. 1991, 1993a; Robert et al. 1989). In accord with this assignment, the quartet of bands A, B, C, and D is accompanied by a corresponding set of A*, B*, C*, and D* bands (Fig. 4). Comparison of the normalized relative intensities of all the bands, calculated as $\text{NORM}_A = I_A(I_A + I_B + I_C + I_D)$ and $\text{NORM}_A' = I_A'(I_A' + I_B' + I_C' + I_D')$, indicates that there are systematic differences in the ordering of the C-group cations adjacent to filled A sites and adjacent to vacant A sites. This is not surprising. Comparison of the results obtained here with those of Della Ventura et al. (1993b, 1996) shows that the identity of the A cation (K vs. Na) significantly affects the ordering of both Ni and Co over the M1,2,3 sites. Thus, it is reasonable to expect that □ (vacancy) vs. Na would have an even greater effect on Ni and Co ordering.

**ACKNOWLEDGMENTS**

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