

Site occupancies in monoclinic amphiboles: Rietveld structure refinement of synthetic nickel magnesium cobalt potassium richterite

GIANCARLO DELLA VENTURA*

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

JEAN-LOUIS ROBERT

Centre pour la Synthèse et la Chimie des Minéraux, CNRS, 1A, rue de la Férollerie, Orléans cedex 2, France

MATI RAUDSEPP, FRANK C. HAWTHORNE

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

ABSTRACT

This paper describes the synthesis and characterization of potassium richterite containing variable amounts of Ni, Mg, and Co in the octahedral strip. Monophase amphibole products were obtained at 750 °C, 1 kbar (H₂O) for all compositions in the system studied. Structural variations and site occupancies were characterized by Rietveld structure refinement, with final *R* (Bragg) indices in the range 2–4%. The trends for individual cell dimensions along the Ni-Mg-Co join show a marked discontinuity at the ordered Mg composition, indicating that the behavior of the individual cell dimensions is not controlled just by the size of the substituent cations, whereas cell volume and grand mean (M-O) bond length are linear with constituent cation size. Refined site occupancies show that both Ni, Mg and Mg, Co distributions are ideal. The partition coefficients for Ni and Co over M1,3 and M2, defined as $K_{M^{2+}} = (M^{2+}/Mg)_{M1,3}/(M^{2+}/Mg)_{M2}$, with $M^{2+} = Ni^{2+}$ or Co^{2+} , are $K_{Ni} = 4.26 \pm 0.56$ and $K_{Co} = 1.92 \pm 0.29$. Both K_d values are >1.0 , indicating that cation size is not the primary factor affecting the ordering of Ni-Mg and Mg-Co over the octahedral sites. The Rietveld method proves to be an extremely powerful method for the characterization of fine-grained synthetic products.

INTRODUCTION

Natural and synthetic amphiboles show long-range and short-range order-disorder that must be characterized for a proper interpretation of the results of synthesis and phase equilibrium experiments. Despite a considerable number of experimental studies on amphibole stability (see Gilbert et al., 1982, for a review) and on end-member synthesis during the last few years (Jenkins, 1987; Raudsepp et al., 1987a, 1987b, 1991; Robert et al., 1989; Robert and Della Ventura, 1990; Della Ventura and Robert, 1990; Della Ventura et al., 1991), few synthetic amphiboles have been adequately studied by modern methods. This is of particular importance with regard to cation order-disorder, microstructural defects, composition, and structural parameters. The detection of microstructural defects such as chain-width disorder and high density of stacking faults (especially common in iron manganese magnesium amphiboles: Maresch and Czank, 1983) is particularly crucial when using results derived from synthesis and stability experiments in thermodynamic modeling and in the interpretation of natural occurrences (Graham et al.,

1989). Moreover, the assumption that the product amphibole is of nominal composition is often unwarranted (Hawthorne, 1983a), even for the ideally simple case of tremolite (Jenkins, 1987).

The experimental techniques by which cation ordering may be characterized have undergone considerable development during the last decade. These include XRD (single-crystal and powder) and spectroscopy (IR, Raman, MAS NMR, EXAFS, XANES, ESR, Mössbauer, etc.; Hawthorne, 1988). In particular, the Rietveld method has been used for the characterization of cation site populations in synthetic amphiboles (Raudsepp et al., 1987a, 1987b; Della Ventura et al., in preparation; Robert et al., 1993). With this method (Rietveld, 1967, 1969), the structure of a material may be refined using only the powder diffraction pattern. Although originally used only for simple compounds (Young et al., 1977), the Rietveld method has been used to derive structural data of adequate accuracy for complex structures (Baerlocher, 1984; Ercit et al., 1985; Baerlocher and Schicker, 1987; Post and Bish, 1989; Burns and Fleet, 1990; Post and Buchwald, 1991).

Here we present the results obtained for the characterization of synthetic potassium richterite containing variable amounts of Ni, Mg, and Co atoms in the octahedral strip.

* Present address: Dipartimento di Scienze della Terra, Sezione Mineralogico-Cristallografica, Università degli Studi di Roma "La Sapienza", P. Aldo Moro 5, I-00185, Roma, Italy.

TABLE 1. Data collection and structure refinement details for synthetic potassium richterite samples

	KNi ₀	KNi ₂₀	KNi ₄₀	KNi ₆₀	KNi ₈₀	KNi ₁₀₀	KCo ₂₀	KCo ₄₀	KCo ₆₀	KCo ₈₀	KCo ₁₀₀
2 θ scan range (°)	9–100	9–100	9–100	9–100	9–100	9–100	9–100	9–100	9–100	9–100	9–100
Step interval (°2 θ)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Integration time/step (s)	5	5	5	5	5	5	5	5	5	5	5
Maximum step intensity (counts)	2705	3721	4452	4337	4375	4519	2397	2132	3091	3284	2503
No. of unique reflections	526	526	526	526	525	522	528	527	531	531	533
No. of structure parameters	35	38	38	38	38	35	38	38	38	38	35
No. of experimental parameters	13	13	13	13	13	13	13	13	13	13	13
<i>N</i> – <i>P</i>	863	860	860	860	860	860	860	860	860	860	860
<i>R</i> _p	9.0	7.4	6.0	5.8	5.8	5.5	6.2	6.7	7.5	6.8	7.7
<i>R</i> _{wp}	11.9	9.6	7.9	7.7	7.6	7.4	8.3	8.6	9.7	9.0	9.9
<i>R</i> _B	4.0	2.9	2.3	2.2	2.3	1.9	2.7	2.8	2.9	2.7	2.5
Durbin-Watson <i>d</i> statistic	1.77	2.17	1.63	1.92	1.89	1.97	1.57	1.48	1.69	1.77	1.86
Esd to be multiplied by*	1.54	1.24	1.27	1.21	1.28	1.28	1.08	1.15	1.18	1.28	1.11
<i>U</i>	0.018	0.052	0.227	0.157	0.188	0.173	0.139	0.288	0.194	0.086	0.204
<i>V</i>	0.064	0.021	–0.094	–0.055	–0.074	–0.067	–0.053	0.144	–0.054	–0.038	–0.127
<i>W</i>	0.030	0.028	0.055	0.048	0.056	0.063	0.055	0.067	0.031	0.030	0.044
γ_1	0.467	0.619	0.674	0.648	0.576	0.572	0.543	0.637	0.789	0.782	0.674
γ_2	0.001	–0.002	–0.003	–0.002	–0.0002	–0.0002	–0.002	–0.005	–0.006	–0.006	–0.001

Note: *N* – *P* = no. of observations (steps) – no. of least-squares parameters.

* Correction for local correlations (Bérar and Lelann, 1991).

EXPERIMENTAL DETAILS

Synthesis

Hydrothermal syntheses were done in cold-sealed, externally heated Tuttle-type vessels. Starting materials were prepared as silicate gels according to the method of Hamilton and Henderson (1968). Ni and Co were introduced into the gels as metals, and transformed to nitrates by reaction with HNO₃. Three end-member compositions were prepared: (1) magnesium-potassium richterite: K(NaCa)Mg₅Si₈O₂₂(OH)₂; (2) nickel-potassium richterite: K(NaCa)Ni₅Si₈O₂₂(OH)₂; and (3) cobalt-potassium richterite: K(NaCa)Co₅Si₈O₂₂(OH)₂. Intermediate compositions were prepared along the binary joins Ni-Mg and Mg-Co in steps of 1 atom pfu of the substituting octahedral cation. H₂O was added to the charge in a quantity roughly equal to 10 wt% to ensure complete filling of the anionic site plus extra H₂O as a mineralizing agent. Experiment conditions were *T* = 750 °C and *P*_{H₂O} = 1 kbar. Experiment times were as long as 30 d for each composition.

X-ray data measurement

Experimental products were ground in an alumina mortar for 30 min to a grain size < 2 μm and then mounted in standard Al holders with cavities 20 × 15 × 1.6 mm. In order to minimize preferred orientation, considerable care was used in the sample preparation. The powder was back loaded and gently pressed against a frosted glass slide. The already textured surface was then serrated with a razor blade in a direction parallel to the path of the X-ray beam. This manipulation tends to randomize the orientation of anisotropic crystals that are aligned during filling but maintains a reasonably flat surface (Raudsepp et al., 1990). For the determination of the cell dimensions, a second set of data was obtained for sam-

ples prepared by densely packing the powder against the glass slide to obtain a flat surface level with the top of the holder. However, cell dimensions from patterns obtained in this way were within the standard deviations of the Rietveld values. Step-scan powder diffraction data were obtained with a Philips PW1710 automated diffractometer system, using a PW1050 Bragg-Brentano goniometer equipped with incident- and diffracted-beam Soller slits, 0.5 mm divergence and antiscatter slits, 0.2 mm receiving slit, and a curved graphite diffracted-beam monochromator. The normal-focus Cu X-ray tube was operated at 40 kV and 40 mA, using a take-off angle of 6°. The spectra were recorded using a step interval of 0.10 2 θ and a step counting time of 5 s. As discussed by Hill and Madsen (1986), these are approximately the optimum conditions for reducing serial correlation without adversely affecting the accuracy of the results. Information pertinent to data measurement is given in Table 1.

Rietveld structure refinement

The structures were refined by the program LHPM1 (DBW 3.2, originally written by Wiles and Young, 1981; modified by Hill and Howard, 1986). The peaks were defined as pseudo-Voigt with variable percentages of Lorentzian character. The peak full-width at half-maximum height (FWHM) was varied as a function of 2 θ using the expression of Caglioti et al. (1958). Peak asymmetry was corrected using the semiempirical relation of Rietveld (1969). The profile step intensity was calculated over the interval of four FWHM on either side of each peak centroid. Backgrounds were fitted with a simple polynomial function. The monochromator correction was experimentally derived for the instrument used. Initial structural parameters were taken from the single-crystal study of synthetic potassium fluor-richterite (Cameron et al., 1983). Isotropic displacement factors were fixed at values

approximately correct for amphiboles. During the initial refinements, the A site was constrained to the special position 2b at the intersection of the twofold axis with the (010) mirror plane. Refinements were then repeated, allowing the A site K to become disordered along the mirror plane (special position 4i). Better agreement was obtained with this second model, and all subsequent refinements were made with the A cation occupying the special position 4i. The correction for preferred orientation was of the form $I_{\text{corr}} = I_{\text{calc}}[P_1 + (1 - P_2)\exp(P_1\alpha_k^2)]$, where P_1 and P_2 are refinable parameters, and α_k is the acute angle between the scattering vector and the normal to the crystallites; P_2 was not refined. Information pertinent to the structure refinements is given in Table 1. After estimating as closely as possible the initial structural and experimental parameters both from the single-crystal structure and the powder pattern, refinements were done in the following sequence. The scale factor, zero-point correction, background parameters, and cell dimensions were refined with all other parameters fixed. Next the half-width parameters were refined. The remaining parameters were added to the refinement in the following order: peak shape (percentage Lorentzian character), atomic positions, peak asymmetry, overall temperature factor, correction for preferred orientation, and site occupancies. Final convergence was assumed when the parameter shifts in the final cycle were <30% of their respective standard deviations.

EXPERIMENTAL RESULTS

For each starting composition along both the joins nickel-magnesium and magnesium-cobalt potassium richterite, a single-phase product of amphibole was obtained, suggesting a complete solid-solution along the limiting binary joins of the pseudoternary system nickel richterite–magnesium richterite–cobalt richterite, under the experimental conditions used. Additional phases were not detected using a binocular microscope, by scanning electron microscopy (SEM) or by X-ray powder diffraction. Crystals were acicular in shape, 5–10 μm in length along *c*, and <3 μm in diameter. The typical morphology of end-member cobalt-potassium richterite is shown in Figure 1. Oxidizing conditions were close to the Ni-NiO buffer. The color of the experimental product was green (Ni-Mg series) or violet-pink (Mg-Co series), the intensity increasing with the content of the transition metal present in the phase. No trace of unreacted material was detected. We expended a considerable amount of effort trying to analyze the experimental products by electron microscope but were defeated by the small size of the crystals, which never exceeded 3 μm in diameter and were usually considerably less than that. Mark Welch has examined, by HRTEM, a range of potassium sodium richterite samples synthesized by us and Co-bearing richterite samples of his own and has shown that these are largely free of chain multiplicity and chain arrangement faults. His work indicates that the richterite syntheses at 750 °C, 1 kbar,

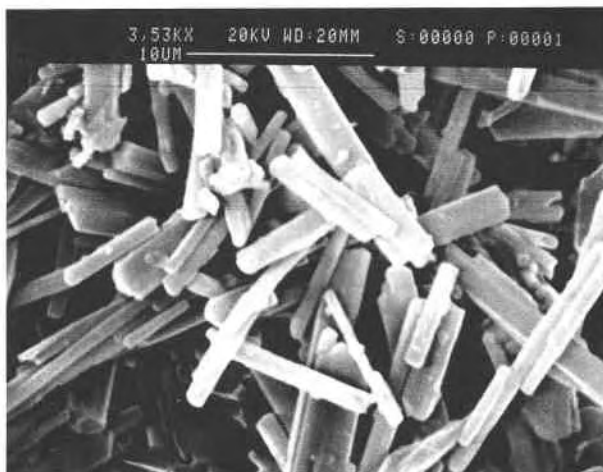


Fig. 1. SEM image showing the typical morphology of the synthetic amphiboles. The sample is the end-member cobalt-potassium richterite.

produce defect-free amphiboles (Welch, 1992 personal communication).

Unit-cell dimensions for the synthesized amphiboles are given in Table 2. Final atomic positions and selected interatomic distances are listed, respectively, in Tables 3¹ and 4. Observed and calculated step intensities are listed in Table 5. As shown in Table 1, the Durbin-Watson *d* statistic (Durbin and Watson, 1950, 1951, 1971; Hill and Flack, 1987) is generally within the range 2.0 ± 0.2 , suggesting little or no serial correlation in the data; this indicates that the assigned standard deviations should be accurate. However, the multiplicity factors for *esd*'s (Table 1) calculated with the method of Bézar and Lelann (1991) are in the range 1.2–1.5, which shows that minor serial correlation should be taken into account. Typical observed, calculated, and difference X-ray powder diffraction patterns for an intermediate composition are shown in Figure 2.

Cell dimensions

The variation in cell dimensions for the synthesized amphiboles are shown in Figures 3 and 4.

In the two series, the cell volume increases regularly (Fig. 3) in response to the increasing size of the substituting cations ($r_{\text{Ni}} = 0.690 \text{ \AA}$, $r_{\text{Mg}} = 0.720 \text{ \AA}$, $r_{\text{Co}} = 0.745 \text{ \AA}$, Shannon, 1976).

It is well known that, in isostructural series, the cell volume is a linear function of the cube of the mean cation radius of the sites involved in the substitution (Prewitt and Shannon, 1969). Although Hawthorne (1978) and

¹ Tables 3, 4, and 5 may be ordered as Document AM-93-527 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 2. Cell dimensions and volumes for synthetic potassium richterite samples

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)
KNi ₀	10.0547(8)	17.997(1)	5.2746(4)	104.832(5)	922.66
KNi ₂₀	10.0536(7)	17.982(1)	5.2702(4)	104.879(5)	920.82
KNi ₄₀	10.0492(7)	17.975(1)	5.2661(4)	104.904(4)	919.45
KNi ₆₀	10.0436(7)	17.962(1)	5.2633(3)	104.936(4)	917.44
KNi ₈₀	10.0382(7)	17.954(1)	5.2610(3)	104.954(5)	916.06
KNi ₁₀₀	10.0297(7)	17.942(1)	5.2576(3)	104.982(5)	913.96
KCo ₀	10.0547(8)	17.997(1)	5.2746(4)	104.832(5)	922.66
KCo ₂₀	10.0711(6)	18.015(1)	5.2760(3)	104.836(4)	925.30
KCo ₄₀	10.0817(8)	18.021(1)	5.2753(4)	104.832(5)	926.50
KCo ₆₀	10.0923(8)	18.032(1)	5.2742(4)	104.829(5)	927.85
KCo ₈₀	10.1065(7)	18.052(1)	5.2743(4)	104.844(4)	930.12
KCo ₁₀₀	10.1166(9)	18.066(1)	5.2752(4)	104.846(6)	931.94

Zhang et al. (1991) show the intrinsic nonlinearity of this relationship, the range in variation along the studied join is small enough to allow the use of a linear model. The measured increase in cell volume for the nickel magnesium cobalt potassium richterite samples synthesized here shows an excellent linear trend as a function of the cube of the mean cation radius at M1,2,3, testifying to the accuracy of both the refined cell dimensions and the site occupancies.

On the other hand, the relative variation of individual cell dimensions are significantly different between the two series. Along the Ni-Mg join (Fig. 4), the three cell parameters *a*, *b*, and *c* increase with increasing cation size; the β angle decreases markedly but *a* sin β increases. In other words, the unit repeat across facing double chains increases.

Significantly different behavior is observed for the Mg-Co series, for which anisotropic variation of the cell parameters as a function of the substitution of Co for Mg is observed. In fact, *a* and *b* increase, whereas *c* remains practically constant, and there is only a very slight increase in the β angle.

For monoclinic amphiboles, a comprehensive model relating the variation of individual cell parameters to composition has never been proposed, although some major relationships between composition and cell dimen-

sions have been established (Whittaker, 1960; Colville et al., 1966). The major problem involves quantifying the behavior of the octahedral strip and the tetrahedral double-chain, together with the effects of the linking M4 and A cations, in response to a chemical variation at a particular site. Any local distortion affects the overall geometry of the structure in such a way as to allow the best fit among the different units in the module. In our case, the problem is greatly simplified because of the controlled chemistry of the system: the tetrahedral sites are exclusively occupied by Si, and the M4 and A-site occupancies are fixed for all samples. The differences in size among Ni, Mg, and Co are very small: $r_{\text{Mg}} - r_{\text{Ni}} = 0.030 \text{ \AA}$, whereas $r_{\text{Co}} - r_{\text{Mg}} = 0.025 \text{ \AA}$, and similar evolutions of cell parameters and volumes are expected in both series. However, this is not the case; Figure 4 shows that the rate of increase of the individual cell parameters along the two joins are significantly different.

Bond lengths

Previous work (Raudsepp et al., 1987a, 1987b) on structural refinement of amphiboles by the Rietveld

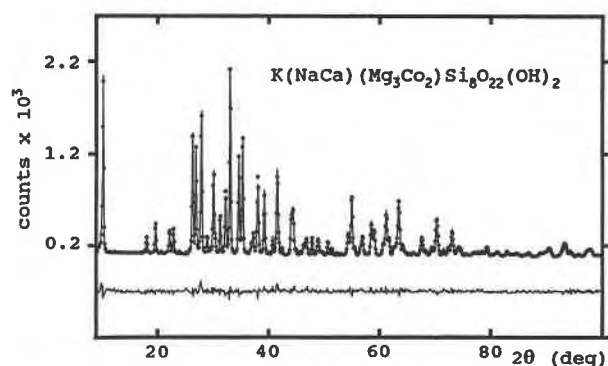


Fig. 2. Observed (full line), calculated (dots), and difference (bottom full line) X-ray powder diffraction patterns for richterite $\text{K}(\text{NaCa})(\text{Mg}_3\text{Co}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$.

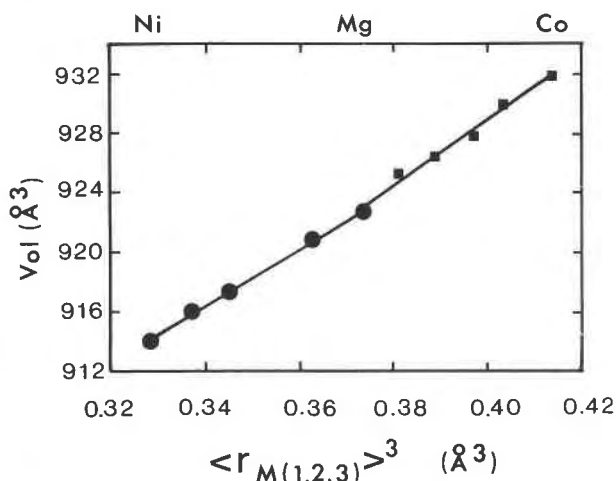


Fig. 3. Variation of the cell volume for the synthetic potassium richterite samples as a function of the cube of the average cation radius at the M1,2,3 sites.

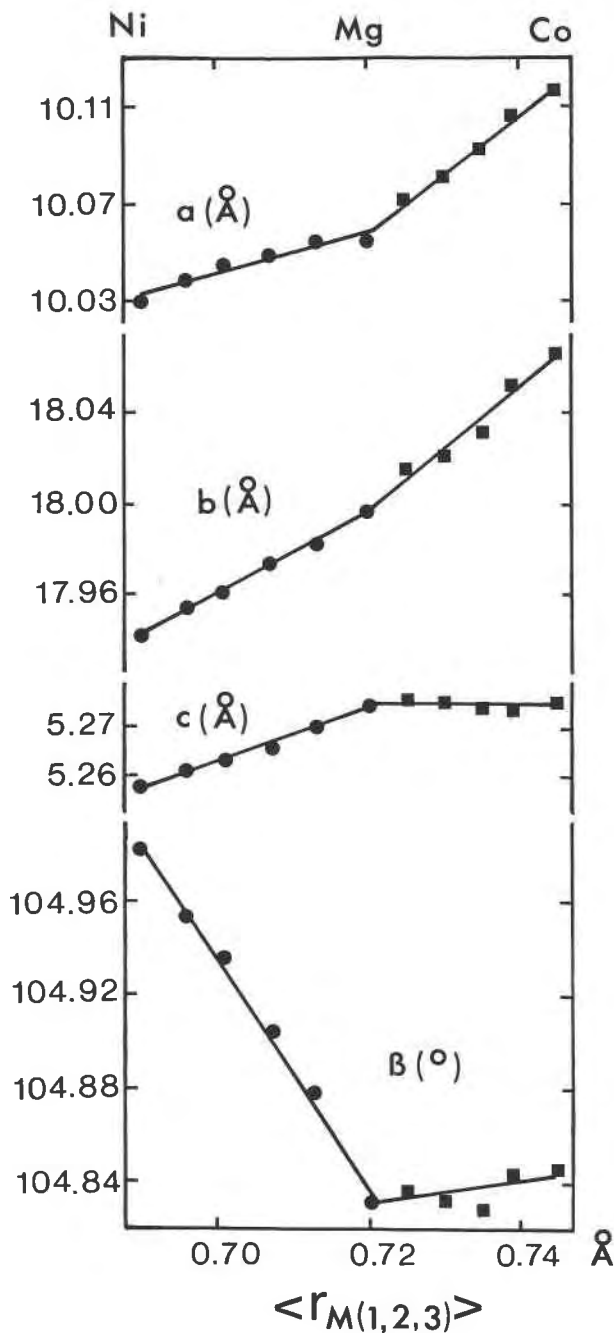


Fig. 4. Variation of the cell parameters for the synthetic potassium richterite samples as a function of the average refined cation radius at the M1,2,3 sites.

method pointed out the low accuracy of the resulting individual bond lengths caused by pseudosymmetry in the amphibole structure. The major discrepancies were in the individual T-O distances with respect to those determined by single-crystal diffraction studies on amphiboles of similar composition. The present study confirms those findings. In comparison with single-crystal data from similar phases (e.g., Cameron et al., 1983, and Oberti et

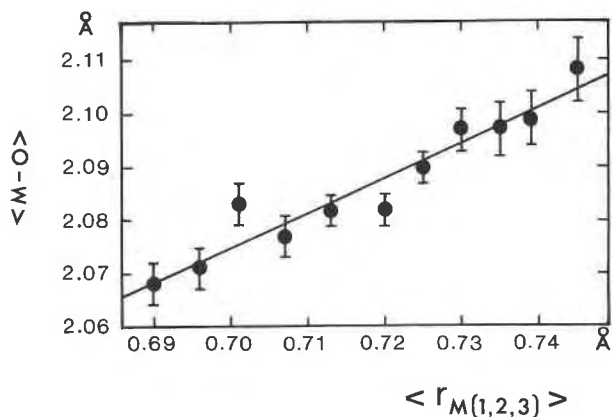


Fig. 5. Variation of the grand (M-O) bond distance for the synthesized potassium richterite samples as a function of the mean cation radius at M1,2,3. Vertical bars represent the esd; the solid line is a linear least-squares fit to the data points.

al., 1992, for richterite; Hawthorne and Grundy, 1976, for tremolite), T1-O5 distances are systematically too short and T1-O6 distances are too long. However, the mean tetrahedral bond distance is in close agreement with single-crystal data for purely siliceous amphiboles: $\langle T1-O \rangle$ is in the range of 1.620–1.630 Å, whereas $\langle T2-O \rangle$ ranges within 1.630–1.640 Å.

In isomorphous series, mean octahedral bond-lengths are linearly related to the radius of the constituent cations (e.g., garnets: Novak and Gibbs, 1970; olivines: Brown, 1970; pyroxenes: Hawthorne and Grundy, 1974, 1977; Cameron and Papike, 1981; Raudsepp et al., 1990). For amphiboles, the variation of individual $\langle M-O \rangle$ lengths as a function of the constituent cation radius is well characterized (Ungaretti, 1980; Hawthorne, 1983b). The grand mean $\langle M-O \rangle$ bond lengths for the nickel magnesium and magnesium cobalt potassium richterite series (Fig. 5) show linear variation with the refined mean octahedral radius, and are in close agreement with the relationship proposed for a large number of amphiboles (Fig. 6). However the values obtained here are somewhat larger than predicted. The individual $\langle M-O \rangle$ bond lengths also show a reasonable agreement with the general trends for monoclinic amphiboles, but again the Rietveld data are somewhat larger than the curves derived from single-crystal diffraction.

Site occupancies

The refined site occupancies of the synthesized amphiboles are listed in Table 6. The Rietveld method provides quite accurate site occupancies and bulk compositions, if reasonable values for isotropic displacement factors are used (Raudsepp et al., 1990).

Comparison of the refined and nominal Ni-Mg and Mg-Co compositions (Fig. 7) shows good agreement. However, for the Ni-Mg series the refined values are slightly larger than the expected ones. No additional phases were found by XRD and SEM observations, so

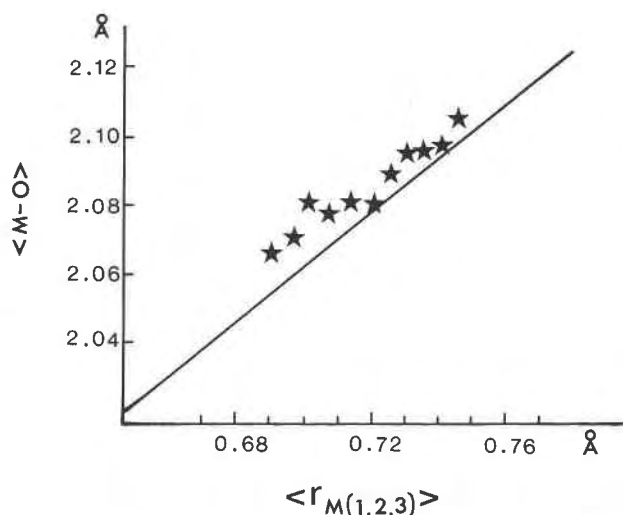


Fig. 6. Plot of the grand mean $\langle M-O \rangle$ bond distance as a function of the mean cation radius at M1,2,3 for several well-characterized amphiboles (from Hawthorne, 1983b). Stars: synthetic potassium richterite, this work.

this slight disagreement may be an artifact of the displacement model used, as already suggested by Raudsepp et al. (1990).

For end-member compositions, the scattering at the M1, M2, and M3 sites are known exactly, and consequently the unconstrained occupancy refinement for these compositions should converge to the ideal occupancy. This is a good check on the accuracy of the site-occupancy refinement procedure. For each end-member, an occupancy equal to nominal (within 1 sd) was obtained.

Along the substitutional joins, both Ni and Co preferentially enter the OH-coordinated M1 and M3 sites (Table 6), whereas Mg prefers M2. The Ni and Co distribution over M1 and M3 is 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 series. The relationship between Ni and Co at M1,3 and at M2 is shown in Figure 8. The data of Table 6 allow the calculation of the partition coefficients for Ni and Co over the OH-coordinated M1,3 and OH-free M2 sites, defined as $K_{M2+} = (M^{2+}/Mg)_{M1,3} / (M^{2+}/Mg)_{M2}$, with $M^{2+} = Ni^{2+}$ or Co^{2+} . For the Ni-Mg series $K_{Ni} = 4.26 \pm 0.56$; for the Mg-Co series, $K_{Co} = 1.92 \pm 0.29$.

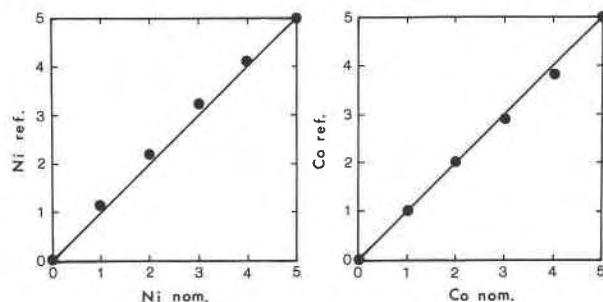


Fig. 7. Relationship between the nominal and refined Ni and Co occupancies on the octahedral strip of synthetic potassium richterite (this work).

DISCUSSION

Comparing the behavior of the cell parameters along the two joins, there is a marked break in the trend at $\langle r \rangle = 0.720 \text{ \AA}$ (corresponding to Mg). For a mean cation radius at M1,2,3 $> 0.720 \text{ \AA}$, a and b keep increasing, with a steeper slope, whereas c remains essentially constant along the range from Mg to Co. There is also a spectacular discontinuity of the β angle, which ceases to decrease and slightly increases for $\langle r \rangle > 0.720 \text{ \AA}$. The overall trend for the cell volume is approximately linear, indicating that the relative anisotropy of expansion in the Mg-Co series is such that the constant volume increase is maintained. If the cell volumes for the Ni-Mg and Mg-Co series are fitted separately, a slight nonlinearity is apparent (Fig. 3), but it is not clear if it is significant or not.

Two factors enter into the behavior of the cell dimensions with different compositions in the octahedral strip: (1) cation size, and (2) electronic configuration. In the mineralogical literature, previous discussions regarding this point have maintained that 1 is the principal variable. However, the unusual discontinuities and marked different behavior of the different transition metal compositions indicate that 2 is also a major factor. Detailed discussion of these results will be deferred until data are available on other transition-metal series and the effect of electron configuration can be properly assessed. The K_d values observed here also indicate that electronic structure has a major effect on the relative ordering of cations in the amphibole structure. Ni^{2+} is smaller than Mg, whereas Co^{2+} is larger than Mg. Thus if cation ordering were controlled solely by cation size (for a specific

TABLE 6. Refined site occupancies for synthetic potassium richterite samples

		KNi ₀	KNi ₂₀	KNi ₄₀	KNi ₆₀	KNi ₈₀	KNi ₁₀₀	KCo ₂₀	KCo ₄₀	KCo ₆₀	KCo ₈₀	KCo ₁₀₀
M1	Mg	1.00	0.72(2)	0.46(2)	0.25(2)	0.10(2)	—	0.76(1)	0.55(2)	0.38(3)	0.21(3)	—
	M ²⁺	—	0.28(2)	0.54(2)	0.75(2)	0.90(2)	1.00	0.24(1)	0.45(2)	0.62(3)	0.79(3)	1.00
M2	Mg	1.00	0.90(2)	0.73(2)	0.54(2)	0.33(2)	—	0.86(2)	0.71(2)	0.50(3)	0.30(3)	—
	M ²⁺	—	0.10(2)	0.27(2)	0.46(2)	0.67(2)	1.00	0.14(2)	0.29(2)	0.50(3)	0.70(3)	1.00
M3	Mg	1.00	0.62(3)	0.37(3)	0.20(3)	0.07(3)	—	0.75(2)	0.50(3)	0.32(3)	0.16(4)	—
	M ²⁺	—	0.38(3)	0.63(3)	0.80(3)	0.93(3)	1.00	0.25(2)	0.50(3)	0.68(3)	0.84(4)	1.00
M ²⁺ _{nom}		0.00	1.00	2.00	3.00	4.00	5.00	1.00	2.00	3.00	4.00	5.00
M ²⁺ _{exp}		0.00	1.14	2.25	3.22	4.07	5.00	1.01	1.98	2.92	3.82	5.00

Note: M²⁺ = Ni, Co.

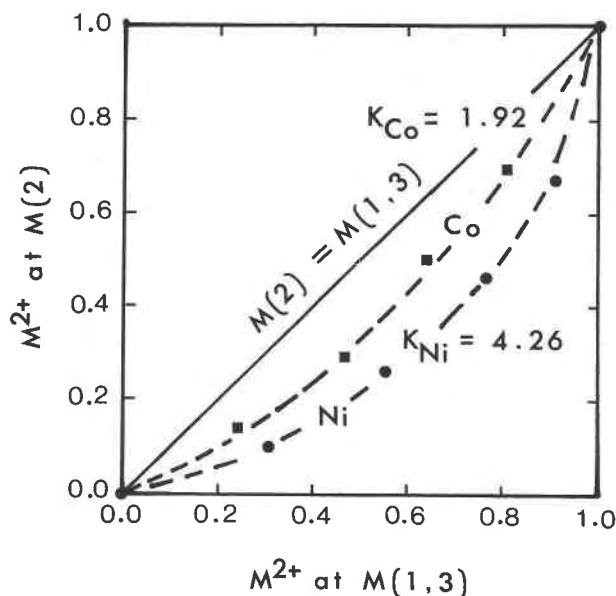


Fig. 8. Relationship between the refined Ni-Mg and Co-Mg occupancies at the M1,3 and M2 sites. Circles: Ni,Mg series. Squares: Mg,Co series.

structure type), then K_d for (Ni²⁺,Mg) ordering should lie on one side of 1.0, and K_d for (Co²⁺,Mg) ordering should lie on the other side of 1.0. The fact that K_d for both these orderings is >1.0 indicates that the primary factor controlling the ordering is not cation size. The other obvious factor involved is the electronic structure of the transition metal. Co and Ni have d⁷ and d⁸ configurations, respectively, and the relationships between bond length and constituent cation radii indicate that they are both in the high-spin configuration. For Ni, there is an octahedral stabilization energy associated with complete occupancy of the t_{2g} levels and single occupancy of the e_g levels. For Co, the situation is a little more complicated. As well as a different octahedral stabilization energy, there is also an electronic degeneracy in the t_{2g} levels for a holosymmetric octahedral environment and hence an additional stabilization energy (compared with Ni) for distorted environments. This argument could be developed further, but we regard it as premature to do so. Further work is planned on other transition metal richterite samples (Fe²⁺,Mn²⁺) in order to put these qualitative arguments on a more quantitative basis.

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