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

GIANCARLO DELLA VENTURA,[1] JEAN-LOUIS ROBERT,[2] MATI RAUDSEPP,[3]
FRANK C. HAWTHORNE,[4] AND MARK D. WELCH[5]

[1]Dipartimento di Scienze Geologiche, Terza Università di Roma, Viale Ostiense 169, Rome, I-00154, Italy
[2]Centre pour la Synthese et la Chimie des Mineraux, CNRS, 1A, rue de la Ferollerie, Orleans cedex 2, France
[3]Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada
[4]Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada
[5]Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.

ABSTRACT

Amphiboles were synthesized at 750 °C, 1 kbar (H_2O) 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 $K^{M2+} = (M^{2+}/Mg)_{M1,3}/(M^{2+}/Mg)_{M2}$, and $M^{2+} = Ni^{2+}$ or Co^{2+}, $K_d^{Ni} = 2.98 \pm 0.37$ and $K_d^{Co} = 1.34 \pm 0.31$. Both K_d values are greater than 1.0, whereas $^{[6]}r(Ni^{2+}) < ^{[6]}r(Mg) < ^{[6]}r(Co^{2+})$; 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 $3I_o^A + 2I_o^B + I_o^C$ and $I_o^B + 2I_o^C + 3I_o^D$ 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.