

X-ray Rietveld and ^{57}Fe Mössbauer studies of epidote and piemontite on the join $\text{Ca}_2\text{Al}_2\text{Fe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$ – $\text{Ca}_2\text{Al}_2\text{Mn}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$ formed by hydrothermal synthesis

MARIKO NAGASHIMA^{1,2,*} AND MASAHIDE AKASAKA¹

¹Department of Geoscience, Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan

²Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

ABSTRACT

Fe^{3+} and Mn^{3+} distributions on octahedral M1, M2, and M3 sites in synthetic epidote/piemontite from $\text{Ca}_2\text{Al}_2\text{Fe}_q^{3+}\text{Mn}_{1-q}^{3+}\text{Si}_3\text{O}_{12.5}$ starting material and their effects on the crystal structure were investigated using X-ray Rietveld and ^{57}Fe Mössbauer methods. Epidote and piemontite were crystallized as almost single phases from $q = 1.0, 0.75, 0.5,$ and 0.25 starting materials at P_{fluid} of 200–400 MPa and a temperature of 500 °C, using standard cold-seal pressure vessels. The Mn_2O_3 - MnO_2 buffer was used to produce f_{O_2} adequate to maintain Fe^{3+} and Mn^{3+} . The Rietveld refinements converged to goodness-of-fit ranges from 1.21 to 1.60.

At this temperature, site preferences of $\Sigma(\text{Fe}^{3+}+\text{Mn}^{3+})$ for octahedral sites are $\text{M3} > \text{M1} (>> \text{M2})$. K_D values of $\Sigma(\text{Fe}^{3+}+\text{Mn}^{3+})$, where $K_D = [(\text{Fe}^{3+}+\text{Mn}^{3+})/\text{Al}]^{\text{M1}}/[(\text{Fe}^{3+}+\text{Mn}^{3+})/\text{Al}]^{\text{M3}}$, (0.05–0.13) are similar to those of individual Mn^{3+} and Fe^{3+} vs. Al^{3+} , respectively. However, the K_D values of Fe^{3+} and Mn^{3+} for M1 and M3, where $K_D = (\text{Fe}^{3+}/\text{Mn}^{3+})^{\text{M1}}/(\text{Fe}^{3+}/\text{Mn}^{3+})^{\text{M3}}$, vary with $\text{Fe}_{\text{total}}^{3+}:\text{Mn}_{\text{total}}^{3+}$ ratios. In epidote with Fe^{3+} content larger than 0.4 atoms per formula unit (apfu) and $\text{Mn}^{3+} < 0.6$ apfu, Fe^{3+} has a stronger preference for M1 than Mn^{3+} . In piemontite with 0.12 Fe^{3+} and 0.73–0.78 Mn^{3+} apfu, the preference of Mn^{3+} for M1 is greater than that of Fe^{3+} . The site occupancies of individual Mn^{3+} and Fe^{3+} are governed by the individual K_D values and the Mn^{3+} and Fe^{3+} concentrations in corresponding epidote and piemontite. Variations of the unit-cell parameters indicate the combined result of linear variation due to $\text{Al} \leftrightarrow \text{Fe}^{3+}$ substitution and nonlinear variation due to $\text{Al} \leftrightarrow \text{Mn}^{3+}$ substitution.

Keywords: Epidote, piemontite, synthesis, Rietveld refinement, Mössbauer spectroscopy