

Crystal chemistry of the natrojarosite-jarosite and natrojarosite-hydronium jarosite solid-solution series: A synthetic study with full Fe site occupancy

LAUREL C. BASCIANO* AND RONALD C. PETERSON

Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada

ABSTRACT

Members of the natrojarosite-hydronium jarosite $[(\text{Na}, \text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]$ and jarosite-natrojarosite $[(\text{K}, \text{Na})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]$ solid-solution series were synthesized and investigated by Rietveld analysis of X-ray powder diffraction data. The synthesized samples have full Fe occupancy, where in many previous studies there were significant vacancies in the B site. Well-defined trends can be seen in the unit-cell parameters across the solid-solution series in the synthetic samples. The majority of the samples in this study were directly synthesized under hydrothermal conditions at 140 °C. End-member natrojarosite was synthesized using a two-step method, where the initial sample was heated in a 1.0 *m* H_2SO_4 -0.5 Na_2SO_4 solution at 200 °C for 3 days, yielding a sample with 100% Na occupancy. Many of the samples were initially zoned and required grinding and re-heating in the reactant solution for homogenization. Substitution of H_3O and K into natrojarosite changes unit-cell parameters in a linear fashion. The unit-cell parameters presented here are significantly different than the majority of previous studies on synthetic samples, as samples in the current study have full Fe occupancy and the Na-K jarosite series has no H_3O substitution in the A site. Substitution in the A site mainly affects unit-cell parameter *c* with little change in *a*. As Na occupancy increases there is a decrease in A-O2 and A-O3 distances and a consequent increase in Fe-O2 and Fe-O3 distance leading to an overall decrease in unit-cell parameter *c* in both the Na- H_3O and Na-K jarosite series. The synthetic samples are compared to natural samples from mine waste deposits in Rio Tinto (Huelva, Spain), Ely Mine (Vermont), and a mineral collecting locality near Sharbot Lake (Ontario), as well as natural and synthetic samples documented in the literature. Based on unit-cell parameters many of the natural samples appear to have full Fe occupancy and correlate well with the synthetic samples from this study. The infrared spectra of the samples were analyzed, and there is a gradual change in the spectral features across the solid-solution series between end-members. The results from this study will aid in the interpretation of the possible chemical compositions of natural jarosite group minerals in mine waste and on Mars.

Keywords: Jarosite, hydronium jarosite, natrojarosite, solid-solution series, crystal synthesis, crystal structure, IR spectroscopy, Rietveld refinement