

Jarosite–hydronium jarosite solid-solution series with full iron site occupancy: Mineralogy and crystal chemistry

LAUREL C. BASCIANO* AND RONALD C. PETERSON

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

ABSTRACT

Structural changes within the jarosite–hydronium jarosite solid-solution series, $(K, H_3O)Fe_3(SO_4)_2(OH)_6$, were investigated by X-ray Rietveld analysis of powder diffraction data collected from synthetic samples. All previous studies of jarosite solid solution consisted of samples that were non-stoichiometric with respect to iron. In this study, stoichiometric samples in the series were synthesized under hydrothermal conditions at 140 °C using starting materials of $Fe_2(SO_4)_3 \cdot 5H_2O + K_2SO_4 + H_2O$ in hydrothermal conditions. End-member potassium jarosite was also synthesized under similar conditions from a stoichiometric mixture of $FeCl_3 + KCl + LiCl + Fe(SO_4)_3 \cdot 5H_2O + H_2O$. Crystals were initially zoned with potassium-rich cores and hydronium-rich rims. Samples were homogenized by grinding and re-heating in the reactant solution. One iron deficient sample was synthesized to determine the effect of non-stoichiometry. Substitution of H_3O by K changes the unit-cell parameters in a linear fashion; c increases significantly and a decreases to a lesser degree. Unit-cell parameters from stoichiometric samples determined in this study are larger than synthetic samples analyzed in previous studies as a result of full iron occupancy. Potassium substitution in the alkali site (A site) mainly affects the A-O2 bond length, which causes the Fe-O2 and Fe-O3 bonds to lengthen and shorten, respectively. As potassium substitutes into the structure, there is an overall increase in the c axis. Iron deficiency leads to a significant decrease in unit-cell volume (large in c , minor in a), which is caused by bond length Fe-O3, which is markedly shorter than stoichiometric samples with similar potassium occupancy. The synthetic samples are compared with natural samples of jarosite and hydronium jarosite collected from mine waste deposits in Rio Tinto, Huelva, Spain. The natural samples have close to full iron occupancy, resulting from high iron content in solution and correlate well to the synthetic samples. Samples were also analyzed using short-wave infrared spectroscopy (SWIR). It was found that there is a subtle difference in spectra between end-members hydronium jarosite and potassium jarosite that can be tracked across the solid-solution series.

Keywords: jarosite–hydronium jarosite solid-solution series, crystal synthesis, IR spectroscopy, SWIR, crystal structure, XRD data, Rietveld refinement