EXPERIMENTAL STUDIES OF JAROSITE AND ALUNITE AT HYDROTHERMAL CONDITIONS. R.E. Stoffregen, AWK Consulting Engineers, Inc., 10 Duff Road, Suite 304, Pittsburgh, Pennsylvania, 15218, Stoffregen@verizon.net.

Introduction: The minerals jarosite (KFe₃(SO₄)₂(OH)₆), alunite (KAl₃(SO₄)₂(OH)₆), and their sodium analogs have been studied in a variety of hydrothermal experiments over a temperature range of 100 to 450°C. Due to mineral stability and reaction rate considerations, experiments on jarosite were conducted mainly in the temperature range of 100-250°C, and those for alunite from 250-450°C. These experiments have defined the stability field of jarosite relative to hematite [1]; determined mineral-fluid Na-K distribution coefficients and provided constraints on the mixing behavior along the jarosite-natrojarosite [1] and alunite-natroalunite [2] binaries; measured the fractionation of oxygen isotopes between water and the sulfate and hydroxyl sites in alunite, and the D-H fractionation between water and alunite [3]; and provided reconnaissance information on these mineral-water isotope fractionation factors for jarosite [4]. In addition, the experiments provide rates of alkali and isotope exchange between these minerals and co-existing aqueous solutions that can be extrapolated to lower temperatures with some confidence [1,5].

Jarosite Stability: Jarosite is stable relative to hematite below a log m H₂SO₄ of -0.35 ± 0.5 at 250°C and -0.58 ± 0.12 at 200°C (corresponding to m H₂SO₄ of 0.45 and 0.26). Natrojarosite could not be produced from hematite at 250°C, but was stable below a log m H₂SO₄ of -0.17 ± 0.08 at 200°C (corresponding to a m H₂SO₄ of 0.63). These extreme sulfurous acid concentrations required for jarosite stability are consistent with the rarity of jarosite in hydrothermal environments on earth. Decreasing temperature increases the jarosite stability field, consistent with the common occurrence of jarosite in terrestrial surface environments where pyrite serves as a source of sulfurous acid during weathering.

Alkali Exchange and Mixing: The distribution coefficient for the exchange reaction

\[(1) \text{jarosite} + \text{Na}^+ \rightarrow \text{natrojarosite} + \text{K}^+ \]

is -4.9 at 150°C, -3.7 at 200°C, and -3.1 at 250°C, and values for the analogous alunite-natroalunite reaction are -2.56 at 250°C, -1.73 at 350°C, and -0.99 at 450°C. These values indicate that partitioning of alkalis is similar for jarosite and alunite, and that increasing temperature favors the sodium end-member for both phases.

Experimental results suggest that jarosite-natrojarosite can be modeled as an ideal solid solution at 200°C. Increasing departures from ideality with decreasing temperature are not precluded by the experimental data, but a solvus in the system jarosite-natrojarosite is considered unlikely. In contrast, the alunite-natroalunite binary shows a substantial departure from ideality that increases with decreasing temperature from 450 to 250°C. An asymmetric solvus is considered likely with decreasing temperature.

Isotope Exchange: Alunite-water oxygen and hydrogen isotope fractionations were determined in couple alkali and isotope exchange experiments. Results were used to develop an intra-mineral geothermometer based on oxygen isotope fractionation between the alunite sulfate and hydroxyl sites. Reconnaissance jarosite-water isotope fractionation experiments were also conducted, but their interpretation was complicated by apparent non-equilibrium effects.

Reaction rates: The experimentally determined rate of jarosite-fluid alkali exchange over the temperature range of 200-108°C was

\[\log t_\alpha = -14.38 + 6.28 \left(1000/T \text{ (K)}\right)\]

where \(t_\alpha\) is equal to the time required for 50% exchange, in days. When extrapolated to 25°C, this equation suggests that jarosite will rapidly equilibrate (at geologic times scales) with co-existing fluids even at earth-surface conditions. This should be taken into consideration when studying the stable isotope systematics of jarosite, or using it for K-Ar dating. Experimentally determined alunite-fluid exchange rates are roughly three orders of magnitude slower than those for jarosite, which suggests that alunite, unless it is fine-grained, will not re-equilibrate at surface conditions.