

COMPARING NA-JAROSITE AND K-JAROSITE DISSOLUTION RATES TO DETERMINE THE EFFECTS OF CRYSTAL CHEMISTRY ON JAROSITE LIFETIMES. S. K. Zahrai¹, M. E. Elwood Madden¹, A. S. Madden¹ and J. D. Rimstidt², ¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, shayda.k.zahrai-1@ou.edu, ²Dept. of Geosciences, Virginia Tech, 4044 Derring Hall, Blacksburg, VA 24061, jdr02@vt.edu.

Introduction: On Earth, the ferric sulfate mineral jarosite forms in volcanic fumaroles, acidic soils, and acid mine drainages. Observations of jarosite on Mars by the Mars Exploration Rover (MER) Opportunity [1, 2, 3, 4] have been interpreted as an indicator of water-limited aqueous diagenesis at Meridiani Planum [5, 6, 7, 8, 9]. Therefore, by measuring the dissolution rates of jarosite, jarosite lifetimes and the duration of water in jarosite-bearing sediments on Mars can be determined. In this study, Na-jarosite dissolution experiments were conducted and compared to previous K-jarosite results [10]. By comparing these two phases, the effect of crystal chemistry on jarosite dissolution rates can be determined.

Methods: Na-jarosite used in this study was synthesized using the method previously described by Driscoll [11]. The mineralogy was confirmed with X-ray powder diffraction and surface area measured by BET nitrogen adsorption method ($2.645 \text{ m}^2 \text{ g}^{-1}$). Morphology of the synthesized Na-jarosite was imaged using Transmission Electron Microscopy (TEM).

Dissolution experiments were conducted at 277 K, 295 K, and 323 K in ultrapure water, as well as buffered room temperature experiments at pH 1, 6, and 8. Solutions were mixed on a stir plate with a magnetic stir bar constantly stirring the solution. The 277 K, 295 K, 323 K, and pH 6 experiments initially contained 0.25 g Na-jarosite and 250 g of solution in a 600 mL beaker, while the pH 1 and pH 8 experiments were conducted in a 150 mL beaker initially containing 0.15 g jarosite and 160 g of solution. The 277 K experiments were conducted in an ice bath on top of a stir plate within a standard refrigerator, while heated stir plates were used for the 323 K experiments. In each experiment, an experimental blank was collected before adding Na-jarosite. After adding the Na-jarosite, 10 mL samples were collected at regular intervals and filtered through a $0.2 \mu\text{m}$ syringe filter. The timing interval for sample collection was based on the predicted reaction progress from previous results [10]. Experiment time initiated once Na-jarosite was added to the solution. Experiments were replicated 2-4 times to ensure reproducibility of the results.

Samples were stored in a refrigerator until the concentration of Na^+ was analyzed using a Perkin Elmer Analyst 800 Flame Atomic Absorption Spectrometer (AAS). AAS settings were determined according to the manufacturer's instructions. Samples were analyzed three times, resulting in an average concentration. Jar-

osite dissolution rate was determined by plotting the reported Na^+ concentration versus reaction time of each experiment and then fitting the curve with a second order polynomial. The second derivative of this curve gives the instantaneous slope at $t=0$, providing an initial rate of dissolution [12].

Results: Na-jarosite dissolution rates are temperature and pH dependent. Dissolution rates increase with increasing temperature (Figure 1), which yield an activation energy of 52 kJ/mol. The pH data form a "V" shape with dissolution rates that increase at low and high pH, similar to previously conducted K-jarosite experiments. However, the Na-jarosite dissolution rates were slightly faster than the K-jarosite dissolution rates, except for the pH 6 experiments (Figure 2).

TEM images taken of a Na-jarosite pH 6 experiment after five days of reaction show dissolution occurring along the edges of the hexagonal Na-jarosite crystals. Hematite was also observed forming as a reaction product.

Particle lifetimes of 1 mm Na-jarosite grains were calculated using a shrinking sphere equation:

$$\Delta t = d/2V_m r$$

where d is the diameter (m), V_m is the molar volume ($\text{m}^3 \text{ mol}^{-1}$), and r is the rate of dissolution ($\text{mol m}^{-2} \text{ s}^{-1}$). Na-jarosite lifetimes were longer for slower reaction rates corresponding to lower temperatures and pH 6; lifetimes were shorter at higher temperatures, pH 1, and pH 8. Lifetimes ranged from 1 year at pH 1 to ~200 years at 277 K.

Discussion: Rates of Na-jarosite dissolution are very similar to previous data reported for K-jarosite dissolution. This suggests that cation substitution in the A site does not have a significant effect on dissolution rates. The "V" shaped trend of the pH data indicate that dissolution rates increase with more H^+ or OH^- in solution. The dissolution rates of Na-jarosite are slightly faster than K-jarosite dissolution rates and yield marginally shorter lifetimes in aqueous systems. The relatively short lifetimes of Na-jarosite indicate short-term aqueous diagenesis on Mars is required to preserve jarosite within outcrops at Meridiani Planum.

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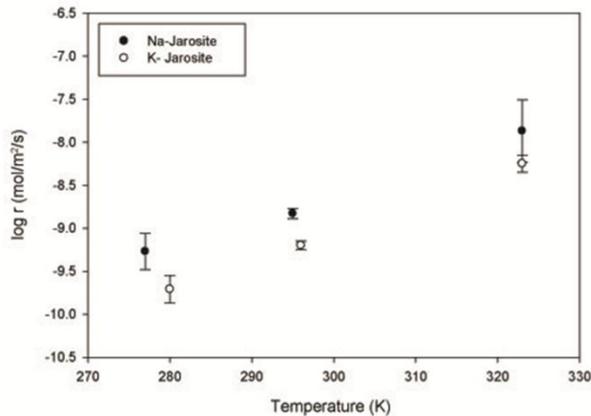


Figure 1. Both Na-jarosite (solid circles) and K-jarosite (open circles) dissolution rates at pH ~4 increase with increasing temperature. However, Na-jarosite rates are slightly faster than K-jarosite dissolution rates. Error bars show the standard deviation of the average dissolution rates.

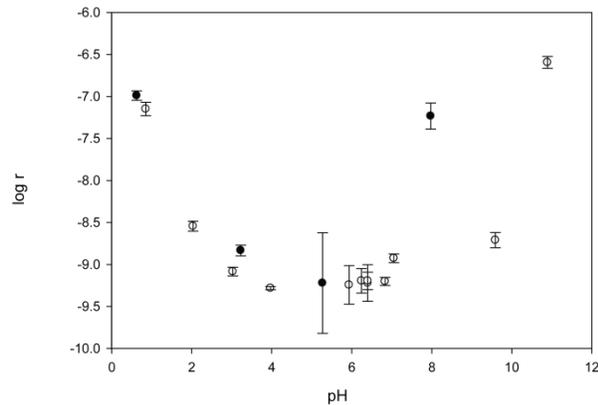


Figure 2. Na-jarosite (solid circles) dissolution rates and K-jarosite (open circles) dissolution rates form a "V" shape showing that rates increase at low and high pH [10]. Error bars show the standard deviation of the average dissolution rates.

References: [1] Christensen P.R. et al. (2004) *Science*, 306, 1733-1739. [2] Klingelhofer G. et al. (2004) *Science*, 306, 1740-1745. [3] McLennan S.M. et al. (2005) *Earth Planet. Sci. Lett.*, 240, 95-121. [4] Squyres S.W. et al. (2006) *J. Geophys. Res.-Planet.*, 111, E12S12. [5] Bibring J.P. et al. (2007) *Science*, 317, 1206-1210. [6] Bibring J.P. et al. (2006) *Science*, 312, 400-404. [7] Elwood Madden M.E. et al. (2004) *Nature*, 431, 821-823. [8] King P.L. and McSween H.Y. (2005) *J. Geophys. Res.-Planet.*, 110, E12S10. [9] Tosca N.J. et al. (2008) *J. Geophys. Res.-Planet.*, 113. [10] Elwood Madden M.E. et al. (2011) *GSA*, Abstract #167-5. [11] Driscoll R. and Leinz R. (2005) *U.S. Geol. Surv. Tech. Methods* 05-D1. [12] Rimstidt J.D. and Newcomb W.D. (1993) *Geochim. et Cosmochim. Acta*, 57, 1919-1934.