

SALINITY AND TEMPERATURE EFFECTS ON THE DISSOLUTION OF NATROJAROSITE AND K-JAROSITE. B. N. Pritchett¹, M. E. Elwood Madden¹ and A. S. Madden¹, ¹ConocoPhillips School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, Brittanyp@ou.edu

Introduction: Jarosite is a ferric sulfate salt, ((K, H, Na)Fe₃(SO₄)₂(OH)₆), that forms both on Earth and on Mars. The presence of jarosite, along with iron oxides, has been used to determine the duration of aqueous alteration on Mars [1, 2]. APEX spectra also detected the presence of Fe₂(SO₄)₃, MgSO₄, AlCl₃, Na₂SO₄, CaCl₂, MnSO₄ and KH₂PO₄ within the outcrops, indicating that high salinity brines may have been associated with jarosite deposits at Meridiani Planum, Mars [3,4, 5]. Previous studies have measured jarosite dissolution in dilute fluids but have not examined jarosite dissolution rates within saline brines. Ionic strength reduces the activity of water ($\alpha\text{H}_2\text{O}$) and therefore the potential reactivity of the solution [6] Jarosite lifetimes in high salinity brines could therefore be longer than particle lifetimes in dilute fluids. This study examines the effects of $\alpha\text{H}_2\text{O}$ on the dissolution rates and the lifetimes of Na- and K-jarosite.

Methods: K-Jarosite and Na-Jarosite were first synthesized following the method of Driscoll et al. [7] and then analyzed using X-Ray Diffraction to determine mineralogy and their surface area determined using the BET method. Dissolution rates of K-jarosite and Na-Jarosite were measured in 4 different fluids (ultra pure water, NaCl-saturated brine, CaCl₂-undersaturated brine and CaCl₂-saturated brine) covering a range of water activity ($\alpha\text{H}_2\text{O}$ of 1.0, 0.75, 0.75, and 0.35, respectively) in batch reactor experiments at room temperature. One K-jarosite batch reactor experiment, measured in a NaCl brine, was conducted at -8 °C within a standard freezer to examine the dissolution process in extreme cold and better understand the effects of Martian conditions on jarosite dissolution rates.

For the room temperature experiments, 0.1g of either K-jarosite or Na-jarosite was mixed with 100mL of each fluid and 10 mL samples were removed and passed through a 0.2 μm filter at predetermined intervals over several hours and/or days. The -8°C experiment was conducted in a freezer and samples were taken over the course of 9 days.

The aqueous samples were diluted 1:8 and one Na-jarosite experiment ($\alpha\text{H}_2\text{O}$ 0.75) was diluted 1:32. The K⁺ and Na⁺ concentrations were then analyzed using matrix-matched flame Atomic Absorption Spectrophotometry. The lifetimes of a 1mm particle were determined using a shrinking sphere model:

$$\Delta t = \frac{d}{2V_m k} \quad (1)$$

where Δt is the lifetime of the particle (sec), d is the diameter of the particle (cm), V_m is the molar volume of the mineral ($\text{cm}^3 \text{g}^{-1}$), and k is the rate of dissolution ($\text{g cm}^{-2} \text{sec}^{-1}$).

Results: The data (Table 1) show that both K-jarosite and Na-jarosite dissolution rates are significantly affected by $\alpha\text{H}_2\text{O}$. With decreasing $\alpha\text{H}_2\text{O}$ (1, 0.75, 0.35) the dissolution rates of both end-member jarosites decrease by approximately one order of magnitude. This shows that $\alpha\text{H}_2\text{O}$ does provide a control on the dissolution rate of Na- and K-jarosite. The low-temperature K-jarosite experiment showed that temperature, as well as ionic strength, could influence the dissolution rate. The dissolution rate from the low temperature experiment (0.75 $\alpha\text{H}_2\text{O}$) decreased from the room temperature rate and was comparable to the rate found for the 0.35 $\alpha\text{H}_2\text{O}$ experiment.

Table 1. Dissolution rates of K- and Na-jarosite in solutions with three different activities of water (1, 0.75, and 0.35).

Activity of Water	Na-Jarosite (Log r)	K-Jarosite (Log r)	K-Jarosite Low-T (Log r)
1.0	-8.8	-9.0	
0.75	-10.4	-10.0	-11.6
0.35	-11.0	-11.5	

Particle lifetime data (Table 2) shows that decreasing both $\alpha\text{H}_2\text{O}$ and temperature can significantly extend the lifetime of jarosite particles. By decreasing the temperature 30°C the lifetime of a K-jarosite particle increased by ~30,000 times. These results show that K- and Na-jarosite lifetimes are extended in high salinity and cold environments, allowing for prolonged periods of aqueous alteration at Meridiani Planum.

Table 2. Calculated lifetimes of a 1mm jarosite particle in solutions with three different activities of water (1, 0.75, and 0.35).

Activity of Water	Na-Jarosite (yr)	K-Jarosite (yr)	K-Jarosite Low-T (yr)
1.0	68	113	
0.75	2,357	1,102	36,506
0.35	10,289	35,675	

References: [1] Elwood Madden M. E. et al. (2009) *Geology*, 37, 635–638. [2] Elwood Madden M. E. et al. (2011) *GSA, Abstract #167-5*. [3] Barron V et al. (2006) *EPSL*, 251, 380-385. [4] Reider R. et al. (2004) *Science*, 306, 1746-1749. [5] Keller J. M. (2006) *Journal of Geophysical Research Planets*, 111, 1-18. [6] Pitzer K. S. (1973) *J. Phys. Chem.*, 77, 268-277. [7] Driscoll, R. L. and Leinz R. W. (2005) *U.S. Geological Survey Techniques and Methods*, 5-D1, p. 5.

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