

FERRIHYDRITE TRANSFORMATION PRODUCTS IN NEAR-SATURATED MARTIAN BRINES K.S.R. Barbre¹, M.E. Elwood Madden, A.S. Elwood Madden, and C.A. Hodges, ¹School of Geosciences, University of Oklahoma, 100 E. Boyd Street, Norman, OK, kaydra.s.barbre-1@ou.edu.

Introduction: Iron cycling is an important function of soil and regolith development, and recent data from Mars orbiter and rover missions shows that Martian soils contain abundant iron oxides and iron-bearing minerals. Our understanding of how Mars mineral assemblages change and develop by aqueous alteration is still poorly understood. *Curiosity* and *Opportunity* detected amorphous iron oxide phases in Gale Crater and Meridiani Planum, notably signs indicative of ferrihydrite and other iron oxide phases that form through aqueous alteration [1]. Aqueous alteration on Mars is possible by the presence and transport of near-saturated brines, including sulfates, chlorides, perchlorates and other salts [2].

Ferrihydrite, a metastable iron oxide phase, is often the first to crystallize during oxidative weathering of iron-bearing minerals and is a precursor to more stable iron oxides such as goethite and hematite. Due to high surface area and poor crystallinity, ferrihydrite transforms to more stable iron oxides relatively quickly in terrestrial environments. However, ferrihydrite stability, as well as other iron oxide formation pathways, are influenced by temperature and the chemistry of the weathering solutions. Since near-saturated brines can exist at the low temperature and vapor pressure conditions present at the surface of Mars [3], including sulfates, chlorides, and perchlorates [2], these brines may affect ferrihydrite stability and subsequent iron oxide phases [4].

Mars brine chemistry differs significantly from Earth. Whereas carbonates and chlorides often dominate surface waters on Earth, sulfates and chlorides brines were active and at some stage the dominant form of surface water on Mars [2, 3]. Only brines with a eutectic point well below that of pure water's freezing point may maintain a liquid state, originating either through deliquescence or large-scale evaporation of Mars' ancient oceans [5, 6].

Here we investigate the effects of anion chemistry and bulk concentration on ferrihydrite stability and transformation products in near-saturated brines.

Materials and Methods: We synthesized 2-line ferrihydrite using a method modified from [4]. We added 1M KOH to 0.1M Fe(NO₃)₃ until pH reached 7-8, then centrifuged to create a thick slurry. We dialyzed the slurry to remove excess electrolytes from the ferrihydrite. For the first batch, we freeze-dried the ferrihydrite, then confirmed the final product with X-Ray Diffraction (XRD) and Raman spectroscopy.

Based on results from our first set of experiments, we synthesized a second batch of ferrihydrite, which we also centrifuged and dialyzed, but did not freeze dry prior to the experiments to prevent clumping and maintain dispersed crystallites.

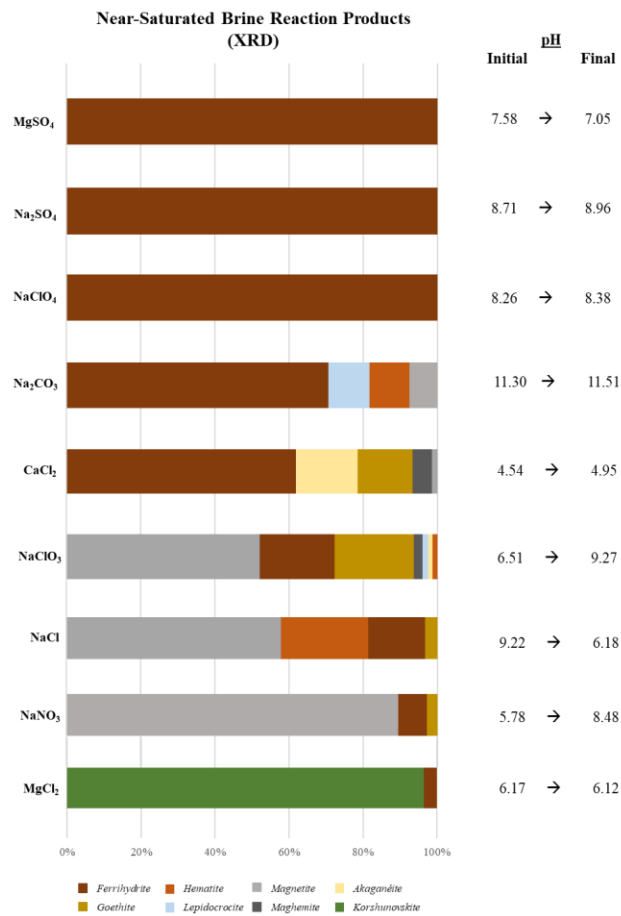
We created NaCl, CaCl₂, MgCl₂, NaNO₃, Na₂SO₄, Na₂CO₃, MgSO₄, NaClO₃, and NaClO₄ near-saturated brine solutions by adding reagent grade salt to 1.5 L of ultra-pure water (UPW) based on the solubility product of each solution. We set aside 250 mL of each near saturated brine, then mixed diluted solutions representing 10% and 50% of the near-saturated form, totaling 28 experimental solutions (three concentrations of nine brines and one ultra-pure water [UPW]). For each experiment, we added 0.25 g of ferrihydrite to each 250 mL solution, then mixed the sealed 250 mL plastic bottles on an incubator stirring station at 20°C for 30 days.

After 30 days, we filtered the solutions via vacuum filtration with 0.45 µm filter paper, then freeze-dried the resulting solids to remove excess water. We analyzed the transformation products using a Rigaku Ultima IV XRD with a Cu tube with a curved graphite post-sample monochromator. To determine changes in the shape and size of the reaction products, we analyzed the solid reaction products with a Thermo Fisher Field-Emission Scanning Electron Microscope (SEM) for secondary electron imaging and Energy Dispersive X-Ray Spectroscopy (EDS). Further analysis of the reaction products from replicate experiments from the second batch of ferrihydrite are underway using the JEOL 2000FX Transmission Electron Microscope (TEM) for high magnification imaging and electron diffraction.

Results: Freeze-drying the ferrihydrite slurry caused significant particle clumping, creating a particle size range of roughly 10 nm – 500 µm. This resulted in difficulty observing other iron oxides phases that may have formed in each solution in TEM and SEM. Ferrihydrite clumps appeared as blocky fragments with sharp, jagged edges. Some smaller sphere-shaped particles in the range of 5-10 nm were observed in the near-saturated solutions of NaCl, Na₂SO₄, and MgSO₄, and 10% saturated solutions of Na₂SO₄ and MgSO₄.

XRD data collected from the reaction products (see Figure 1) indicate that ferrihydrite was preserved in near-saturated MgSO₄, Na₂SO₄, and NaClO₄, with no other iron oxide phases apparent. Ferrihydrite was

Figure 1: Near-saturated brines with their respective XRD reaction product results. Initial and final pH conditions also shown on the right for each experiment.



completely preserved in all concentrations of Na₂SO₄, was increasingly altered in more diluted concentrations of MgSO₄, whereas alteration was observed with no clear pattern across changing concentrations of NaClO₄. Ferrihydrite appeared to be largely preserved in solutions where changes in pH were minimal (± 0.5 or less). Additional iron oxide reactions products were observed in several experiments, including hematite (Fe₂O₃), goethite [α -FeO(OH)], lepidocrocite [γ -FeO(OH)], magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃), and akaganéite [Fe⁺³O(OH,Cl)]. Akaganéite only formed in NaCl and CaCl₂ solutions, and was present in all three concentrations of NaCl, but only in the 10% and near-saturated concentrations of CaCl₂. More ferrihydrite was preserved in the lower concentration NaCl and MgCl₂ experiments, while ferrihydrite preservation did not follow a consistent trend in increasing concentrations from 10% to near-saturated in CaCl₂, NaNO₃, Na₂CO₃, NaClO₃, and NaClO₄. In the MgCl₂ solutions, Mg₂Cl(OH)₃ • 4H₂O (Korshunovskite) was

also observed, with the greatest abundance observed in near-saturated MgCl₂ brine.

Significance and Future Work: Anion chemistry of different brines appears to have a significant impact on the preservation of ferrihydrite and its transformation pathways. Ferrihydrite may be best preserved in near saturated sulfate solutions, and reaction products diversify as concentration of anions decreases in certain brines. As studies show sulfate salts dominate brine chemistry on Mars [2, 5, 6], our results suggests that ferrihydrite may be more stable against dissolution and transformation over a longer period of time on Mars compared to conditions commonly observed on Earth.

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References: [1] Dehouck, E. et al (2017), *JGR*, 122, 358-382. [2] Mianping, Z. et al (2013), *Acta Geologica Sinica - English Edition*, 87, 885-897. [3] Sears, D.W.G. and Chittenden, J. (2005), *Geophysical Research Letters*, 32, L23203. [4] Cornell, R.M. and Schwertmann, U. (2003). [5] Toner, J.D. et al (2014), *Geochimica et Cosmochimica Acta*, 136, 142-168. [6] Möhlmann, D. and Thomson, K. (2010), *Icarus*, 212, 123-130.