**PYRITE WEATHERING IN HYPERSALINE SOLUTIONS.** A. J. Rodriguez\(^1\) and M. Elwood Maden\(^2\), 
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**Introduction:** Understanding the geochemical reactions of pyrite and hypersaline solutions can provide valuable insight into the past and present conditions on terrestrial planets as well as bodies with active hydrothermal vents. Hematite found within sulfate-bearing sedimentary layers on Mars allude to an aqueous system where redox reactions of iron and sulfur play a key role \(^{1-3}\). In addition, the surface of Mars has evidence of high concentrations of salts on the surface where deliquescence is possible in many areas, forming modern near-saturated brines\(^4\).

Here we examine pyrite-brine interactions in laboratory experiments to investigate processes that may have formed iron oxides on Mars in the past and current aqueous activities that may be active today \(^{5,6}\). Our aim is to observe secondary minerals from the reaction of pyrite with brines composed of end-member salts at concentrations near saturation and at one tenth the near-saturated concentration. We also analyzed the liquid reaction products to observe any bulk chemical changes in solution chemistry as well as direct observations of secondary minerals.

**Methods:** Stock solutions of Na-Cl-H\(_2\)O, Na-SO\(_4\)-H\(_2\)O, Mg-Cl-H\(_2\)O, Ca-Cl-H\(_2\)O, and Mg-SO\(_4\)-H\(_2\)O near saturated brines were synthesized from laboratory grade salts. A hand sample of natural pyrite was crushed and micronized, then placed in HDPE reaction bottles containing the solution. The bottles were mixed on a shaker table, with replicate bottles sampled after seven, 14, 30, and 90 days. The solid reaction products were filtered using a 0.22μm Millipore filter and freeze dried to remove any remaining liquid, then placed on a glass slide for Raman analysis using a 785nm LD laser at ~4mW for one minute per location (15 total) using a Renishaw InVia Raman spectrometer and the spectra analyzed with WiRE 4.2 software. The samples were immediately placed in a Rigaku Ultima IV diffractometer for XRD analysis utilizing a Cu-K\(_\alpha\) radiation at 40KV and 44 mA and at scintillating detector. XRD data analysis was completed using MD Jade Pro with the ICDD PDF4+ database. A small amount of the freeze-dried solid sample was re-suspended in methanol then dripped onto a 200-mesh lacey carbon supported Cu TEM grid for transmitted electron microscopy, scanning electron microscopy, and electron diffraction. The liquid fraction was stored in HDPE bottles, with separate fractions used for pH measurements, atomic absorption (AA) analysis, and ICP-OES analysis.

**Results:** Analysis of the liquid samples show an initial pH drop due to pyrite dissolution and iron hydrolysis leading to acidification (Fig.1). AA analysis of the solutes show an increasing trend of Fe release due to pyrite dissolution (Fig. 2).

![Figure 1. pH versus time graph of the 18.2 MΩ H\(_2\)O (UPW), 2.3 wt% Na-Cl-H\(_2\)O, and 23 wt% Na-Cl-H\(_2\)O.](image)

![Figure 2. Fe concentration in solution versus time. Aqueous Fe was preserved and any colloidal precipitates re-dissolved using 0.3M HCl.](image)

The amount of iron in solution indicates pyrite dissolved fastest in ultrapure 18.2 MΩ H\(_2\)O, with similar rates observed in the 2.3 wt% Na-Cl-H\(_2\)O solution. Pyrite dissolution slowed significantly in the hypersaline 23 wt% Na-Cl-H\(_2\)O solution. (Fig. 2).

The solid reaction products show evidence of iron oxides detected in Raman spectroscopy (Fig. 3). The majority of the Raman spectra show evidence of only pyrite and marcasite, which are present in the unreacted control samples. The SEM images of the samples show evidence of pyrite dissolution, and TEM images show secondary minerals found near pyrite crystals (Fig. 4 & 5).

**Discussion:** The concentration of iron in solution as well as the pH change observed in each replicate is correlated to the amount of salt in solution. While there is no evidence to suggest a significant difference in the reaction products between the 18.2 MΩ H\(_2\)O and the 2.3 wt% Na-Cl-H\(_2\)O solutions, the 23 wt% Na-Cl-H\(_2\)O solution shows a significant difference in the pH
attained at the end of the experiment from the other two solutions.

The reaction products observed in the Raman spectra and XRD data show no distinct differences between the three solutions, suggesting that techniques other than XRD and Raman spectroscopy are needed to observe any significant differences in the secondary minerals formed from solutions of varying salt solutions and concentrations, as secondary minerals appear to be in concentrations too low for bulk analysis. Preliminary TEM and SEM have begun to analyze the solid reaction products at the micron to nm scale, including electron diffraction. Such evidence will allow us to further interpret the mineral assemblages observed on modern Mars so as to better understand geochemical conditions and processes in the past.

Figure 3. Raman spectra of hematite from pyrite reacting in 23 wt% Na-Cl-H2O for 30 days collected with a 785nm laser. Hematite is indicated by the peaks at 223, 289, and the small peak near 400 cm⁻¹. Pyrite is indicated by the peaks at 341 and 377 cm⁻¹.

Figure 4. Transmission electron micrograph of pyrite after reacting in 23 wt% Na-Cl-H2O for 30 days. Scale bar is 100nm.

Figure 5. Above) Scanning electron micrograph of a control sample of pyrite. Below) Scanning electron micrograph of pyrite after reacting in 23 wt% Na-Cl-H2O for 30 days. Scale is 100nm at 25 KV accelerating voltage.