

MARS ANALOGOUS BASALT INTERACTION IN NEAR SATURATED BRINES. A. J. Rodriguez¹, M. E. Madden², L. Hunt³. ¹University of Oklahoma, School of Geosciences Andrew.rodriguez@ou.edu), ²University of Oklahoma, School of Geosciences (Melwood@ou.edu). ³University of Oklahoma (lehunt@ou.edu).

Introduction: Understanding the geochemical interaction of near-saturated brines with the surface and subsurface of Mars is imperative for delving into the processes that control secondary mineral formation and nutrient transport. Brines on Mars are a potential driving force for current geochemical alteration on Mars as well as being a possible biome for life.

Basalt has been observed to be common across Mars, including the Southern Highlands [1]. Mars basalt is abundant in olivine and pyroxene, with higher concentrations than those observed in terrestrial basalt. Basalts from the Craters of the Moon National Monument [2] are a good Mars analog, as they are also high in pyroxene, TiO₂, and P₂O₅. Basalt-brine experiments aid interpretations of secondary mineral assemblages observed on Mars. By studying how brines interact with basalt, we can also develop models of nutrient transport that can help us determine the availability of major nutrients necessary for life.

Salts on Mars. Salts such as perchlorates, chlorides, and sulfates have been observed with orbiters to be common and widespread on Mars [3]. Chlorine-bearing salts have been detected at each lander site and have been observed at several locations along the paths of the *Spirit*, *Opportunity* and *Curiosity* rovers. Perchlorate and sulfate salts have been measured to be prevalent in the Martian soil and dust, which have been measured to be mostly homogenous and widespread across the Martian surface.

These salts have the ability to lower the triple point of water to allow liquid to be at or near the Martian surface. Additionally, salts have the ability to deliquesce water vapor from the atmosphere to produce liquid brines at the surface. Such brines are thought to have been directly observed on the Phoenix lander struts [4] and are currently hypothesized as a mechanism for recurring slope lineae [5].

On the surface of Mars, brines may exist as either a thin film on rock surfaces or a few centimeters below the topsoil as evidenced by the Mars Exploration Rovers' tire tracks exposing salts in the near subsurface. Geophysical evidence also suggests a large subsurface "lake" of brine under the Martian South pole [6].

Methodology: This study aims to examine how Mars analog basalt reacts with different near-saturated brines and document the secondary minerals that form during basalt-brine alteration. A sample of vesicular porphyritic basalt from the Grassy Cone eruption event

of the Craters of the Moon National Monument (54.3% of the sample is labradorite, 27.5% forsterite, and 13% hedenbergite, with trace amounts of ilmenite and quartz based on powder X-ray diffraction) was used in the experiments. The basalt was broken into small chips (1-5 mm) and 11 small chips and one larger chip were selected for each of the nine reactors. Each of the larger chips were polished with AlO₂ abrasives to create a near flat surface. The polished chips will be used to obtain a crosscut with a reference line to observe the depth of reaction with few imperfections, cavities, or fractures to obscure wavelength dispersive x-ray spectroscopy (WDS) elemental analysis.

Each reactor contained 100 ml of endmember brine (NaCl, Na₂SO₄, NaClO₄, CaCl₂, MgCl₂, MnSO₄), ultrapure water, or a mixed brine (a 50% mixtures by volume) of Na₂SO₄+NaClO₄ or MgSO₄+MgCl₂. A 10 mL aliquot of each brine was collected before we added the rock samples for baseline pH and Raman analyses. After we added the rock samples, we placed the nine reactor bottles on a shaker table. We collected 7 mL samples of the brines within 24 hours of the beginning of the experiment and measured the pH. Subsequent brine and basalt samples were collected after 1 month, 3 months, 6 months, and 12 months of reaction. At each sampling interval we collected 7 mL of the brine for pH measurement of the solution and Raman analysis and 3 rock chips for scanning electron microscopy and Raman analysis.

We collected the polished chip during the 6 month sampling and both a rough surface and the polished surface using Raman spectroscopy and SEM imaging. We then polished a second surface perpendicular to the initial polished plane to prepare the sample for WDS measurements. WDS analysis will allow us to observe any chemical variations in the rock below the surface that may be related to solution infiltration and chemical weathering.

Results: pH measurements show 8 of the 9 solutions were buffered towards 6.5 after the addition of the basalt. The other solution, CaCl₂, skewed away from 6.5 initially. After 12 months, CaCl₂ was the only brine solution not between pH 5.9-7.1, remaining more acidic.

Raman Spectroscopy: Secondary iron oxide minerals were observed on multiple samples. (fig. 1). These minerals were not observed on the unreacted chips or in the first month collection samples but became more abundant as the experiment continued.

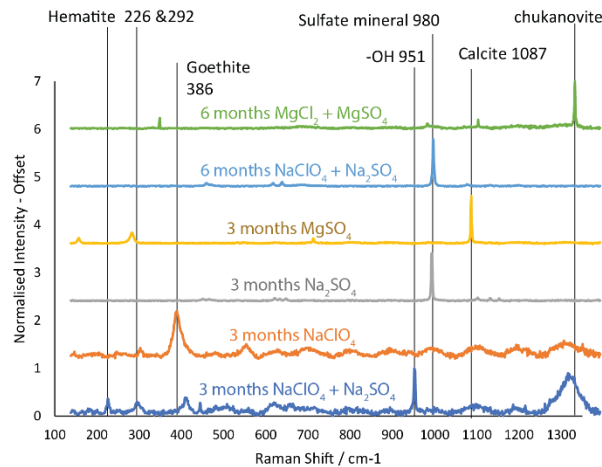


Figure 1: Stacked plot of Raman spectra peaks indicative of iron oxides, sulfates, and carbonate minerals precipitating on chip surfaces.

Scanning Electron Microscopy: Images show evidence of both dissolution of the basalt and precipitation of secondary minerals, likely clays, on the surface (Fig. 2).

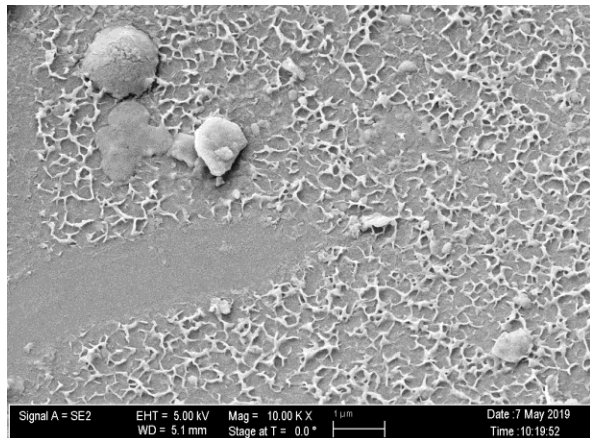


Figure 2: SEM image of basalt reacted with CaCl_2 for 6 months at 10,000X. The corn-flake texture is indicative of clay formation the surface. The area in the center-left without clays may be due to heterogeneity of the surface or sample handling post-experiment.

Results and discussion: The Raman spectrometer is able to detect secondary minerals formed due to the interactions of the basalt in near-saturated brines, even over relatively short periods of duration. As the basalt dissolves in the brine, it releases ions that then reprecipitate as secondary minerals. One spectra of interest is of chukanovite, which was detected in the mixed MgSO_4 and MgCl_2 brine. This mineral is not found in large quantities on Earth and the published properties of this mineral are from synthesized samples

or from terrestrial alteration of iron meteorites [7]. While the initial basalt did not contain carbonate, some CO_2 from the ambient air was trapped in the bottle headspace, providing a potential source of carbon.

This study provides data that will aid the Mars 2020 and the ExoMars missions, as it not only expands our understanding of how high salinity brines may alter rock surfaces on Mars, but also how this alteration may be observed with Raman spectroscopy, instruments available on these rovers. Understanding how near-saturated brines alter and modify the spectra of basalt will aid us in piecing together a fuller understanding of hydrology, geochemistry, and nutrient availability on Mars.

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