

ANOTHER POTENTIAL ROUTE TO MARTIAN JAROSITES: REACTION PRODUCTS OF HYDRATION-DEHYDRATION CYCLING OF FERRIC SULFATE – REGOLITH MIXTURES. E. C. Sklute¹, R. J. Hopkins², R. McKeegan³, M. D. Dyar^{1,4}, A. D. Rogers⁵, and R. L. Clark¹, ¹Planetary Science Institute, 1700 E. Fort Lowell Rd Suite 106, Tucson, AZ 85719; ecsklute@psi.edu, ²University of Massachusetts, Amherst, Dept. of Geoscience, 727 N. Pleasant St. Amherst, MA 01003, ³Amherst College, Dept. of Geology, 220 S. Pleasant St. Amherst, MA 01002, ⁴Mount Holyoke College, Dept. of Astronomy, 50 College St. South Hadley, MA 01075, ⁵Stony Brook University, Dept. of Geoscience, 255 ESS Building, Stony Brook, NY. 11794.

Introduction: The presence of jarosite, an ephemeral salt that precipitates in acidic environments, has been interpreted as evidence for episodes of hydration in Martian history [1-3]. However, new experiments designed to look at the dehydration products of regolith + concentrated ferric sulfate + NaCl brine mixtures have also produced jarosite. Specifically, mixtures of magnesite ($MgCO_3$), halite (NaCl), and anhydrous ferric sulfate ($Fe_2(SO_4)_3$) that have undergone a single hydration-dehydration sequence have been observed to form natrojarosite ($NaFe_3(SO_4)_2(OH)_6$). Thus, grain scale hydration/dehydration cycling could provide another route to jarosite formation across Mars.

Methods: Six regolith-analog starting materials were used in this study: two different magnesite samples (stones Mag(S) and nuggets Mag(N)), gypsum (Gyp), hematite kidney ore (Hem), fresh Hawaii basalt (Bas), and nontronite sample Nau-1 (Non). Each material was prepared in two grain sizes through the combination of shatterboxing, grinding with an agate mortar and pestle, and dry sieving. Anhydrous ferric sulfate (AFS) was prepared by heating ferric sulfate hydrate at 350°C for 2 h. For each experiment, 0.5 g of AFS was mixed with 0.5 g of one of the regolith analogues. A duplicate of each binary mixture was also made to which 0.5 g of NaCl was added. All mixtures were placed in separate sealed containers buffered to 92% RH using DI water for 4 days, after which each sample was dehydrated for 4 days at 11% RH in an individual LiCl-buffered container. Samples were analyzed at the end of the hydration-dehydration cycle using Raman, Fourier Transform attenuated total reflectance, and visible and near infrared spectroscopies.

Samples were then kept in 11% RH and monitored for 2.5 months, at which time they were analyzed by x-ray diffraction (XRD) using Rigaku Smartlab II SE x-ray diffractometer. All samples were loaded under ambient conditions onto a zero background sample holder and analyzed in Bragg-Brentano geometry with Cu K α radiation. Samples were photographed before and after XRD to qualitatively monitor hydration. However, no changes were observed in any of the samples.

Results: XRD results show baseline swell in all

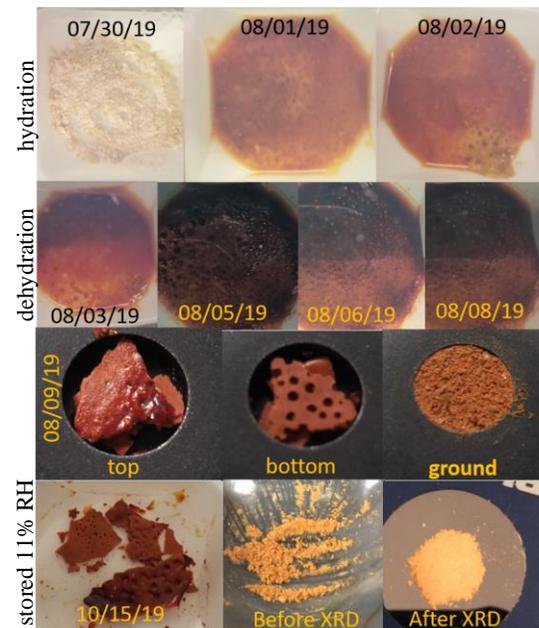


Figure 1. Hydration-dehydration and analysis cycle of AFS with Mag(S) 25-63 μ m.

cases and do not have sufficient crystalline phases to account for the ferric sulfate in the starting material.

Figure 1 follows the hydration-dehydration and analysis cycle of AFS with 25-63 μ m Mag(S) and **Figure 2** follows that of AFS with Mag(S) and NaCl. XRD results for Mag(S) + AFS (**Fig 3**) show magnesite, iron hydroxide sulfate ($FeSO_4(OH)$), gypsum, and a small amount of quartz that was present in the original sample. The iron hydroxide sulfate, a.k.a. basic ferric sulfate (BFS) [4], is present in the AFS prior to hydration but is not seen in the XRD of the hydrated-dehydrated AFS alone, indicating it is a phase that dissolves and reforms under certain conditions. Gypsum is present in reacted Mag(S) but not in reacted Mag(N) and correlates with a dolomite contamination in Mag(S). XRD results for Mag(S) + AFS + NaCl (**Fig 3**) show magnesite, quartz, gypsum, natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), and possibly a very small amount of siderite ($FeCO_3$). Slightly more natrojarosite forms from the finer-grained sample. **Figure 4** displays the baseline swell common to all regolith mixtures, compares it with two mixed salt samples

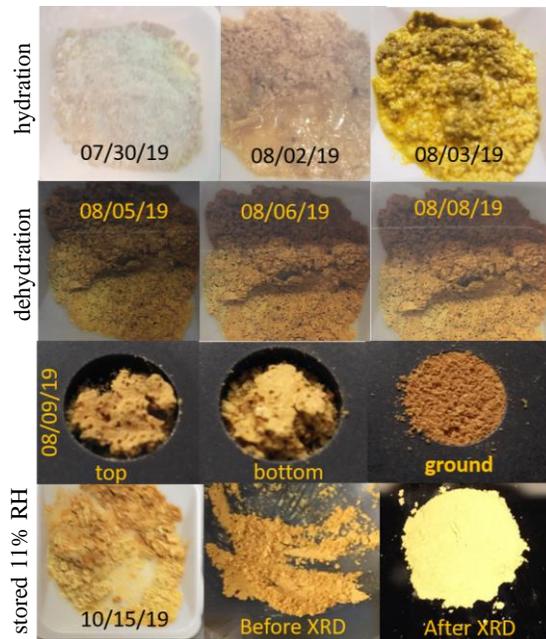


Figure 2. Hydration-dehydration and analysis cycle of AFS with Mag(N) 25-63 μm and NaCl.

from [5], and highlights the BFS to natrojarosite transition with the addition of NaCl.

Gyp + AFS only displayed peaks of gypsum with minor BFS. When NaCl was also added, some of the BFS may have converted to natrojarosite, though the spectrum is dominated by gypsum and NaCl. Hem + AFS XRD patterns match with a combination of protohematite, quartz (impurity in Hem), and BFS. The addition of NaCl to this mixture adds NaCl to the XRD pattern but does not change any of the other phases.

Bas and Non samples are difficult to interpret because the starting materials are also largely XRD amorphous and match poorly with XRD database phases. Comparison of starting and reacted materials shows that Bas + AFS only displayed additional peaks for BFS. Samples with NaCl show many more peaks than those without NaCl. The Smartlab software matches these to butlerite and metasideronatrite. Closer examination of patterns and Raman results calls these matches into question, but no other suitable matches could be found in any database. Non + AFS samples only display peaks for Non and BFS. Non + AFS + NaCl samples show additional peaks that can be partially matched to sodium sulfate. More work is needed to clarify these results.

Conclusions: Regolith materials reacted with concentrated ferric sulfate solutions and rapidly dehydrated form amorphous ferric sulfate coated regolith along with several accessory phases. When Mag and NaCl are in the starting materials, natrojarosite can form. NaCl without Mag forms an amorphous solid [5].

Additional Information: Additional results can be

found in abstracts 1684 and 2051: Follow the project at <https://www.lionsandlamms.com/>

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References: [1] McLennan, S. M. et al. (2005) *Earth Planet. Sci. Lett.*, 240, 95-121. [2] Elwood Madden, M. E. et al. (2009) *Geol.*, 37, 635-638. [3] Pritchett, B. N. et al. (2012) *Earth Planet. Sci. Lett.*, 357-358, 327-336. [4] Gomez et al. (2013) *RSC Adv.*, 3, 16840-16849. [5] Sklute, E. C. et al. (2018) *JGR Planet.*, 302, 285-295.

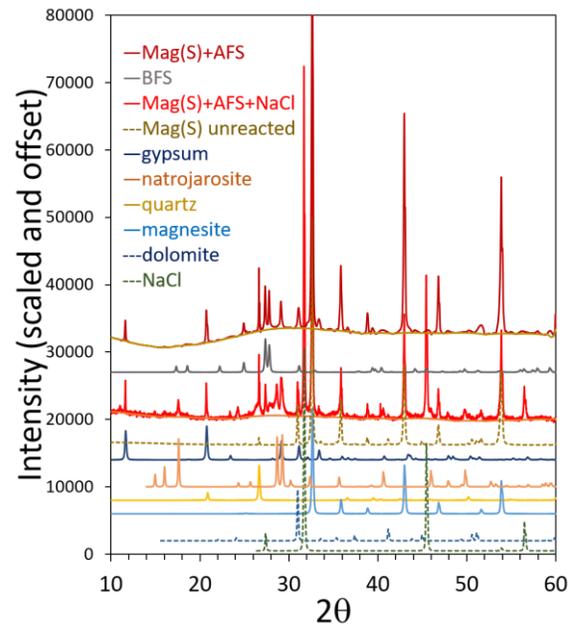


Figure 3. XRD of Mag(S) 25-63 μm experiments along with reference patterns from the Match! COD database. Dashed lines indicate starting materials.

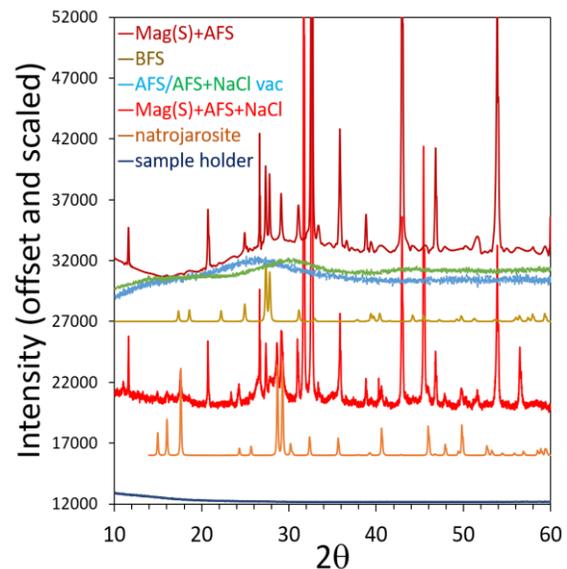


Figure 4. Expanded view of Mag(S) 25-63 μm experiment XRD patterns showing baseline swell, two amorphous phases from [5] and the sample holder.