CHEMICAL AND SPECTRAL PROPERTIES OF IRON-SULFATE ACID SOLUTIONS THROUGH A HYDRATION/DEHYDRATION CYCLE: IMPLICATIONS FOR THE MARTIAN REGOLITH.

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Introduction: With the continuing influx of Mars Science Laboratory Curiosity data and Mars Perseverance 2020 data on the horizon, it is increasingly necessary to characterize mixed Martian regolith spectra. Specifically, the consistent findings of high weight percentages of as yet unidentified amorphous material in the Martian sediment creates a need to understand geochemical processes associated with the formation of amorphous phases [1]. In this study, we add representative Martian regolith materials and sodium chloride (NaCl) in equal dry mass ratios to anhydrous ferric sulfate, (Mikasaite), which forms an amorphous film after a hydration/dehydration cycle [2].

Methods: Gypsum (Gyp), forsterite (Fo90), and magnesite (Mag) were chosen as representative Martian regolith minerals because they have been definitively identified on Mars, and so that sulfate, silicate, and carbonate were all covered in the composition space of these experiments [3,4,5]. Mixtures were made with 0.5g of one of these three minerals, 0.5g of Mikasaite, and 0.5g of NaCl. Mixtures were deliquesced to saturation at 92% relative humidity (RH), and then rapidly dehydrated at 11% RH (RH maintained by DI water and LiCl buffering salt, respectively). Mixtures were prepared at specific grain sizes ($<25\mu m$, 25-63μm, and 63-180μm), however, grain size did not appear as a significant factor in the final spectra. The materials, resulting from one such hydration/dehydration cycle, were analyzed with x-ray diffraction (Rikagu Smartlab II, 10-60 2θ, CuKα, 0.01° step sampling 3°/min), Fourier-transform infrared (Bruker Alpha FTIR-diamond ATR, 360-4000 cm^{-1}, 4 cm^{-1} spectral resolution, KBr beam-splitter, Merz phase correction, Norton-Beer Strong Apodization, 128 scans), and visible to near-infrared (VNIR; ASD Fieldspec 4, 30° incidence, 0° emission, average of 100 1s integrations) spectroscopies. Resulting spectra were compared to spectra of potential mineral products. Additional samples were made to measure the pH of the mixture solutions during deliquescence, using an Apera Instruments PH60 Flat pH Tester.

Results: For these experiments, two trends are apparent: inclusion of NaCl in the starting sample mixture leads to a substantially more complex final spectrum, and the dissolution of NaCl in the mixture significantly reduces the pH of the solution. It is clear from XRD analysis, as well as VNIR and FTIR spectra (Figures 1 and 3), that sideronatrite is a likely product of the gypsum, mikasaite, and NaCl mixtures. VNIR and FTIR spectra of these mixtures are also consistent with containing amarantite and butlerite. XRD analysis indicates natrojarosite is likely present in the magnesite, mikasaite, and NaCl mixtures. Spectrally, natrojarosite is also a good match, specifically in regions associated with Fe-O and Fe^{3+} bonding, as well as in the hydration features. The sulfate energetic environment, however, seems to differ, indicating a related but distinct structure or (more likely) the admixture of an additional sulfate phase, like amorphous ferric sulfate. From XRD identification and spectral comparison, hexahydrite is plausible in the magnesite, mikasaite, NaCl mixtures. However, hexahydrite is a simple hydrated magnesium sulfate, and many other minerals would have a similar spectral signature (e.g. epsomite). The identification of these minerals on Mars may indicate a past aqueous Martian environment that was both acidic and saline.

From FTIR analysis alone, natrojarosite is also a likely product of the forsterite, mikasaite, and NaCl mixtures (Figure 2). Olivine is extensively abundant on the surface of Mars [3], so this connection between natrojarosite and forsterite has important implications for the formation of jarosite found on Mars [6]. It is also significant that natrojarosite is a likely product of both the forsterite and magnesite saline mixtures. Olivine is readily dissolved from acidic chemical weathering on both Earth and Mars, and the fluids associated with the acidic weathering of olivine would be enriched with the elements found in olivine [7]. From the dissolution of forsterite, these species would include aqueous Mg^{2+} and aqueous $Si(OH)_4$ [8]. This aqueous Mg^{2+} could react with dissolved atmospheric CO_2 to form magnesite [9]. Aqueous species consistent with dissolved magnesite may have also formed in the forsterite sample mixtures. Within the hydration times in this study (10 days), Mg^{2+} is quickly removed from the surface layers of forsterite and dissolved into solution at pH values around and less than 3 [10]. In our samples, with a pH around 2, a significant amount of Mg^{2+} would have leached from the forsterite into the concentrated solution during deliquescence. With dissolved Mg^{2+} in solution along with Na^+, Cl^-, Fe^{3+}, and sulfuric acid, the compositions of the forsterite and magnesite solutions would be similar after reaching saturation. The evaporation of a Fe- and Mg-rich fluid under low-pH Martian conditions results in the formation of Fe- and Mg-sulfates and Fe-oxides [11], whose combined features are consistent

with the final products of both forsterite and magnesite saline mixtures, including natrojarosite. Natrojarosite was identified by XRD for the magnesite mixture, and the magnesite and forsterite mixtures spectral similarities lead us to conclude it is present in the forsterite mixture as well. Further studies would take spectra from a wider range of forsterite mixtures.

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Figure 2. Full FTIR spectrum of the Fo90-Mik-NaCl mixture product compared to that of natrojarosite, taken from the RRUFF database.
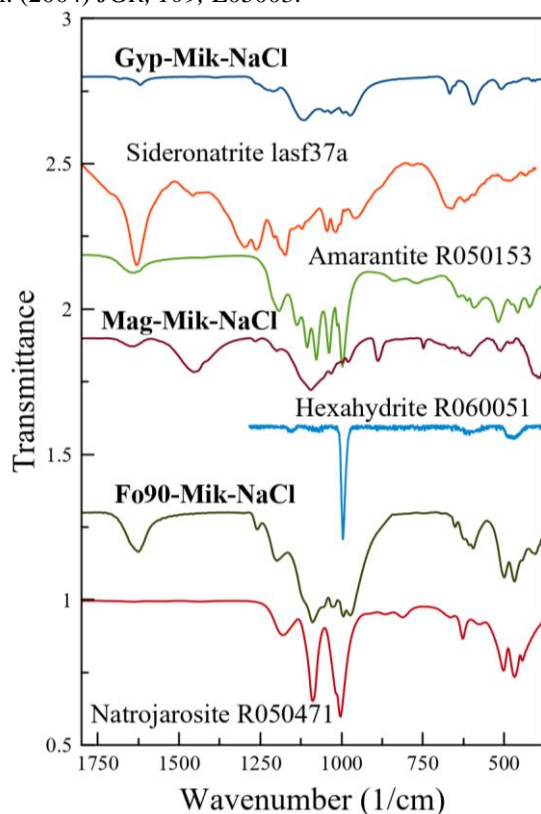

Figure 1. FTIR spectra of experimental mixture products (bold) compared to potential components. The R###### refers to the RRUFF database. The Sideronatrite was taken from the RELAB database. Spectra are staggered for clarity.
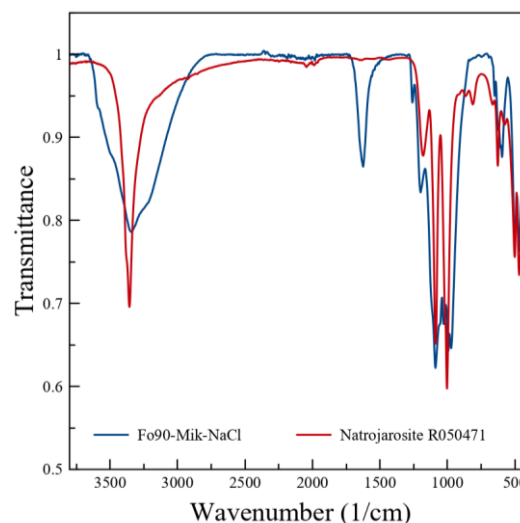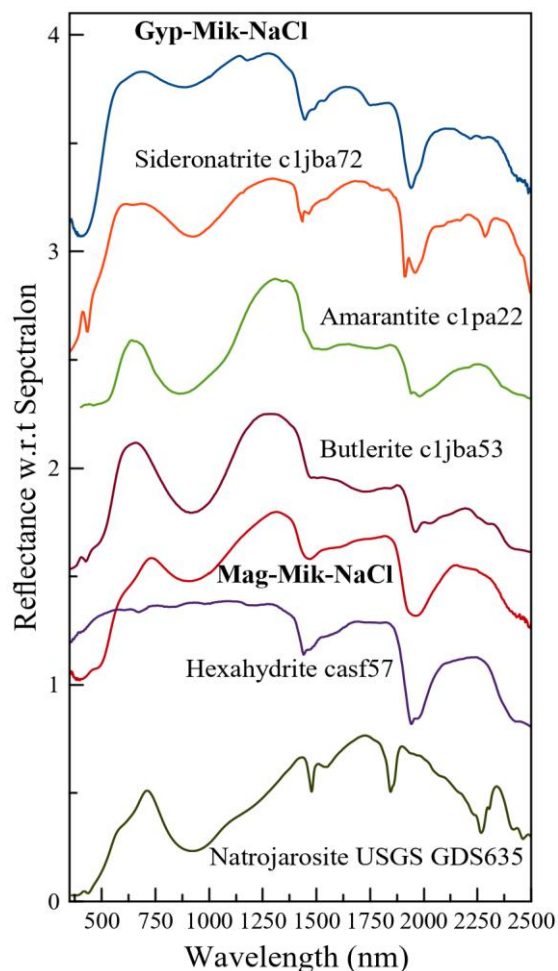

Figure 3. VNIR spectra of gypsum and magnesite experimental mixtures (bold) compared with potential mineral products from RELAB and USGS. Spectra are staggered for clarity.