Laboratory Simulations of Potential Martian Evaporites and their Spectral Signatures.

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Introduction: Evaporite deposits, including chlorides, sulfates, and carbonates, have been detected on the surface of Mars remotely [1]. Evaporite salts both indicate the presence of water and can provide clues to their formation and environmental conditions [2]. Briny solutions have been proposed to explain past evaporite deposits [3], and several studies have previously examined those briny solutions most likely to have formed under past Martian conditions [4-7]. Brines have also been invoked to explain geologically recent surface flow features and previous work has suggested brines which would be metastable within the present-day Martian surface or subsurface [8-10]. However, to date, no evaporites have been detected in association with these features [11].

In this study, we create previously proposed theoretical Martian brines, and evaporate them under monitored conditions. We analyze the constituent salts using a variety of techniques including visible and near-infrared (VNIR) spectroscopy. The bulk VNIR spectra of each complex brine was examined to determine the influence of the constituent salts on the spectra, and to constrain the minimum threshold for detection both of mineral groups and specific minerals.

Methods: Solutions were chosen from previously proposed, theoretical Martian brines to represent diverse potential compositions [6, 12-14]. Where necessary, those brines which were too dilute to be feasible for our experiment were modeled in FREZCHEM [6] to the appropriate concentrations. These brines were evaporated within a fume hood under monitored "Earth" conditions (20-22°C, 30-45% humidity). A portion of the precipitates were placed within a desiccator to control humidity, and any mineralogical changes were noted. Precipitates were analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM), and VNIR (350 - 2500nm) spectroscopy.

Preliminary Results: Eight brines are reported here (Fig 1). Two brines (ASW and TB) have salinity levels similar to terrestrial seawater, the other six have ionic strengths 2-3x higher. ASW is an artificial terrestrial seawater [14], MB1 and MB2 represent two stages in a model for Martian water that does not involve a reintroduction of iron [6], TB is a previously experimentally evaporated brine derived from the acid-fog model for water interaction [12], and TH1-6 were brines modeled down from equivalent starting cation proportions but trending from strongly alkaline to strongly sulfate dominated [13]. Those brines with highest ionic strength, particularly those with highly soluble initial chemistries, produced copious amounts of microcrystalline and amorphous salts, while the more dilute compositions (ASW and TB) produced predominantly crystalline precipitates.

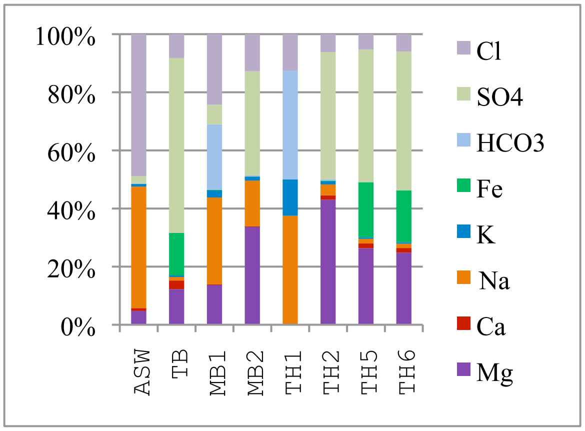

Fig. 1. Ratioed major consituent ion starting chemistry for the eight reported brines.

All brines produced halides detectable with either SEM or XRD. In the brines with small amounts of chloride, crystalline halite (NaCl) was produced, with chloride as the limiting ion. Brine ASW precipitates were dominated volumetrically by halite, >80% by volume, and TH1 had >20% by volume sylvite (KCl). Brine MB2 also had a signficant volume of halite, >10%. Neither halite nor sylvite have distinct VNIR absorptions outside of the ~1.4µm and 1.9µm water absorptions (Fig. 2) and, despite their prevalence in a few brines, were undetectable spectrally. Halite did, however, appear to brighten the spectra overall when present in significant quantities. An amorphous Mg chloride was identified by the SEM in ASW. The spectrum exhibited 1.0, 1.22, 1.46, and 1.94 µm absorptions consistent with bischofite ($MgCl_2•6H_2O$), but these absorptions could also have been caused by magnesium or calcium sulfates. A broad 1.77 µm feature in ASW could be a combined absorption of bischofite and/or gypsum ($CaSO_4•2H_2O$).

Bicarbonate was a constituent ion in a majority of the brines, but was dominant in MB1 and TH1, and carbonate minerals were only detected in the precipitate salts of these two brines. TH1's most prevalent constituent mineral was trona ($Na_3(CO_3)(HCO_3)•2H_2O$), identified by a 1.24 µm and a 1.52µm absorption, as well as a 1.95 and 2.05µm doublet absorption in the spectra. Brine MB1's spectral signature was dominated by its most prevalent constituent salt outside of the halides, the magnesium carbonate, nesquehonite ($Mg(HCO_3)(OH)\bullet 2H_2O$), uniquely identified by doublet absorptions at 1.18 and 1.23 µm as well as 1.43 and 1.49 µm. Both trona and nesquehonite were confirmed by XRD and SEM analysis.

The primary anion in the majority of the brines tested was sulfate. In all brines with calcium and sulfate, regardless of sulfate concentration, crystalline gypsum formed. With the exception of the possible aforementioned 1.77 µm absorption in ASW however, gypsum was not detected spectrally. Gypsum is calculated to be present in quatities of ≤10% by volume. Brine TH2 and MB2 had little to no iron, and their spectra were dominated by 1.0, 1.23, 1.46, and 1.94 µm absorptions consistent with epsomite ($MgSO_4 \bullet 7H_2O$). In MB1, an amorphous hydrated sulfate detected in the SEM may explain the spectral slope between 1.5 and 1.9 µm.

Broad absorptions at 0.9 and 1.2µm are seen in TH5, TH6 and TB, associated with hydrated ferrous iron sulfates [15]. SEM analysis confirmed a magnesium and iron-bearing hydrated sulfate as the dominant precipitate of TH5, TH6, and TB (largely amorphous in TH5 and TH6). Flattening of the spectra around 2.2µm for both TH5 and TH6 is more representative of hydrated magnesium sulfates and could also be produced by this iron-magnesium sulfate. Ferric iron absorptions between 0.4 and 0.65µm were detected in TH2, TH5, TH6, and TB and could be associated with iron sulfates or iron oxides, though no iron oxides were detected in either SEM or XRD analysis. For TH2, no iron precipitates of any type were detected by XRD or SEM analysis; iron precipitates are calculated to represent <0.5% of the sample by volume.

Discussion: We find that VNIR spectra represent constituent salts to varying degrees. The halides produced in this study (halite and sylvite) were undetectable in the spectra even when volumetrically significant, due to lack of unique absorption features in the VNIR. The carbonates that were produced in this study, nesquehonite and trona, were precipitated in high abundance (>20% and ~70% by volume, respectively), and were readily detectable by their VNIR signatures. Iron, when present with magnesium and sulfate as major ions, formed mixed iron and magnesium-bearing hydrated sulfates, which had been previously identified in evaporations of the TB solution [12]. The spectral signature of these sulfates does not exactly match either the iron-bearing or magnesium-bearing endmembers, though ferrous absorptions are evident in each case. Ferric iron absorptions are detectable for oxides/sulfates present at trace levels in each of the iron-bearing samples. This substantiates the dominance of iron-bearing species in VNIR spectra even at small volumes. Amorphous and microcrystalline materials (primarily sulfates) are common and volumetrically significant in those brines with high ionic strengths; these may contribute to broad spectral features consistent with hydrous sulfates in some samples. The amorphous materials, always the later sequence salts in evaporation, are likely a result of the speed of evaporation. This should be considered with regard to Mars, particularly as it relates to high salinity solutions with episodic, short-lived occurrences.

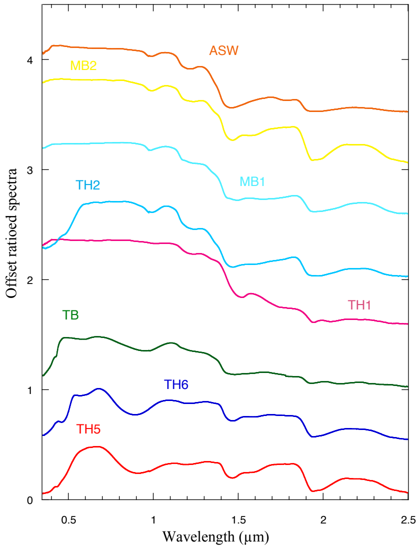

Fig. 2. Ratioed VNIR (350-2500nm) spectra of precipitates from eight reported brines.

Continuing Work: Tests to determine volatile loss are underway, and surface modal mineralogy is being estimated by SEM/EDS X-ray mapping. In addition, the brines are currently being evaporated under simulated Martian conditions, and will undergo similar analysis.

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