

Modeling and Mineralogical Analyses of Potential Martian Chloride Brines. P. E. Martin, M. S. Gilmore, and J. P. Greenwood, Dept. of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459 (pemartin@wesleyan.edu)

Introduction: The discovery of salts in the Viking soils prompted investigation into the stability and composition of theoretical martian brines [e.g., 1, 2]. Such brines may be metastable on modern Mars and have been invoked in the formation of modern fluvial features on Mars such as gullies and slope lineae [3-5]. The evaporation of such brines should result in the formation of mineral deposits that could potentially be recognized in visible-near-infrared (VNIR) spectra collected by the CRISM instrument on the Mars Reconnaissance Orbiter, although this has not yet occurred [3]. In this work, we measure the VNIR spectra of analogue chloride-rich martian evaporite assemblages in an attempt to better understand which minerals are detectable using CRISM and how well VNIR spectra represent the assemblages.

Methods: We selected fourteen chloride-rich compositions from the literature to represent a wide range chemistries [1, 6-12]. These brine recipes were concentrated using the program FREZCHEM 9.2 [6] to both model further evaporation of the theoretical brines and create a solution of a reasonable volume for evaporation in the lab. In the model, we allowed each solution to concentrate until the final iteration before the last liquid water evaporated; if the solution did not fully evaporate in the model, the final iteration, assuming an ionic strength of >3.0, was used as the brine composition. If the ionic strength was still low, the output of the final iteration was run through FREZCHEM again, creating a satisfactorily concentrated brine.

The concentrated model compositions were then created in the lab by adding the proper stoichiometric amounts of salts to double distilled water and are shown in Fig. 1. MKS and KS are both artificially created seawater [6, 12]. MKC, CV1, CV2, CV3, CAM, and CMM are brine compositions that are based on dissolution of ultramafic rocks to create aqueous solutions, which are then slightly altered to better match the modal surface composition of Mars [1, 6-7]. TPR and CLM are brines based on data from Phoenix and the Mars exploration rovers, respectively [8, 10]. SDJ is the composition of Don Juan Pond in Antarctica, which serves as a terrestrial analogue for potential highly concentrated brines on Mars in an environment with a similar temperature regime [11]. TB1, TB2, and TB5 were modeled from the same starting material, and reflect a range in alkalinity by varying the amount of sulfate and bicarbonate [9]. All brines were allowed to evaporate in a hood under normal laboratory conditions (~20-23°C and 15-40% humidity). After evaporation was completed, the resultant minerals were examined using X-ray diffraction (XRD) and VNIR (0.35-2.5 μm) spectra collected by an ASD FR spectrometer.

Results: The evaporation of the brines generally took place over a two to five week period, which depended on the concentration of the brine and its composition (i.e. more deliquescent solutions took more time). CLM, and SDJ remained in solution and were not analyzed further. TPR did not fully evaporate, but crystals formed, and these were harvested and put in a dessicator for analysis. Many samples (MKS, KS, TB1, TPR, TB5, CV2, CV3) contained residual water, possibly due to deliquescence. MKS, KS, and TB1 were analyzed with the water still present, while TPR, TB5, CV2, and CV3, were placed in a dessicator to facilitate evaporation before analysis.

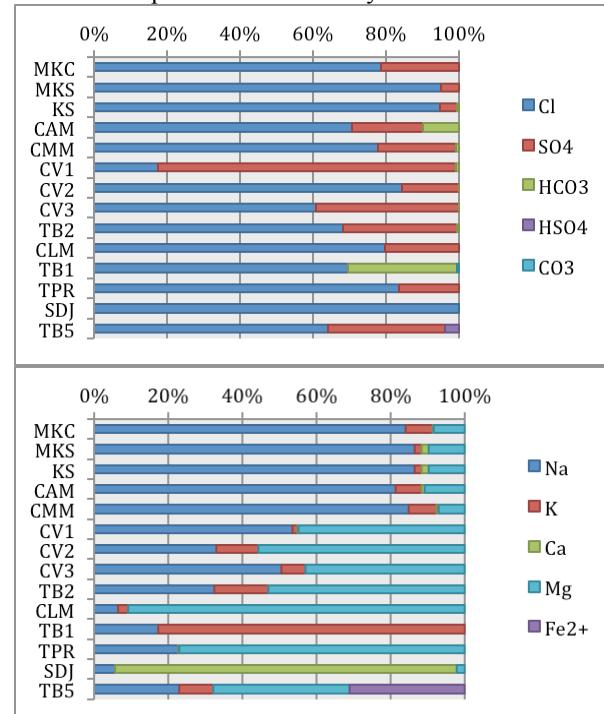


Fig. 1: Ratioed ion concentrations for all fourteen brines created in this experiment.

XRD analyses showed halite (NaCl) in each of the twelve analyzed samples with the exception of TB1 and TB5. In fact, halite was the only recognized XRD pattern in several samples: MKC, MKS, KS, CAM, and CMM. Sylvite (KCl) was identified in TB1. TB5 also had a unique halide: kremersite ($K_2FeCl_5 \cdot H_2O$).

The other minerals identified in XRD were sulfates, with hexahydrite ($MgSO_4 \cdot 6H_2O$) appearing in CV1, CV3, and TB2. Pentahydrite ($MgSO_4 \cdot 5H_2O$) was measured in TPR and bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$)

was present in CV1. Picromerite ($K_2Mg(SO_4)_2 \cdot 6H_2O$) may have been present in MKC, but the pattern was not strong enough for a positive identification of this mineral.

TB1 had characteristic peaks of both natron ($Na_2CO_3 \cdot 10H_2O$) and trona ($Na_3(CO_3)(HCO_3) \cdot 2H_2O$). However, like the picromerite, the peaks were weak.

In the VNIR spectra, all of the samples exhibited absorptions at around 1.0, 1.2, 1.4, and 1.9 μm , which we attribute to water and/or hydroxyl in all samples (Fig. 2). Although halite is dominant in the XRD patterns, it has no notable features in the VNIR [13] and cannot be detected in the data.

The spectra of 4 samples (MKC, CAM, CMM, CV1) are characterized by broad overlapping absorptions at ~ 1.50 and $\sim 1.65 \mu m$. These features can be attributed to epsomite ($MgSO_4 \cdot 7H_2O$) or picromerite, although the shape of the $1.9 \mu m$ feature also suggests some contribution of bloedite or leonite ($K_2Mg(SO_4)_2 \cdot 4H_2O$). Picromerite, bloedite, and hexadrite were measured by XRD.

The spectra of samples KS, TB2, MKS, and CV2 have a absorption centered at $1.76 - 1.80 \mu m$. This feature is present in a number of hydrated chloride minerals, including antarcticite ($CaCl_2 \cdot 6H_2O$), $CaCl_2 \cdot 4H_2O$, sinjarite ($CaCl_2 \cdot 2H_2O$), carnalite ($KMgCl_3 \cdot 6H_2O$), kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$) and bischofite ($MgCl_2 \cdot 6H_2O$). Because Ca is in minute quantities or absent in these brines, bischofite and kainite are the more likely candidate minerals. TB2 has an additional absorption at $1.54 \mu m$ that matches well to mirabilite ($NaSO_4 \cdot 10H_2O$). None of these minerals were identified by XRD.

TB1 has an absorption at $1.50 \mu m$ we attribute to natron. The shape of the 1.94 and $1.74 \mu m$ feature is best matched by trona. A small absorption at $1.66 \mu m$ is consistent with sylvite. Each of these were identified by XRD.

CV3 and TPR have an absorption at 1.61 and $1.53 \mu m$, respectively. This feature may be attributed to hexahydrite or pentahydrite, both of which were identified in XRD. A feature at ~ 1.8 micron in each of these may be attributed to a hydrated chloride or sulfate, as above. This feature is also present in TB5 which has absorptions at 0.49 , 0.63 and $0.92 \mu m$ consistent with a number of iron-bearing sulfates. Although kremersite was identified in this sample, we could find no VNIR spectrum of this mineral for comparison.

Discussion: Many of the minerals predicted to form from these brines [e.g., 9] were not observed in XRD. This may be due to: 1. the evaporites formed as amorphous salts and/or 2. there are so many distinct minerals in each sample that only the main peak of each appears unless the mineral is volumetrically significant. The second scenario is believed to be the more likely of the two, since volumetrically significant

minerals (such as halite in samples where $>80\%$ of the ions were Na and Cl) do appear in the XRD patterns. We will verify this with modal mineralogy in the SEM.

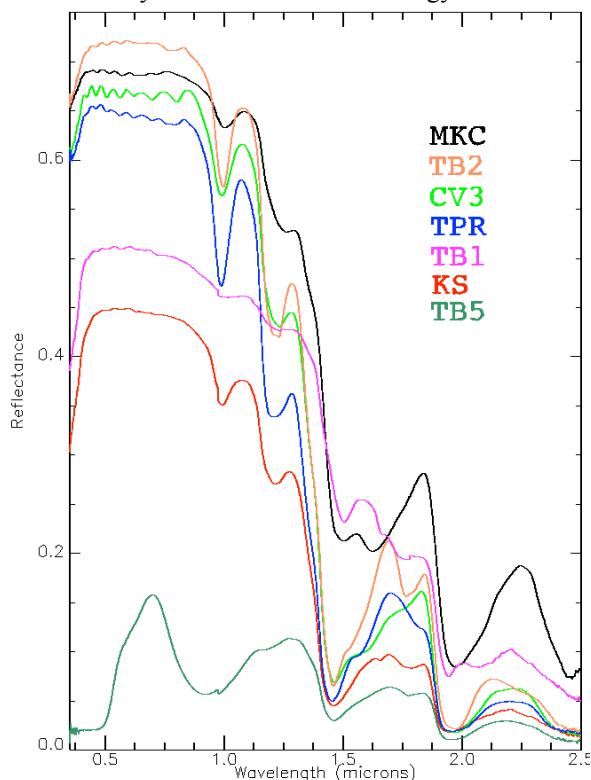


Fig. 2: Reflectance spectra of representative mineral assemblages evapoated from the brines in Fig. 1.

Although anhydrous halides dominate these samples, their weak spectral features preclude their positive identification through VNIR. However, hydrated chlorides, sulfates and carbonates are recognized in these brines by features over the $1.6 - 1.8 \mu m$. These minerals may be expected deposits from these very concentrated chlorine-rich brines.

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