Modeling and Analysis of Potential Martian Chloride Brines

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Background and Methods

Brines depress the freezing point and may allow liquid water to exist at Mars temperatures [1]. Recent modeling efforts have made attempts to understand the possible chemical nature of these brines [e.g., 2]. The discovery of chloride [3] other evaporate deposits on the surface of Mars [e.g., 4] has led to investigation into whether the evaporites resulting from these brines could be detected spectrally. **This study models various theoretical compositions of potential martian chloride brines, creates and evaporates them and determines the mineralogy using XRD, SEM/EDS and VNIR reflectance spectra.** These spectra can be used to better interpret CRISM data.

A broad literature survey was conducted to find theoretical compositions based on a range of sources: modeling data, rover and lander data, and Earth analogues (Figure 1). Where appropriate, these brines were modeled to higher concentration using the program FREZCHEM [5] under Earth conditions. The compositions were modeled to dryness to predict mineralogy and physically created in the lab by addition of salts to deionized water. These brines were allowed to evaporate in the fume hood, and were then examined using VNIR, XRD and SEM/EDS to determine mineralogy.

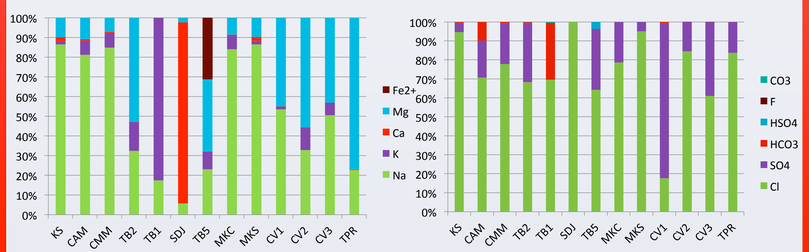

Figure 1: The composition of brines in this study by cation and anion

Red = found in XRD, blue found in VNIR, purple = found in both

Spectral Group 3- Mg/Na, Cl/SO_4 brines

- Group 3 consists of TPR [6] and CV3 [7]
- Modeling predicts (in descending order of abundance): halite (NaCl), pentahydrite ($MgSO_4 \cdot 5H_2O$), bischofite ($MgCl_2 \cdot 6H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$), espomite ($MgSO_4 \cdot 7H_2O$)
- Spectrum includes a shoulder at approximately 1.55 µm, explained by either pentahydrite/hexahydrite/epsomite or bischofite. Bischofite has other absorptions at ~1.0, 1.2, 1.4, 1.75, and 1.9 µm seen in this group.
- Bischofite was identified in both samples using XRD, while pentahydrite was observed in TPR and both hexahydrite and epsomite were seen in CV3.
- SEM/EDS was run on TPR. Various interlocking crystals and amorphous material composed of magnesium sulfate and magnesium chloride was apparent.

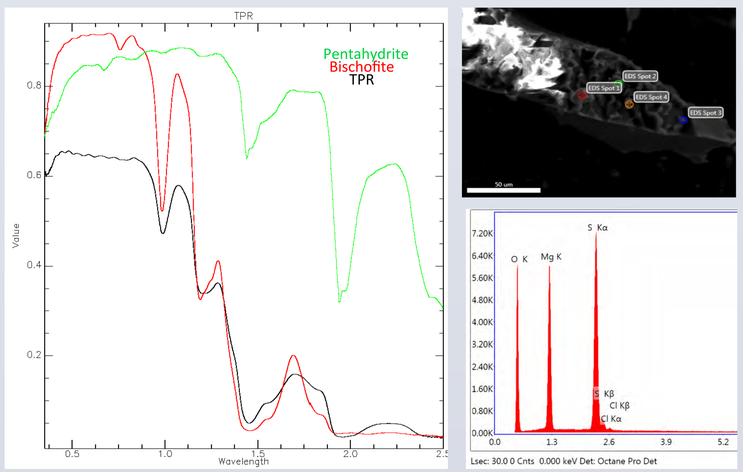

Figure 4: VNIR and EDS analyses of TPR. Left is the VNIR spectrum of TPR with candidate mineral spectra. Top right is an SEM image of a large magnesium sulfate crystal, and lower right is the EDS point analysis of spot 1.

Spectral Group 1- Na/Mg/K, Cl/SO_4 Brines

- Group 1 contains CMM [8], CAM [8], MKC [5], and CV1 [7]. Modeling predicts: halite, thenardite (Na_2SO_4), hexahydrite, bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$), epsomite, picromerite ($K_2Mg(SO_4)_2 \cdot 6H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), aphthitalite ($(K,Na)_3Na(SO_4)_2$, loewite $Na_{12}Mg_7(SO_4)_{13} \cdot 15H_2O$, magnesite ($MgCO_3$), sylvite (KCl).
- Spectral features are almost entirely explained by picromerite (spectrum in [9]) and/or epsomite. Bloedite explains the 1.9 µm feature. CV1, with a lower K concentration, appears more like epsomite spectrally.
- Hexahydrite was also seen in the XRD may have been epsomite prior to dehydration by the x-rays. Picromerite, Bloedite, and hydrous magnesium chloride were all consistent with EDS spot analyses.

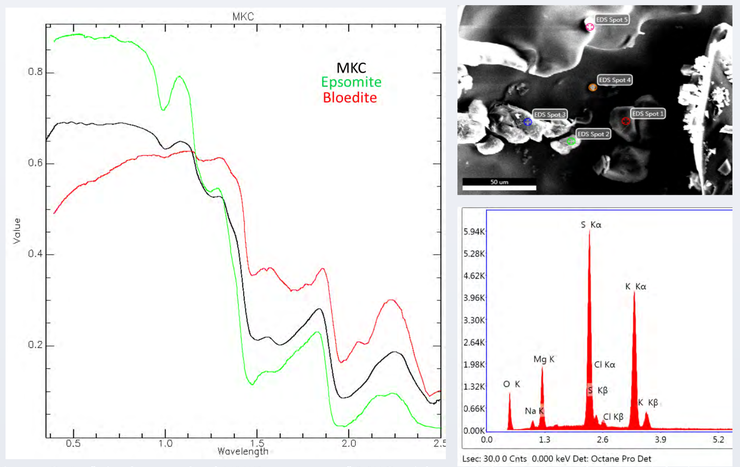

Figure 2: Left is the stacked VNIR spectra of MKC with candidate minerals. Top right is an SEM image of mixed mineralogy, and lower right is the EDS point analysis of spot 1, a likely picromerite crystal.

Brines with unique Spectra

- Several brines could not be grouped spectrally. These were: TB1 (a carbonate brine, [10]), TB5 (an iron brine [10]), and SDJ (a calcium brine [11] recipe for Don Juan Pond, Antarctica).
- TB1 contained trona ($Na_3(CO_3)(HCO_3) \cdot 2H_2O$) and picromerite in the VNIR spectrum, and halite (NaCl) in XRD. Trona dominated the spectrum. Sylvite, trona, kalicinite were predicted by the model.
- TB5 was modeled to precipitate epsomite, ferrous chloride tetrahydrate, bischofite, melanterite, halite and matteuccite. None of these were identified through XRD; we suspect the spectrum is that of $FeCl \cdot 4H_2O$. EDS showed amorphous solids of varied composition.
- Antarcticite ($CaCl_2 \cdot 6H_2O$) and halite were predicted in the model for SDJ and antarcticite was the only mineral identified in XRD. Calcium chloride is so deliquescent that the sample was very wet, leading to a VNIR spectrum that matches with various hydrous minerals.

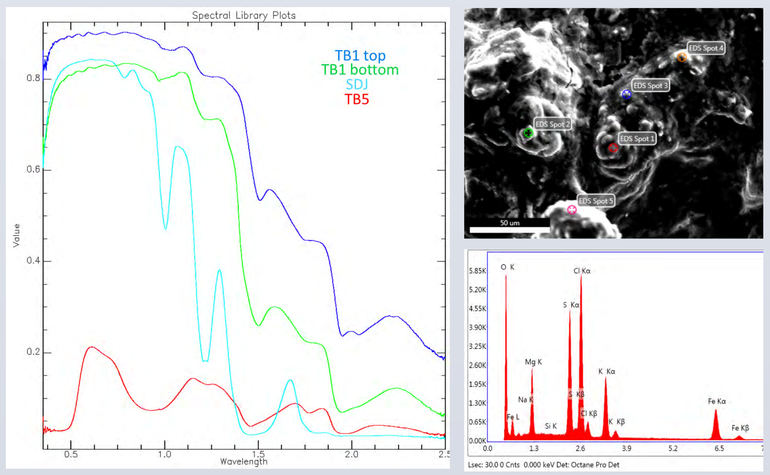

Figure 5: VNIR of miscellaneous samples and EDS analyses of TB5. Left is the stacked VNIR spectra of the miscellaneous samples. Top right is an SEM image of amorphous material with mixed composition, and lower right is the EDS point analysis of spot 2.

Spectral Group 2- Na/Mg/K, Cl/SO_4/HCO_3

- Group 2 is comprised of KS [12], MKS [5], TB2 [10], and CV1 [7].
- Modeling predicts: halite, bischofite, carnallite ($KMgCl_3 \cdot 6H_2O$), anhydrite, magnesite, kieserite, hexahydrite, hanksite, kainite, sylvite, bloedite, epsomite, picromerite.
- Most spectral features are explained by bischofite, the shape of the 1.75 µm feature implies the presence of mirabilite ($NaSO_4 \cdot 10H_2O$) or carnallite.
- Thenardite present in the XRD may have been mirabilite before being dehydrated by X-rays.
- EDS point analyses are consistent with bischofite and carnallite in the samples. Other chlorides including halite (NaCl) were also observed, but no sulfates were observed in this preliminary scan.

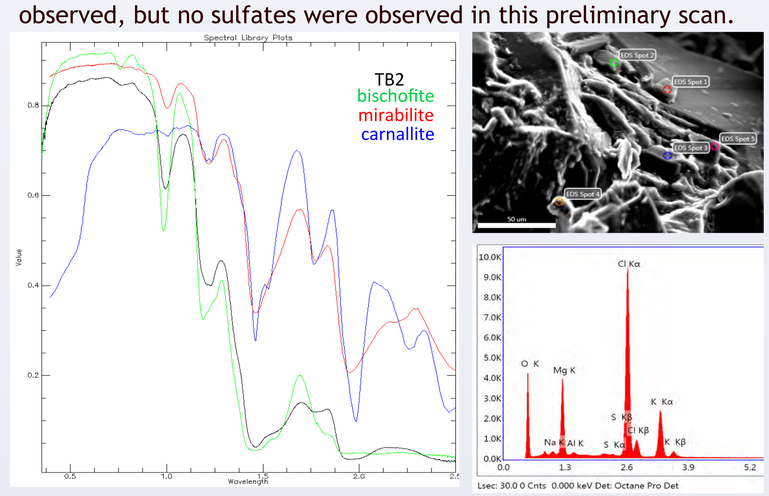

Figure 3: Left is the VNIR spectra of TB2 with bischofite, mirabilite, and carnallite. Top right is an SEM image of a magnesium/potassium chloride, and lower right is the EDS point analysis of spot 1, most likely bischofite with carnallite.

Conclusions

- A range of hydrous chloride, sulfate and carbonate mineral assemblages precipitated from solutions created from modeled brine compositions that may be relevant to Mars.
- Hydrous magnesium sulfates and hydrous magnesium and calcium chlorides are precipitated in these brines as modeled and are detected in the VNIR. **These minerals are best recognized among hydrous minerals by features in the 1.5-1.8 µm range.** Halite is the most common precipitate in most brines but has no diagnostic features the VNIR.
- XRD recognized fewer minerals than were predicted from modeling and were detected using other methods. This could be due to: 1) several of the materials observed in SEM were amorphous in nature. 2) The X-rays were altering (dehydrating) the minerals over the course of a sample run. 3) Minerals, especially ferrous chlorides, whose XRD peaks were apparent are not published and so would not be identified. **These issues may be relevant to the detection of salts using XRD on the Mars surface.**

Acknowledgements

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References

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