

VNIR AND RAMAN SPECTRAL CHARACTERIZATION OF MARTIAN ANALOGUE CHLORIDE AND SULFATE BRINES.

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Introduction: The low atmospheric pressure and desiccating conditions of the modern martian surface are inhospitable to stable pure liquid water [1]. If water were to be stable or metastable on Mars it would likely be in the form of a brine, allowing for depressed stable eutectic temperatures and pressures of liquid water [2]. Ephemeral brines have been modeled to be stable on Mars [3]; the widespread presence of chloride, carbonate and sulfate salts demonstrates that water was once at least transiently stable on Mars [4]. However, the formation of these salts, as well as potential brine compositions, require further investigation. Likewise, the relationship between geochemistry and spectral signatures of multicomponent evaporitic suites remain poorly understood. Here, we present results from an investigation into precipitation pathways of evaporites, as well as methods of characterization, and variations between brines evaporated under terrestrial and martian conditions.

Methods: Brine recipes were generated based on literature regarding anticipated ionic compositions of potential brines present on the modern or ancient martian surface. We concentrated the original recipes using version 9.2 of the FREZCHEM cold aqueous evaporation model, the output of which varied depending on pressure, temperature, and atmospheric conditions of the Earth and Mars systems [5]. Brines based on these recipes were experimentally generated in 200 mL batches by dissolving salts to achieve desired molalities. These recipes were specifically chosen to mimic conditions across a range of martian epochs and chemistries. Once generated, brines were separated into two beakers, one of which evaporated under martian conditions in a Mars analogue chamber (MAC, aliquot “b”), while the other was placed to evaporate under ambient hood conditions (aliquot “a”).

The MAC maintains a temperature of near 0°C, a pressure of ~6 millibar, and CO₂-dominating gaseous conditions. We monitored relative humidity (RH), temperature and pressure daily. Once brines reached full evaporation, we placed a glove box over the chamber and infilled ultra-dry N₂ to prevent atmospherically induced spectral absorptions, and obtained Raman and VNIR spectra of the evaporites. 12 brines were evaporated under both martian and terrestrial conditions, for a total of 24 brines.

Results: Here we report on mixed chloride/sulfate brines (CMM, CV2) and the chloride-dominated brine (TSG). Carbonate/chloride brines are described by [6].

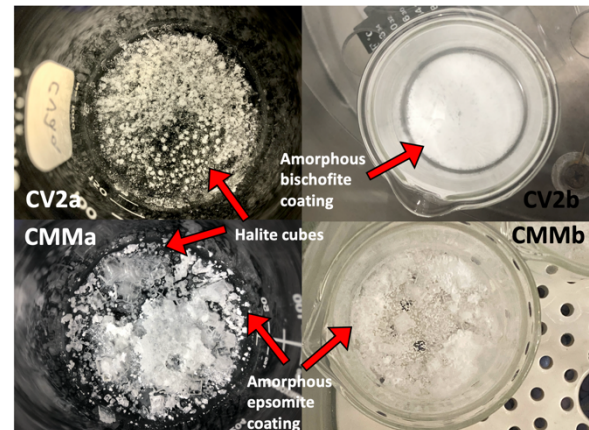


Figure 1. Precipitates from Catling Modern Mars (CMM) [7] and Clark and Van Hart (CV2) [8] brines.

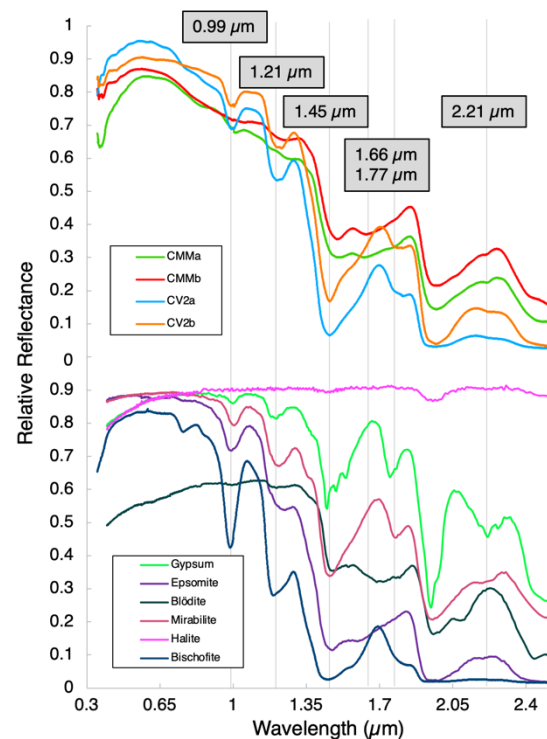


Figure 2. VNIR spectra of CMM and CV2; Bischofite is present in CV2 and epsomite in CMM.

Chloride/sulfate brines. Halite (NaCl) is modeled to make up ~10-50% of evaporites in CV2 and CMM, respectively. Halite is confirmed by XRD analysis and morphologically. Spectrally, however, these brines are dominated by hygroscopic amorphous salts; CMM is dominated by epsomite (MgSO₄•7H₂O) in the VNIR

(Fig. 2) and in Raman, while CV2 was dominated by bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) in the VNIR (Fig. 2) and epsomite in Raman.

Many brines follow this trend. We determine that “coatings” of amorphous hydrous salts are commonly present covering crystalline salts such as halite and sylvite (KCl) (Fig. 1), and dominate VNIR and Raman spectra. Halite has minimal features in VNIR and Raman and thus is unidentifiable by these methods, even if present in bulk.

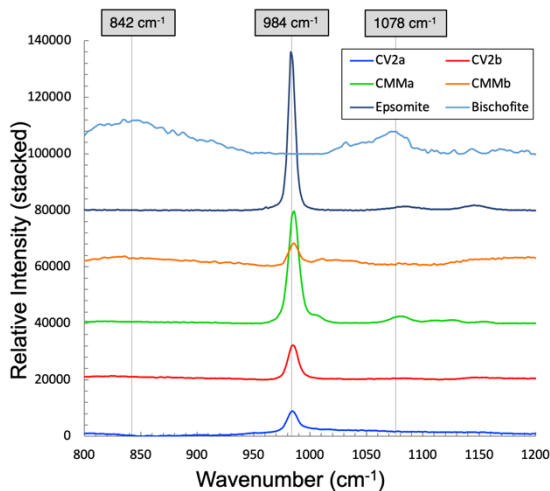


Figure 3. Raman results for CMM and CV2, indicating the presence of epsomite in both evaporitic suites under both martian and Earth conditions.

Chloride-dominated brines. Toner Shallow Groundwater (TSG) [9] contains mixed Mg, Ca, K, and Na chlorides and is modeled to be dominated by an unnamed salt: $\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$. Antarcticite ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is additionally modeled in abundance under Earth conditions (TSGa) and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) under Mars conditions (TSGb). In VNIR and Raman, bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was confirmed in TSGa once it reached complete evaporation (“TSGa Dry”). It could not be confirmed, but may be present, in “TSGa Wet” (post-rehydration). It was not confirmed in TSGb. Under martian conditions, antarcticite was confirmed in VNIR.

Discussion: Observable salts in mixed component evaporite suites differ substantially depending on ID method. The major discrepancy lies between amorphous, hygroscopic salts such as epsomite and bischofite (identifiable in the VNIR and Raman) and crystalline and anhydrous salts such as halite and sylvite (identifiable in XRD). These anhydrous crystalline salts may be undetectable in VNIR and Raman, despite comprising significant volumes of the deposits. It is through a multi-prong approach, then, that components of a mixed evaporite system are best characterized.

In the VNIR spectra of a mixed chloride system, the Mg chloride appears to dominate under terrestrial conditions, and the Ca chloride dominates under martian conditions (Fig. 4). Bischofite is difficult to discern in Raman spectroscopy; the Raman spectra differ structurally between martian and Earth conditions. This indicates possibly significant differences in precipitate signatures between Mars and Earth or wet or dry minerals in the martian surface (e.g., in RSLs), due to variations in temperature and RH conditions between the two systems. As a consequence of their deliquescent properties, chlorides, particularly mixed Mg and Ca chlorides should be considered excellent prospects for modern brine-forming salts on Mars.

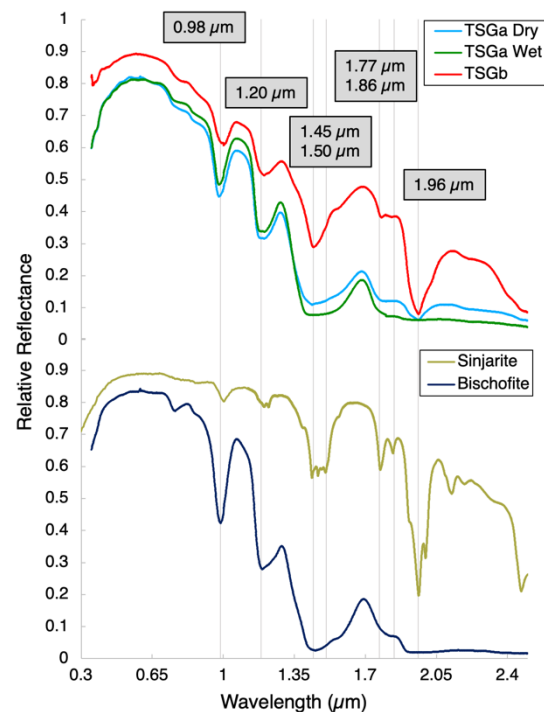


Figure 4. Toner Shallow Groundwater (TSG) in comparison to sinjarite ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and bischofite. Bischofite is present in “TSGa Wet” and “TSGa Dry” and antarcticite is present in TSGb.

Acknowledgements. Thanks to Darby Dyar for use of the Raman spectrometer.

References: [1] Haberle et al. (2001) *JGR* 106, E10 [2] Brass (1980) *Icarus*, 42, 20. [3] Martín-Torres et al. (2015) *Nature Geosci.*, 8 357. [4] Ehlmann and Edwards (2014) *Annu. Rev. Earth Planet. Sci.* 42, 291. [5] Marion and Kargel (2008) *Adv. in Astrobio. and Biogeophys.* Springer-Verlag Berlin. [6] Hughes and Gilmore (2020). *51st LPSC*, Abstract 2106 [7] Catling (1999) *JGR* 104, 16453. [8] Clark and Van Hart (1981) *Icarus* 45, 370. [9] Toner et al. (2017) *EPSL*, 474, 190-197.