

CHARACTERIZATION OF MARTIAN SALTS THROUGH EXPERIMENTAL EVAPORATION AND SPECTRAL ANALYSES OF ANALOGUE BRINES. E. B. Hughes¹ and M. S. Gilmore¹, ¹Department of Earth and Environmental Sciences, Planetary Science Group, Wesleyan University, 265 Church St, Middletown, Connecticut, 06459. Email contact: ebhughes@wesleyan.edu; mgilmore@wesleyan.edu

Introduction: Were liquid water to be stable or metastable on the surface of Mars, it would likely be in the form of a brine, with a lowered eutectic temperature and pressure [1-3]. Water may be present in the form of ice in the regolith that could melt upon interaction with surface or subsurface salts [5], or water vapor in the atmosphere [3], which could be deliquesced by salts. The interaction between available water salts could allow for the formation of stable or metastable brines on Mars. Thus, characterizing potential Martian salts is fundamentally important to understanding modern and ancient aqueous processes on Mars.

Mineral characterization can be performed via remote sensing of Martian surface using the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) aboard the Mars Reconnaissance Orbiter (MRO) operating over 0.35 – 4 μm , on the surface using the Chemistry and Camera (ChemCam) instrument aboard Curiosity, and SuperCam aboard Mars 2020. Chlorides, carbonates, and sulfates all have distinct characteristic spectral absorptions seen best in the spectra of well crystalline single phases [6]. The evaporation of brines may result in intimate mixtures (e.g., coatings) of amorphous phases of variable grain sizes. This makes it difficult to predict which phases will precipitate in a given brine, which phases in real mixtures will be most detectable using VNIR and Raman spectroscopy and how well the spectral signature correlates to the volumes of individual phases.

Here we experimentally investigate evaporation pathways and evaporative phases of modeled martian analogue salts precipitated under Earth and martian conditions. These data can help understand variability between thermodynamic predictions and real mixtures. Spectral data from these mixtures will help us understand which salts can be identified on Mars, and what additional salts may form in tandem with those identified.

Brine Development and Creation: We compiled a list of recipes for potential brines on Mars, derived from available literature and data from Mars rovers, orbiters, and Earth analogue studies, and we experimentally evaporated brines based on these recipes. Initial work in this area was performed by Martin [7]. 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 [8]. These modeled concentrations

allowed for the creation of brines that would evaporate more efficiently.

Six brine compositions were created by dissolving salts into 200 milliliters of water to achieve the cation and anion concentrations in the recipes (Table 1). The resulting brines were divided equally into two different beakers: one was evaporated in a laboratory hood under ambient conditions, while a second was evaporated under martian conditions in a vacuum chamber.

Table 1. Concentrations of cations and anions for each brine used in the initial suite of brines for this study. Concentrations are in mol/kg of solvent.

	Na ⁺	Ca ²⁺	K ⁺	Mg ²⁺	Fe ²⁺	CO ₃ ²⁻	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	HSO ₄ ⁻
CAM [9]	0.889	0.008	0.077	0.120			0.101	0.200	0.722	
CMM [9]	0.889	0.006	0.077	0.074			0.006	0.200	0.722	
CV3 [10]	0.235	0.0003	0.029	0.200			0.0002	0.187	0.292	
MKC [8]	0.810	0.001	0.071	0.082				0.184	0.677	
TB1 [4]	0.219		1.040			0.005	0.377		0.874	
TB5 [4]	0.421		0.167	0.669	0.570			0.745	1.490	0.086

Mars Chamber: The Wesleyan Mars analogue chamber is a vacuum chamber with internal temperature sensors, a relative humidity monitor, and additional ports for environmental control and measurement. The chamber is kept in a freezer held slightly above 0°C to emulate Martian conditions particularly in the summer and autumn seasons, which would be more conducive for modern brine formation [11]. The chamber was maintained at the modern Martian pressure of 0.006 bar and filled with dry CO₂.

Upon complete evaporation of brines, the analogue chamber and freezer were sealed and flooded with ultra-dry N₂ to ensure water-free conditions for spectral analysis. Spectra were collected with an ASD FieldSpecFR spectroradiometer and a Bruker Bravo Raman spectrometer. Precipitates were measured using VNIR spectroscopy and Raman spectroscopy to 1) determine which minerals precipitated from each initial brine, using available methods of analysis, and identify potential discrepancies between suites of minerals precipitated and 2) those modeled and 3) identified spectrally, which could shed light on minerals which are not identifiable using CRISM or Raman spectra but nevertheless are still present.

Results and Conclusions: Brines evaporated to complete dryness over the course of 4-6 weeks, with variations in evaporation rate due to differences in solubility of salts and concentrations of original brines. Multiple brines precipitated cubic crystals, likely

indicating the wide-scale presence of halite (NaCl). Crystal size varied across the brine precipitants. Six of the original twelve brines also resulted in the precipitation of amorphous salts. Morphological differences in precipitated salts can be accounted for by mineralogy, solubility, and presence of additional salts in a suite [12].

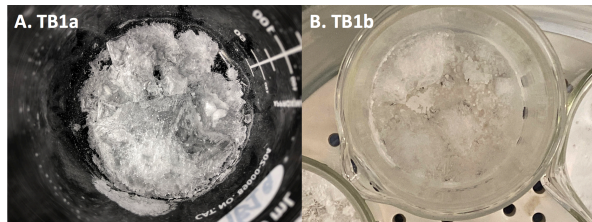


Figure 1. Brine TB1 [4]. TB1a was evaporated in a laboratory hood under earth conditions; TB1b was evaporated in the Mars analogue chamber.

Table 2. Modeled mineral outputs for TB1a and TB1b, and VNIR and Raman detections.

Minerals	TB1a		TB1b			
	% Total Volume	VNIR	Raman	% Total Volume	VNIR	Raman
Sylvite	66.24	M	N/A	53.35	N	/
Magnesite	29.72	N	N/A	23.00	N	N
Trona	4.05	Y	N/A	/	Y	Y
Nahcolite	/	N	N/A	13.39	M	Y
Kalicinite	/	/	N/A	10.26	/	Y

Table 2 demonstrates the differences in suites of precipitates under Mars and earth conditions for the same starting brine TB1 [4], here used as an example of spectral analysis. Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) was recognized in spectra for both experiments, despite not being modeled for TB1b, (Figure 2). VNIR analysis demonstrates the precipitation of trona in both TB1a and TB1b, from absorptions at 1.2, 1.5 and 1.9 microns. However, TB1b's Raman peaks at 227 and 850 cm^{-1} demonstrate differences between the precipitated suite of minerals and trona. This could be due to the influence of other minerals in the suite, which have been known to shift Raman peaks [13]. Nahcolite (NaHCO_3) peaks are recognized in VNIR and Raman data for TB1b as predicted from modeling. Kalicinite (KHCO_3) can account for the strong 1016 cm^{-1} peak in the Raman spectra as modeled for TB1b.

While magnesite (MgCO_3) and sylvite (KCl) are modeled to comprise the highest volume of precipitates, neither were detected with VNIR nor Raman. Such discrepancies help us better understand the sensitivity of remote detection methods at Mars and our interpretation of spectral data.

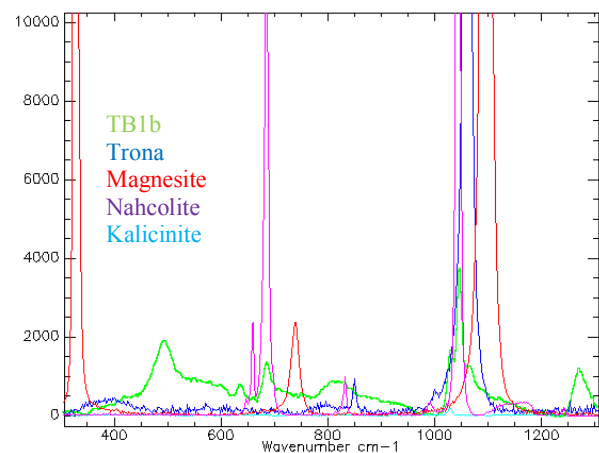
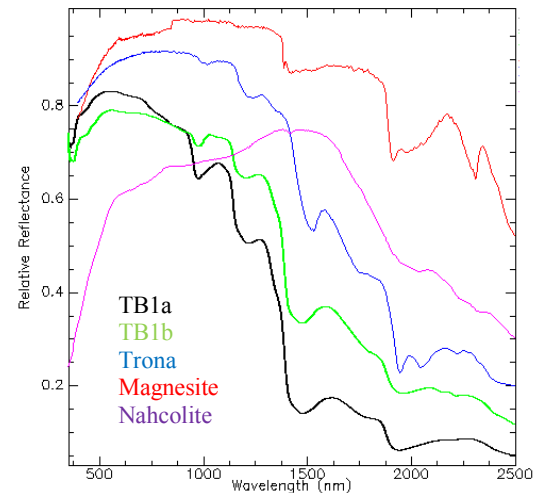


Figure 2. VNIR (above) and Raman (below) spectral plots for brine TB1 [4] evaporated under ambient (TB1a) and martian (TB1b) conditions.

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