

INVESTIGATION OF SODIUM SULFATE SPECTRA FROM THE GREAT SALT LAKE AS A MODEL FOR CHARACTERIZING AQUEOUS GEOCHEMISTRY & CLIMATE HISTORY OF MARTIAN PALEOLAKES. ^{1,2}W. L. Wallentine, ¹K. L. Lynch, ¹G. L. Eggers, ³E. B. Hughes, ³J. J. Wray, ³F. Rivera-Hernández; ¹Lunar and Planetary Institute (USRA), Houston, TX, 77058, USA, ²Dept. of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459, USA. ³School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA. (Contact: wwallentine@wesleyan.edu)

Introduction: There is little debate about the presence of water in the history of Mars. However, there is much debate concerning the climate of early Mars. Was it ‘cold and wet’, ‘cold and icy’, or even ‘warm and wet’? [1]. Perennially ice-covered lakes (PICLs) and salt mounds serve as potential analogs to an early ‘cold and icy’ Mars, or as transition points between an earlier wet Mars to the current cold and dry Mars [2, 3]. On Earth, most PICLs are found in arid polar regions that are below 0°C and have a unique sedimentary record that distinguishes them from open-water lakes [3]. Salt mounds of mirabilite (Na₂SO₄•10H₂O) precipitate out of subsurface fluids near the Lewis Cliffs Ice Tongue (LCIT) in Antarctica [4]. Similarly, in the Great Salt Lake (GSL), mirabilite mounds precipitate out of upwelling saturated spring water during the winter months. Mounds that are morphologically similar to those in the LCIT and GSL occur on Mars, with several explanations relating to upwelling of subsurface fluids, including mud volcanism and pingos [5, 6].

Mirabilite is often not preserved in ancient deposits due to its low melting point and high solubility [7]. As local environmental conditions change mirabilite transforms into more stable minerals, such as thenardite (Na₂SO₄). Mirabilite will also convert to thenardite diagenetically or via burial. This transformation from mirabilite to thenardite, and thereby the cool & arid climate to warm & arid climate, can be detected through identifying several different features within a sedimentary sequence, hence providing a cool climate indicator. This has been used previously as a paleoclimate indicator of a cool and arid period in Central Spain that correlates with an Antarctic ice expansion “Mi” event ~18.4Ma [7].

Here we take the first steps to establishing mirabilite as a paleoclimate indicator and an aqueous geochemical indicator for Martian environments. On Mars, future analysis of thenardite and mirabilite may help constrain paleoclimate conditions, help characterize subsurface hydrology, as well as provide a preserving environment for possible biosignatures of life.

Most studies of mirabilite spectra are based on pure mineralogical samples in lab settings (e.g., Crowley 1991) or in-situ studies in natural settings. As of publishing, there have been no studies of natural (e.g., multicomponent and not synthesized) putative

mirabilite samples observed in lab settings. There are also few studies investigating the spectral impact of the transition from mirabilite to thenardite. Understanding the spectral signatures associated with this transition could aid researchers in remote sensing of cold, dry environments. Here, we perform spectral analysis of analogue samples from the GSL—specifically samples of GSL brines that we allow to evaporate under ambient laboratory conditions.

Analog samples: Brine fluids collected from the north arm of the GSL, where mirabilite mounds have previously formed, served as the sample set for this study. The collected brine samples were kept sealed and in -80 °C conditions until this study.

Spectral collection: Spectra were collected with an SEI SM-3500 OreXpress over the 350-2500 nm range, covering the visible and near-infrared.

Wet samples were transitioned from the -80°C to a -18°C freezer to allow for thawing and manipulation of the sample. Spectra of the GSL water samples were collected under two separate conditions: complete dehydration, and during a 30-minute melting period (from -80 °C to ambient temperature).

Results: For the complete dehydration experiment, a sample of brine precipitate was left to dry in ambient lab conditions for six days. After the six days, a well-defined spectrum indicative of mirabilite was observed (Figure 1). However, the spectrum of evaporated brine precipitate is slightly different from the USGS spectrum of pure mirabilite, likely because of influence by other evaporitic minerals present in the GSL.

For the 30-minute melting experiment, conclusive detection of mirabilite occurred only when the brine sample was frozen to -80°C. As the sample returned to room temperature, mirabilite diagnostic bands disappeared after 25 minutes. In the spectra of the first scan, where the brine sample was coldest, absorption features are well defined. Major absorptions in the first scan occur at 1, 1.23, 1.5, 1.64, 1.8 and 1.98 μm. After 25 minutes at room temperature and humidity, reflectance drops drastically, and features after 1.5 μm are subdued or non-detectable. The only remaining absorption features at this stage, where the sample was a slushy liquid, are found at 1 μm and 1.2 μm.

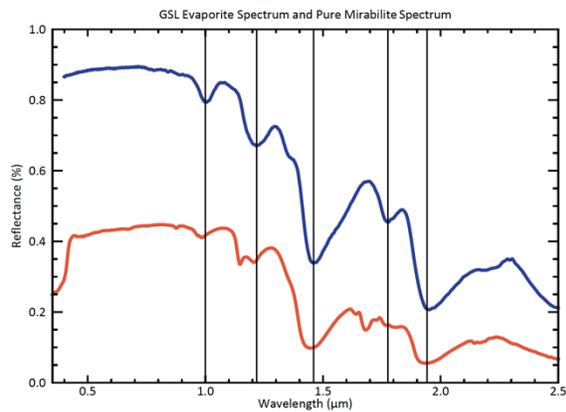


Figure 1. Spectra of pure mirabilite from USGS (dark blue) and GSL evaporite (light red). Lines in black correlate with major absorption features.

Discussion: The absorption features found in the frozen brine samples are consistent with those found by [12] of mirabilite. Being a decahydrated sodium sulfate, most of the spectral absorption features can be attributed to the structural water in the mineral. Specifically, the features at 1, 1.2, 1.5, 1.8, and 1.98 μm , are all overtones and combination features of structural H_2O in the mineral [12]. Many of the spectral features are also consistent with the mirabilite spectra found in the USGS mineral spectral library [10]. However similar the locations of the absorption bands are, the magnitude of reflectance varies. As the sample warmed, the conclusive diagnostic features of mirabilite after 1.5 μm flattened and ultimately disappeared. This could be attributed to spectral masking by halite, as crystals similar in structure to halite were observed to form as the sample warmed, and there's no immediate evidence of rapid mirabilite transformation into thenardite. Loss of the hydration bands after 1.5 μm but not 1 μm and 1.2 μm could be evidence of transformation into a semi-hydrated state, sodium sulfate heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$). It is unlikely that these bands are evidence of thenardite, as thenardite has only one diagnostic band in the VNIR range, at 1.9 μm , which is due to contamination or adsorption of water. This evidence reaffirms that mirabilite forms under cold conditions, and that warming conditions make detection harder.

Indeed, transformation of mirabilite into thenardite is temperature dependent, but also regulated by the chemical context of the environment. It is known that in presence of NaCl , dehydration into thenardite drops from 32°C to 18°C, whereas presence of Mg^{2+} drops it down to 16°C [11]. The Bonneville basin, where the studied brine samples came from, is known for its extensive halite (NaCl) deposits, as well

as its deposits of potassium chloride and magnesium chloride [13].

Conclusion: Evidence of mirabilite in frozen brine and desiccated brine fluid from the GSL was found using VIS-NIR spectroscopy. These preliminary findings shed light on the utility of the GSL as an analog for mirabilite studies. Mirabilite and thenardite have been suggested to exist on Mars, but no mission has prioritized detection of these sulfates [4, 9]. Understanding the processes linked to formation and deposition of these minerals should be a key aspect of planetary science missions in the future.

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