INVESTIGATION OF DEHYDRATION-HYDRATION FEATURES OF IRON-SMECTITE AND SULFATE FROM -90 TO 950 °C AND APPLICATIONS TO MARS. Merve Yeşilbaş1 and Janice L. Bishop1,2. 1SETI Institute (Mountain View, CA 94043; myesilbas@seti.org), 2NASA Ames Research Center (Moffett Field, CA 94035; jbishop@seti.org)

Introduction: Previous studies with visible/near infrared (VNIR) spectra from martian orbit confirmed the presence of hydrous minerals, such as smectites, sulfates, silicates and Cl-bearing salts [1-4]. Here we focused on one of the most widespread phyllosilicates on Mars, nontronite (Fe-smectite), and the hydrated sulfate rozenite (FeSO₄·4H₂O), found at Valles Marineris [5] and Gale crater. Smectite minerals can absorb variable amounts of water on the surface and between the layers, and they are even capable of absorbing organics and gas molecules, e.g CO₂ [6]. Rozenite contains H₂O in its crystal structure as well, which may favor stabilizing water and absorbed organics under the extreme conditions of Mars. Advancing that, these water-bearing minerals may preserve the bio(geo)chemical signatures for determining the geological and aqueous history of Mars [7]. In this study, we aim to understand the interactions of these minerals with water and brine solutions using the mid-IR (4000-600 cm⁻¹) spectral region to probe the activity of water both at elevated temperatures (up to 900 °C) and under cold temperatures (-90 °C) and to help develop a VNIR spectral database for martian orbit analyses.

Methods: We used the Al-poor nontronite (NAu-2, JB791) from the Clay Minerals Society Source Clays Repository [8]. The rozenite sample (JB626-B) is a pure hydrated iron sulfate (FeSO₄·4H₂O) collected from Iron Mountain, CA [7]. Each mineral was crushed and dry sieved to <125 µm and measured either as a powder or in an aqueous suspension.

Thermogravimetric Analyses (TGA). About 4 mg of each sample was heated from 25 to 950 °C under N₂ (g) in a Mettler Toledo TGA/DSC-1 at a rate of 1 °C/min. TGA was performed in two stages: (i) to evaluate dehydration of water on the surface of Mars over geological time the mineral powders were heated to 80 °C to remove weakly (ad)sorbed water and retained there for 180 min. Morris, et al performed similar experiments at ~110 °C [9], (ii) to reveal the loss of the remaining bound H₂O and OH in the samples the powders were heated further to 950 °C.

Temperature Programmed Desorption (TPD)-FTIR. The sample powders were deposited on a tungsten mesh with a pressure of 5 N/m between steel discs, then inserted into the copper heating shaft. Prior to heating, the sample was dried at 30 °C in vacuo (< 0.8 Torr) for 10 min in a transmission optical reaction chamber to ensure the loss of water is time-independent. The sample was then heated from 30 to 400 °C at a rate of 10 °C/min. Spectra were monitored with a Bruker Vertex 70/V FTIR over the range 600-4000 cm⁻¹ at 4 cm⁻¹ resolution, where 100 scans were collected in 89 sec at the spectral range of (6000-1000 cm⁻¹).

Cryogenic-FTIR. We mixed 3 mg sample with 20 µL of H₂O, 0.1 M NaCl and 0.1 M CaCl solutions and equilibrated for 30 min. 10 µL of the nontronite and rozenite suspensions were applied on a precooled attenuated total reflectance (ATR) accessory (Golden Gate, Specac) at -90 °C. We held this temperature for 15 min to confirm stability of the frozen samples. Then, the temperature was increased to 80 °C at a rate of 10 °C/min to monitor changes in the hydration features using ATR spectra from 1800 - 800 cm⁻¹ at 4 cm⁻¹ spectral resolution with 3 sec per scan.

Thermal Decomposition in High Temperatures: The loss of water loading on the minerals was revealed by TGA (Fig 1), whereas TPD-FTIR (Fig 2) exhibited spectral changes in the hydration bands for nontronite and rozenite. TGA revealed a total loss of ~12% water for nontronite, and ~9% for rozenite by heating through 80 °C. This loss could be related to weakly bound ‘free’ physisorbed and interlayer water molecules of nontronite [6]. In the second stage up to 400-450 °C, TGA revealed further loss of ~8% water for nontronite and ~12% for rozenite due to loss of more tightly bound water from the interlayer cations of nontronite and crystalline water of rozenite. In the third stage, dehydroxylation occurs resulting in greater weight loss (~25%) for rozenite and less (~5%) for nontronite.
TPD-FTIR experiments specifically revealed loss of interlayer water from nontronite and crystalline water from rozenite. We focused on the 1626 cm\(^{-1}\) band in the nontronite spectra to probe the loss of interlayer water (Fig 2, left). This band gradually decreased with heating to 400 °C. The band intensity changes at 1626 cm\(^{-1}\) (Fig 2, right) also confirmed the initial water loss of ~50% below 200 °C and ~30% additional loss between 200-400°C. On the other hand, one of the doublet bands of dried rozenite (not shown) (1660 cm\(^{-1}\)) was gradually eliminated through heating up to ~250 °C, and was followed by a gradual decrease in the 1630 cm\(^{-1}\) band from 250 – 400 °C, resulting in a redshift at the 1613 cm\(^{-1}\) band with stronger coordination of water molecules to the cation [11].

![Fig 2. TPD-FTIR 1626 cm\(^{-1}\) band intensity for nontronite to probe the loss of interlayer water (left), changes in band intensity correlated with TGA weight loss in vacuo environment (right), similar to previous results [6].](image)

**Hydration-Dehydration in Cold Temperatures.** We examined the hydration features of mineral-suspension mixtures and determined the temperature range where these suspensions became liquid. All the suspensions of rozenite and nontronite revealed the suspensions were frozen at -90 °C, confirmed with the O-H stretching bands at 3220 and 3150 cm\(^{-1}\), and a characteristic broad ice band centered at 1600 cm\(^{-1}\), comparable to the frozen form of pure aqueous solutions of H\(_2\)O and 0.1 M NaCl [11] as well as 0.1 M CaCl\(_2\) vibrational spectra. As the frozen nontronite brine gradually lost water, the ice signatures disappeared between -50 to -40 °C, whereas the frozen rozenite brine kept the ice features until -30 °C. While the rozenite system revealed no signature of hydrohalite formation, hydrohalite may have formed in the nontronite system, where a band due to liquid water occurred in the spectra from -40 to -30 °C. As the possible phase change for NaCl occurs near -21 °C (triplet point) [11], quite close to -30 °C, liquid NaCl may be contributing to the spectral features and will be investigated further.

![Fig 3. Cryo-FTIR results in O-H bending region for the water and brine mixtures of nontronite (left) and rozenite (right) at -90 °C, and with further heating at -40 °C, 25°C and 80°C.](image)

For the CaCl\(_2\) mixtures of nontronite and rozenite low temperature spectra revealed possible liquid water signatures between -50 to -40 °C. This is close to the eutectic point of ~51 °C, where the CaCl\(_2\)-6H\(_2\)O and ice transform to a solution phase of CaCl\(_2\) coexisting with ice. Upon to heating all of the mixtures from 25 °C to 80 °C, the water bands were progressively eliminated.


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