

CHARACTERIZATION OF GYPSUM USING VIBRATIONAL SPECTROSCOPY AND XRD FROM LOW TO HIGH TEMPERATURE AND APPLICATIONS TO MARS. M. Yeşilbaş^{1,2,3}, T. H. Vu^{3,4}, R. Hodyss^{3,4}, M. Choukroun^{3,4}, P. V. Johnson^{3,4} and J. L. Bishop^{1,3,5}, ¹Carl Sagan Center, SETI Institute, Mountain View, CA 94043, USA, ²Umeå University, Umeå, Sweden (merve.yesilbas@umu.se), ³NASA Astrobiology Institute, USA, ⁴Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA, ⁵NASA Ames Research Center, Moffett Field, CA 94035, USA.

Summary: Gypsum and its related Ca sulfates are important minerals on Mars. We performed a suite of Raman, VNIR and XRD experiments at low and high temperatures to investigate the effects of temperature on gypsum signatures and explore dehydration of gypsum to bassanite or anhydrite. Our XRD analyses observed formation of bassanite from gypsum/CaCl₂ mixtures at elevated temperatures, but not from pure gypsum or gypsum/NaCl mixtures. Although the transition temperature in our experiments was too high to explain gypsum conversion to bassanite with CheMin at Gale crater, a slower heating rate may enable bassanite formation at lower temperatures and higher salt concentrations may facilitate this transition at lower temperatures. VNIR reflectance spectra of gypsum measured under Mars-like temperatures exhibit sharpened bands at largely the same wavelengths as room temperature spectra, providing confidence in the orbital identification of gypsum at Mars.

Background: Gypsum (CaSO₄·2H₂O) occurs in many terrestrial settings on Earth such as marine evaporative environments and hydrothermal veins, as well as on Mars [1], where it has been detected in several locations including Olympia Undae [2], Meridiani Planum [3] and Gale crater [4]. Gypsum can lose its structural water through heating above 100 °C and convert to the dehydrated phases bassanite (CaSO₄·0.5H₂O) and anhydrite (CaSO₄), all of which have unique spectral properties [5]. Further, anhydrite has a complex structure including three subclasses: soluble (γ -anhydrite), insoluble (β -anhydrite) and anhydrite I (α -anhydrite), observed at progressively higher temperatures [6]. Comparing all of these Ca-sulfate phases, the crystal structure of soluble γ -anhydrite exhibits more similarities with bassanite than other forms of anhydrite [4]. This adds complexity to distinguishing XRD patterns of Ca sulfates; nevertheless, gypsum, bassanite, and anhydrite were all identified at Gale crater using CheMin [4]. Characterization of gypsum and formation of its dehydrated phases is important for constraining the aqueous history of Mars and assessing potential water resource for future human missions.

Experimental Methods: Gypsum (JB1464) was ground with a mortar and pestle, then dry sieved <45 μ m for this study. The gypsum grains were then mixed with (i) distilled water, (ii) 1% CaCl₂ solution (500 g/L mass-

water ratio) and (iii) 1% NaCl solution (1000 g/L mass-water ratio) to create a thick paste.

(i) *Cryogenic-Raman.* Raman spectra were acquired with an Horiba Jobin-Yvon LabRam HR dispersive confocal Raman microscope coupled with a green laser (532 nm). The sample pastes were deposited inside a Linkam LTS 350 cryostage at ambient temperature and pressure, then flash frozen to -90 °C. Spectra were collected from 4000-100 cm⁻¹ every 30 °C while heating the sample at a rate of 30 °C/min. up to 180 °C.

(ii) *Cryogenic-VNIR.* VNIR spectra were collected using a Thermo Nicolet 6700 FTIR spectrometer equipped with a DiffusIR reflectance accessory (PikeTech) coupled with a low temperature vacuum chamber. Each spectrum was acquired by averaging 200 scans at 2 cm⁻¹ spectral resolution. The prepared gypsum mixtures were placed into a sample cup at 25 °C under standard pressure (~754 Torr) and frozen at -90 °C. The chamber was then evacuated to 500 mTorr. After stabilizing the sample in this environment, spectra were collected as the sample was heated at a rate of 10 °C/min. up to 25 °C.

(iii) *Cryogenic-XRD.* Samples were sealed in 0.9 mm glass capillary tubes and flash frozen at -90 °C. The samples were then heated at a rate of 10 °C/min. and data were collected every 30 °C up to 120 °C.

Results: (i) *Cryogenic Raman Spectroscopy.* The Raman spectrum of gypsum exhibits peaks due to the SO₄ tetrahedral symmetric (ν_1) and antisymmetric (ν_3) stretching modes at 1008 and 1138 cm⁻¹ and due to H₂O asymmetric (ν_3) and symmetric (ν_1) stretching vibrations at 3406 and 3493 cm⁻¹ [7]. The water stretching bands at cold temperatures are sharper than at 25 °C, likely due to the H-bonding environment of water at low temperatures. Upon heating from 25 to 150 °C,

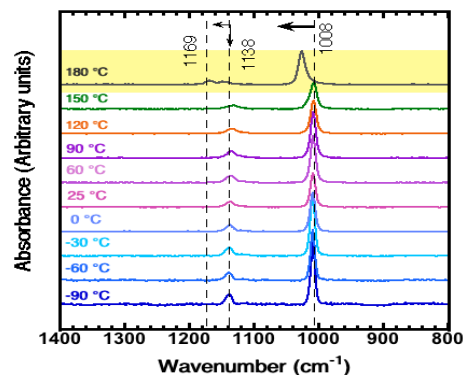


Figure 1. Raman spectra of flash frozen gypsum-water paste from -90 to 180 °C in the S-O stretching region.

these water stretching bands are progressively eliminated, until at 180 °C both bands are completely lost, similar to the anhydrite spectrum in the H₂O stretching region. A corresponding shift in the symmetric SO₄ tetrahedral vibration (ν_1) to higher wavenumbers was observed with decreasing hydration, resulting in a doublet at 1146 and 1169 cm⁻¹ at 180°C (Fig. 1). This spectrum shares strong similarities with the spectrum of γ -anhydrite (soluble anhydrite), formed through microwave heating at 225 °C [6].

(ii) *Cryogenic VNIR Spectroscopy.* VNIR spectra of gypsum and bassanite are sufficiently different to distinguish these minerals [5]. Specifically, the diagnostic gypsum triplet at 1.45, 1.49, and 1.54 μ m shifts to 1.43, 1.48, and 1.54 μ m for bassanite. Similarly, shifts in bands at 1.75 μ m and 1.94 μ m to 1.77 and 1.92 μ m occur from gypsum to bassanite. None of these features are observed for anhydrite. Low temperature spectra of the gypsum powder in our experiments exhibited similar features to [5], but with sharper bands (Fig. 2). Spectra of the gypsum-water mixture at -90 and -60 °C in our study are dominated by the broad water ice band near 1.5-1.6 μ m. This was eliminated at -30 °C as the characteristic gypsum bands became visible and became clearer by 25 °C (Fig. 2). Spectra of the gypsum mixtures with 1 wt.% NaCl and 1 wt.% CaCl₂ followed similar trends with heating from -90 to 25 °C. We did not observe clear signatures of bassanite or anhydrite in these experiments.

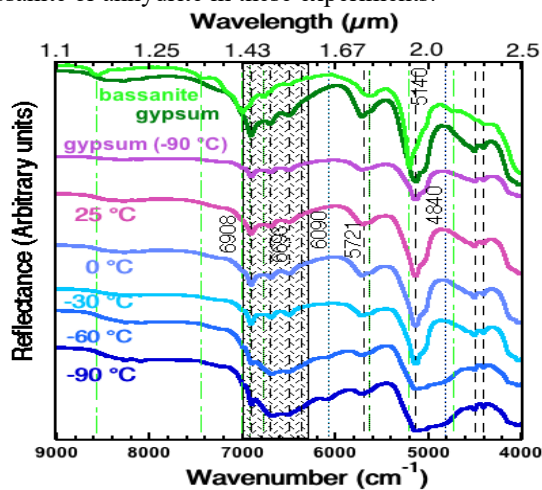


Figure 2. VNIR spectra of flash frozen gypsum/CaCl₂ mixture from -90 to 25 °C compared with bassanite (25 °C).

(ii) *Cryogenic XRD.* The XRD data for the gypsum-water mixture did not exhibit evidence of a phase change upon heating to 120 °C (Fig. 3). However, the mixtures of gypsum with 1% NaCl and CaCl₂ presented features of both gypsum and ice (I_h) at ~23°, 24° and 26° 2 θ , correlated as 100, 002, 101 [8]. These ice bands were eliminated during heating from -30 to 0 °C. As a

noteworthy change, further heating of the mixture of gypsum with 1% CaCl₂ to 120 °C led to the formation of bassanite in this sample, whereas this was not observed for the NaCl-gypsum mixture. We note that previous studies found that bassanite and γ -anhydrite are not easily distinguished so that diffractograms of these phases are similar [4]. We will apply further chemometrical analyses and vibrational spectroscopy experiments to resolve this.

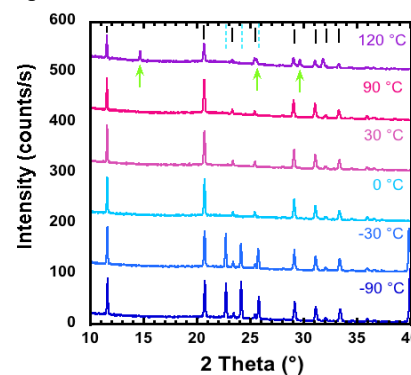


Figure 3. XRD patterns of flash frozen gypsum/CaCl₂ mixture from -90 to 120 °C. Dashed blue lines indicate ice patterns, whereas black patterns mark gypsum.

Implications to Mars: This study includes a wide range of spectral data to help understand gypsum dehydration pathways and identify formation of dehydrated phases. This is particularly important for understanding the aqueous and geochemical history of Mars using orbital spectra and rover measurements. Cryogenic VNIR spectra of gypsum in our experiments provide confidence for gypsum identification on Mars using room temperature data. Further, the low temperature water ice-gypsum spectra may provide insights for interpreting spectra of the gypsum dunes at Olympia Undae where water ice is also present. Previous XRD studies suggested that bassanite formation may depend on the dehydration of gypsum in the warm sample chamber of CheMin during the XRD measurements [4]. They also suggested that gypsum may have dehydrated over martian sols, forming an anhydrite-bassanite-gypsum mixture. The coordinated Raman/VNIR/XRD measurements in our study may enable connecting Raman data from Perseverance with XRD data from Curiosity and VNIR data from orbit at Mars.

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