THE SPECTRAL PROPERTIES OF GYPSUM FROM -90 TO 400 °C AND IMPLICATIONS FOR MARS.

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Summary: Gypsum ($CaSO_4.2H_2O$) is a hydrated sulfate commonly found on Earth and at several locations on Mars. Characterizing the spectral properties of gypsum under different temperature conditions supports remote identification of this mineral. Understanding dehydration of gypsum is also important for interpreting the CheMin data at Gale crater and constraining water in the martian regolith, which has important implications for the geochemical history of Mars, its habitability, and the potential for life. To resolve this, we combined thermal decomposition experiments with cryogenic-FTIR to probe the dehydration of the H-O-H bending (1400-2300 cm^{-1}) region. Our Thermogravimetric Analysis (TGA) and temperature programmed desorption (TPD)-FTIR experiments revealed that H_2O in gypsum is released by ~100-150°C. Additionally, cryogenic-FTIR measurements of 1% NaCl and 1% $CaCl_2$ mixtures with gypsum demonstrated that gypsum is more soluble in 1% $CaCl_2$ solution at -90 °C.

Introduction: Gypsum is an abundant terrestrial sulfate mineral in evaporate settings on Earth along with its dehydrated phases (bassanite and anhydrite), and has been detected at several locations on Mars [1]. This includes detection of gypsum dunes in Olympia Undae by OMEGA/Mars Express in the north polar region of Mars [2], Meridiani Planum [3] and Gale Crater [4]. Understanding the conditions governing dehydration of gypsum will help constrain the aqueous and geochemical history of Mars. Water loss from the mineral gypsum can occur through (i) heating over 100 °C [5, 6, 7] or (ii) the reaction of gypsum with salts at ~83 °C that both lead to the transformation of gypsum and basanite to anhydrite [5]. This study combines thermal decomposition experiments and cryogenic-FTIR spectroscopy of gypsum and Cl-salt mixtures to provide an experimental study to describe the dehydration features of Ca-sulfates and their spectral properties under a range of temperatures to support interpretation of aqueous environments on Mars where Ca-sulfates are present.

Methods: We used gypsum sample JB1464 [5] that was crushed and dry sieved prior to the experiments. Spectra were collected either as a powder or mixed with brine solutions for cryogenic-FTIR measurements.

TGA. 7.2 mg of gypsum was heated from 25 to 400 °C in the Mettler Toledo TGA instrument with a heating rate of 1 °C / min under N_2(g). These experiments were performed in two stages as described in our previous TGA study with the iron-rich sulfate, rozenite [8].

TPD-FTIR. The gypsum powder was coated on a tungsten mesh while applying 5 N/m pressure. Prior to heating, the sample was dried at 25 °C *in vacuo* (< 0.78 Torr) for 10 min in a transmission IR cell. The temperature was increased from 25 to 400 °C at a rate of 10 °C/min and spectra were collected every 89 sec, based on our previous study [8].

Cryogenic-FTIR. We mixed 50 mg sample with 20 µL 1% NaCl and 1% $CaCl_2$ solutions and equilibrated them for 15 min. 10 µL of the aqueous suspensions were applied onto an attenuated total reflectance (ATR) accessory at 25 °C and flash-frozen to -90 °C in 5 min. The temperature was then increased to 25 °C at a heating rate of 10 °C/min to probe the phase variations from H_2O/chloride ice to H_2O bound in gypsum, monitoring the H-O-H bending region at 4 cm^{-1} spectral resolution with 100 scans per spectrum every 89 sec.

Results: Our TGA analysis (Fig. 1) revealed that gypsum lost substantial water (~13.8 wt.%) through dehydration up to 80 °C. An additional ~5.4 wt.% water was lost by 110 °C, after which the sample remained

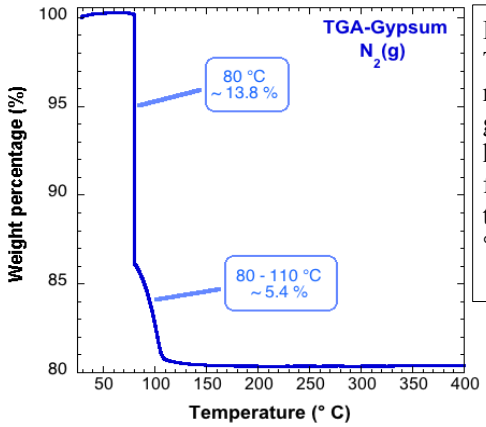

Fig. 1 TGA results for gypsum heated from 25 to 400 °C.

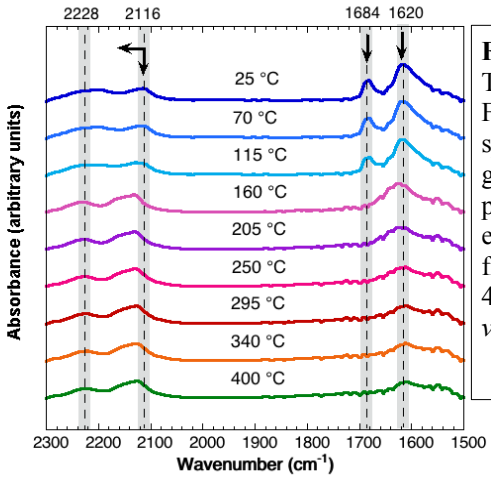

Fig. 2 TPD-FTIR spectra of gypsum progressively heated from 25 to 400 °C *in vacuo*.

stable until 400 °C. This is consistent with a previous study [7] where gypsum lost ~20 wt.% water by 150 °C.

TPD-FTIR spectra of gypsum at 25 °C (Fig. 2) observed a spectral doublet at 1620 and 1684 cm^{-1} in the H-O-H bending region, as expected [5, 9]. Further heating up to 150 °C resulted in the loss of the spectral band at 1684 cm^{-1}, and was accompanied by the progressive elimination of the 1620 cm^{-1} band at elevated temperatures. These changes in the H-O-H bending region also affected the SO_4^{2-} vibrations due to changes in the Ca sulfate structure. Variations in the spectra of gypsum near 2000-2500 cm^{-1} with heating correspond to water loss, consistent with the spectral properties of gypsum, bassanite and anhydrite [5].

Cryogenic-FTIR measurements were designed to establish further insights regarding interactions between gypsum and chloride salts. Gypsum is more soluble at low concentrations of $CaCl_2$ than NaCl solution [10], and this increased solubility could facilitate dehydration of gypsum, (*e.g* formation of bassanite or anhydrite) [5, 10]. Our results indicate that the spectrum of the gypsum/ $CaCl_2$ mixture at -90 °C (Fig. 3) is broader and more similar to the spectrum of H_2O ice than the spectrum of 1% $CaCl_2$ at -90 °C [8]. This could be an indicator for the presence of additional water bound to the $CaCl_2$, contributed by gypsum dehydration. This was surprising because the samples were only equilibrated for 15 min, suggesting dehydration of gypsum occurs rapidly in these conditions. Further heating of the gypsum/$CaCl_2$ mixture produced a slight elimination of the H_2O ice spectral band intensity through heating up to 25 °C, when the spectrum became more liquid-like. We should also note that H_2O ice features were observed up to 0 °C, correlating with the solubility diagram of gypsum/$CaCl_2$ mixtures at low temperatures [10]. We dried the gypsum/$CaCl_2$ mixture at 25 °C at the end of the experiment, which produced bands at 1614, 1626 and 1684 cm^{-1}, that could indicate a mixture of gypsum, bassanite, and $CaCl_2$ that needs further investigation.

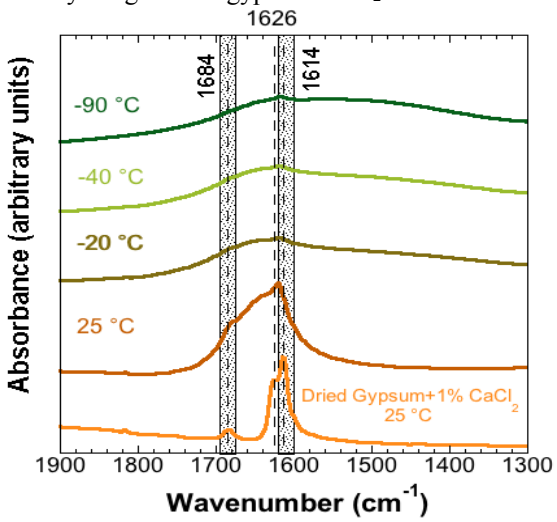

Fig. 3 Cryogenic-FTIR spectra of the gypsum+1% $CaCl_2$ mixture in the H-O-H bending region.

In contrast, the gypsum+1% NaCl mixture spectrum exhibited gypsum and H_2O ice bands at -90 °C (1616, 1640 and 1684 cm^{-1}) (Fig. 4). Following the phase diagram of NaCl, the spectral band intensities were progressively eliminated until the eutectic point of NaCl, resulting in a liquid-like spectrum from ~ -20 °C to 25 °C. After the evaporation of excess water at 25 °C, the gypsum/NaCl mixture contained spectral bands at 1616 and 1684 cm^{-1}, similar to the dried spectrum of gypsum.

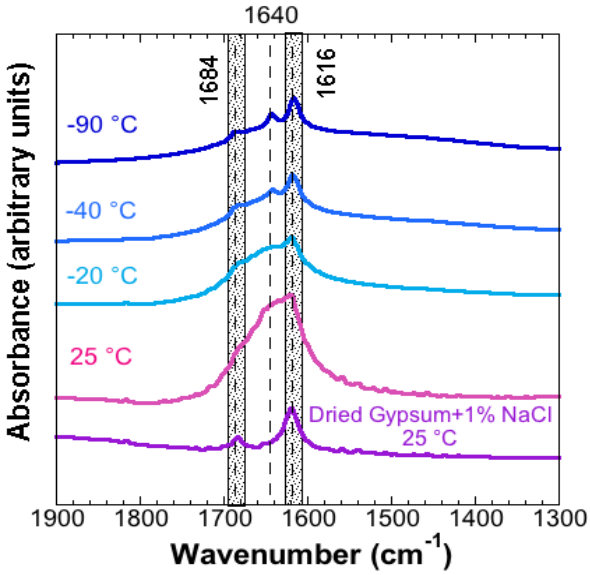

Fig. 4 Cryogenic-FTIR spectra of the gypsum+1% NaCl mixture in the H-O-H bending region.

References: [1] Murchie, S.L. et al. (2019) Ch23 in Remote Compositional Analysis, Cambridge, 453-483. [2] Langevin, Y. et. al. (2005), *Science, 307,* 1584-1586. [3] Grotzinger, J.P. et. al. (2015), *Science, 434,* 1242777. [4] Vaniman, D.T. et. al. (2018), *Amer. Min., 103,* 1011-1020. [5] Bishop, J.L. et. al. (2014) *Amer. Min., 99*, 2105-2115. [6] Lane, M. (2007), *Amer. Min., 92,* 1-18. [7] Van Susante, P.J. et. al. (2018), *AIAA,* Abstract #5292. [8] Yeşilbaş, M. and Bishop, J.L. (2020) *LPSC LI,* Abstract #2610. [9] Liu, Y. et. al. (2009) *LPSC XL*, Abstract #2128. [10] Bishop, J.L. et al. (2021) *Science Advances, 7,* eabe4459.

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