

ALTERATION OF HYDRATION ABSORPTION FEATURES IN REFLECTANCE SPECTRA OF SELECTED SULFATES IN A LOW PRESSURE ENVIRONMENT: 0.45-4.3 μm . M. Craig¹, E. A. Cloutis¹, L. Kaletzke¹, K. McCormack¹, and L. Stewart¹, ¹Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada R3B 2E9 (m.craig@uwinnipeg.ca, e.cloutis@uwinnipeg.ca).

Introduction: Spectral reflectance properties from 0.45 to 4.3 μm have been investigated for a number of mineral samples. Eight mineral samples were placed in one of the environmental simulation chambers in the University of Winnipeg's spectroscopy lab [1,2]. The eight samples and two standards spent 38 days in the chamber. Of the eight samples (three silicates, two carbonates and three sulfates), only the sulfate data are presented here, with specific focus on their hydration features and the changes seen in those features over time. Spectra for two of the three samples, gypsum and hexahydrite, are presented below. The spectra for jarosite is not included as we saw no systematic measurable difference in its spectra over the 38 days.

Experimental Procedure: Samples were crushed and dry sieved to obtain <45 μm fractions. Reflectance spectra of the samples were measured with an ASD FieldSpec Pro HR from 350-2500 nm with between 2 and 7 nm spectral resolution. A bifurcated fibre optic probe was used to provide normal incidence and emission angles. The spectra were measured relative to halon and corrected for minor irregularities in halon's absolute reflectance in the 2-2.5 μm region. A total of 2000 spectra were averaged to increase signal-to-noise ratio. Reflectance spectra from 2-4.3 μm were measured with a Designs and Prototypes Model 102F FTIR spectrometer with $i=35^\circ$ and $e=0^\circ$, and 6 wavenumber resolution, relative to brushed gold. A total of 100 spectra were averaged to reduce signal-to-noise ratio. Prior to being placed in the chamber, the samples sat for 14 days in a desiccating compartment.

Once placed in the chamber, reference spectra were measured in air (but through the sapphire window of the environment chamber). Immediately following pump down to 5 torr CO_2 (0.2 inHg, 6.7 Mb) reflectance spectra were acquired, then every day thereafter for the first 23 days in the chamber, then on average every second day for the next 15 days with the pressure reduced to 8×10^{-3} torr CO_2 (3×10^{-4} inHg, 0.1 Mb). For the last 9 of the 23 days at 5 torr, the samples were illuminated with a deuterium lamp UV source. The use of a sapphire window on the chamber allowed exposure of the samples to UV light with wavelengths as low as 200 nm. Each day of UV exposure in the lab was roughly equivalent to a decade on the Martian surface. For all spectra, the samples were chilled to 12-15°C via a forced water cooling circuit that passes through the chamber.

Results: The spectra taken in the first 23 days (5 torr) for all three samples showed no systematic measurable differences; additionally we saw no measurable difference in the spectra of the jarosite sample over the full 38 day period. The spectra of both the gypsum and the hexahydrite exhibited significant change in the appearance of their various hydration features during the 15 days at 8×10^{-3} torr. Figures 1 and 2 show the reflectance spectra for gypsum from 0.45 to 2.5 μm and 2 to 4.3 μm , respectively. Figures 3 and 4 are the spectra of hexahydrite for the same ranges.

The hydration features common to both minerals occur at ~1.4, 1.9, 2.55 and 3.0 μm ; additionally gypsum has a hydration feature at 1.75 μm not shared with hexahydrite [3]. Excepting the 3.0 μm band in hexahydrite, each absorption feature experienced a gradual decrease in depth over the 15 days at 8×10^{-3} torr. Figures 1 through 4 show only initial in-air reference spectra and the last spectra (day 38) for clarity. For the gypsum sample, band depths decreased for each major water absorption band: 1.4 μm band – from 8 to 3%, 1.75 μm band – from 4 to 0%, 1.9 μm band – from 18 to 5%, 2.55 μm band – from 30 to 16%, and 3.0 μm band – from 93 to 68%, derived via reflectance ratio (reflectance at 1.7 μm used for 1.4, 1.75 and 1.9 μm , reflectance at 2.21 μm used for 2.55 μm and reflectance at 3.8 μm used for 3.0 μm). In addition to the decrease in depths of each band, band centers also shifted subtly towards shorter wavelengths. Band depths in the hexahydrite experienced similar changes but to a lesser degree. Decreases in band depths for the hexahydrite are as follows: 1.4 μm band – from 6 to 4%, 1.9 μm band – from 16 to 10%, 2.55 μm band – from 46 to 42% (reflectance at 1.25 μm used for 1.4 and 1.9 μm , reflectance at 2.25 μm used for 2.55 μm).

Discussion: As expected, the water-associated absorption features of the gypsum and hexahydrite experienced decreases in water band depths, paralleling work done previously addressing montmorillonite at similar low pressures [4,5]. The differences in water band depth changes (slightly greater for gypsum vs. hexahydrite) can likely be attributed to differences in the mineral structures and how tightly bound the water is in each mineral. The lack of change in the spectra of the jarosite sample can be attributed to the lack of molecular water in its structure (it contains only OH); this again parallels previous work done with montmorillonite which showed no alteration of structural OH

bands [4]. The lack of change in the reflectance of hexahydrate at 3.0 μm can be attributed to the large abundance of water in the mineral; a substantial amount of water would need to be lost for the intense 3 μm water band (likely saturated) to show a measurable decrease in band depth. The band at 2.43 μm in hexahydrate as well as the bands at 2.17 μm , 2.22 μm and 2.48 μm in gypsum possibly attributable to S-O overtones [6] show changes in wavelength position and depth despite the probability that they are not hydration features. There are two possible explanations for this change: (1) exposure to low pressure has dehydrated the samples and changed their structure, which is evidenced by the visible cementation of the hexahydrate, or (2) the overriding nature of the 3.0 μm water band and its 2.55 μm shoulder.

Conclusions: Low pressure environments, such as those present on other planets and asteroids, have considerable effect on the hydration features of hydrated minerals. The alteration in hydration feature band depths and positions can make a reflectance spectrum unrecognizable when compared to the spectrum of equivalent terrestrial minerals whose spectra are measured under ambient terrestrial conditions. Alteration in hydration features can virtually eliminate less intense combination/overtone bands due to OH- or H₂O bending, stretching and rotation as well as modifying sulfate S-O bending overtones. Nine days of intense UV irradiation had no measurable effect on the spectra.

Additionally, this work raises several questions: referencing Mars at 5 torr CO₂ had little to no effect on the spectra, but lower pressures altered hydration features significantly. Therefore, do the lower pressures approximate long time periods on Mars or other planets with higher atmospheric surface pressures? And what are the effects, if any, of low pressure on other mineral classes?

References: [1] Craig M., Cloutis E., and Mueller T. (2001) *LPSC XXXII*, Abstract #1368. [2] Cloutis E. A. et al. (2006) *LPSC XXXVII*. [3] Clark R. N. et al., (1990) *JGR*. [4] Bishop J. L. et al., (1993) *LPSC XXIV*. [5] Bishop J. L., and Pieters C. M. (1995) *JGR*. [6] Bishop J. L., and Murad E. (2005) *Amer. Mineral.* 90, 1100-1107.

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Figures: Figures 1 thru 4, blue is first spectra acquired in air at ambient pressure through the sapphire

window, red is last spectra acquired in CO₂ at 8×10^{-3} torr. The inflection seen in figures 1 and 3 at 1.0 μm is a result of detector changeover in the ASD instrument.

Figure 1:

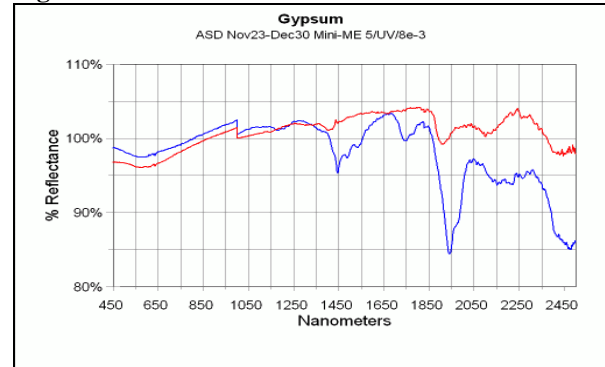


Figure 2:

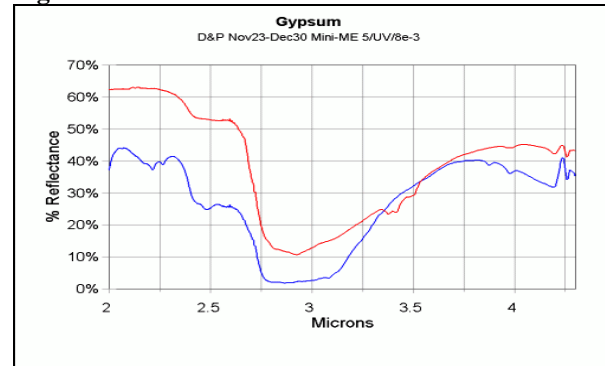


Figure 3:

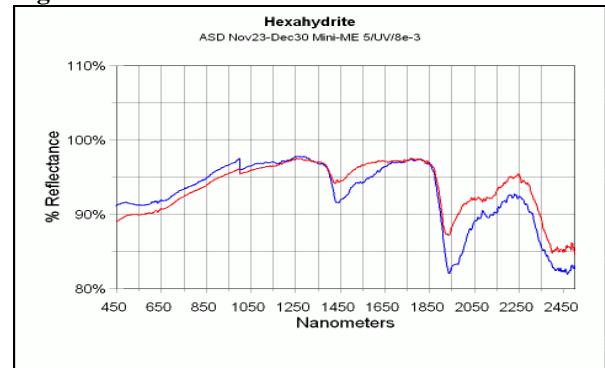


Figure 4:

