

**EXPERIMENTAL VNIR REFLECTANCE SPECTROSCOPY OF GYPSUM DEHYDRATION: CONSTRAINTS ON SULFATE COMPOSITION AT IANI CHAOS, MARS** T. N. Harrison, M. S. Gilmore, and J.P. Greenwood, Department of Earth and Environmental Sciences, Wesleyan University, 265 Church St., Middletown, CT 06459 (tharrison@wesleyan.edu).

**Introduction:** Hydrated sulfate detected by the Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) spectrometer in the Iani Chaos region was identified by [1] as either gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) based on absorptions at  $\sim 1.4$ ,  $1.75$ ,  $1.9$ ,  $2.21$ , and  $2.27 \mu\text{m}$ , and a  $2.4 \mu\text{m}$  drop in reflectance. Gypsum has also been detected in light-toned layered deposits in Juventae Chasma [1] and in dunes in the northern polar region [2]. The goal of this project is to determine whether gypsum and bassanite can be distinguished in the OMEGA data in order to identify the sulfate mineral detected in Iani Chaos. The presence of bassanite (or any calcium sulfate subhydrate ( $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ ,  $0 < n \leq 0.8$ )) could indicate desiccation of primary gypsum due to elevated temperatures, low relative humidity, or crystallization directly by evaporation of highly saline solutions [3, 4].

**Methods:** Four samples of gypsum (selenite, satin spar, alabaster, and massive, from Ward's), were ground in agate and sieved to two grain size fractions,  $63\text{--}125 \mu\text{m}$  and  $<63 \mu\text{m}$ . The samples were verified to be gypsum via VNIR reflectance spectroscopy, and size fractions were verified via SEM observation. In order to study how gypsum behaves upon dehydration, the samples were individually heated in  $15^\circ \text{C}$  increments from  $55\text{--}130^\circ \text{C}$ , plus an increment at  $92^\circ \text{C}$ , for half an hour at each temperature step. After each interval of heating, the samples were removed from the oven, weighed, and their spectra were taken using an ASD FieldSpec Pro FR. Continuum removal was performed on the spectra using ENVI 4.3 in order to measure band depths and positions. Spectra were degraded to OMEGA resolution and compared to a 3-point smoothed, averaged spectrum from Iani Chaos created from 30 OMEGA pixels from orbit 0353\_2, as well as a bassanite spectrum from [5]. The OMEGA spectral data were atmospherically corrected using the method of [6]. Each pixel was also ratioed to a dusty pixel in the same scene.

**Dehydration experiment:** Significant spectral changes were observed in each sample with increased temperature (Fig. 1). Band depths for all absorptions decreased in each sample from the beginning to the end of the experiment (Fig. 1). The  $1.75 \mu\text{m}$   $\text{H}_2\text{O}$  bending and stretching combination and absorptions in the  $2.1\text{--}2.2 \mu\text{m}$  range attributed to S-O bending overtones [7] were present in all samples until  $100\text{--}115^\circ \text{C}$ ,

at which point the bands were lost. These reductions are likely due to dehydration of the sample and are consistent with the pressure-induced dehydration observed by [8].

Major shifts in band position were observed for several bands when the samples reached temperatures of  $\sim 92\text{--}115^\circ \text{C}$ : the  $1.4$  and  $1.9 \mu\text{m}$   $\text{H}_2\text{O}$  combination and overtone bands [7] shift to shorter wavelengths (Figs. 2 and 3), and the  $3\nu_3$  S-O absorption at  $\sim 2.4 \mu\text{m}$  [7] shifted to slightly longer wavelengths, typically by  $\sim 20 \text{ nm}$ . An absorption at  $\sim 1.66 \mu\text{m}$  that was not present in the original unground gypsum samples appeared at  $55\text{--}70^\circ \text{C}$  and remained present continuously in some samples, whereas in others it appeared and disappeared at different temperature intervals.

The shift in band positions at  $\sim 100^\circ \text{C}$  is abrupt, consistent with a fundamental change in crystal structure from gypsum to calcium sulfate subhydrate. The shift in band positions at  $\sim 100^\circ \text{C}$  results in a spectrum that matches the USGS spectrum of bassanite (speclab.cr.usgs.gov), which was itself formed by the dehydration of gypsum at  $60^\circ \text{C}$  for an indeterminate amount of time. This  $\sim 100\text{--}115^\circ \text{C}$  temperature range also coincides with a peak in mass loss which we attribute to dehydration of the gypsum to calcium sulfate subhydrate. Further reduction of the depths of the  $1.4$  and  $1.9 \mu\text{m}$  bands with continued heating likely reflects water contents less than the ideal bassanite composition.

There is no consistent relationship between grain size and temperature at which the spectral changes occur in the  $1.4$  and  $1.9 \mu\text{m}$   $\text{H}_2\text{O}$  bands. The shift occurs at lower temperatures in the alabaster and satin spar samples than other samples, which may be attributable to differences in habit or bulk composition.

**Comparison to OMEGA data:** Degradation of the gypsum and calcium sulfate subhydrate spectra in our experiment to OMEGA resolution demonstrates that these minerals should be distinguishable in the OMEGA data (Fig. 4). The OMEGA spectrum from Iani Chaos differs from both typical gypsum and bassanite (Fig. 4). The OMEGA spectrum contains absorptions at  $1.75$  and  $\sim 2.17\text{--}2.22 \mu\text{m}$  that are consistent with gypsum and absent in the dehydrated samples. The width and depth of the  $1.4$  and  $1.9 \mu\text{m}$  bands in the OMEGA spectrum is also more consistent with the gypsum laboratory spectra. However, the position

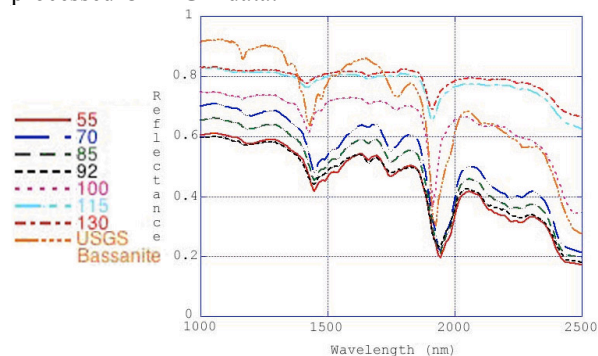
of these absorptions in the OMEGA spectrum is shifted to longer wavelengths compared to the laboratory spectrum of gypsum. The OMEGA spectrum also contains absorptions at 1.45 and 1.95  $\mu\text{m}$  that are best matched by bassanite. Based on these observations, we believe that the hydrated sulfate detected by OMEGA in Iani Chaos is either 1) a combination of gypsum and bassanite, 2) a combination of gypsum and another mineral, or 3) neither gypsum nor bassanite, but rather a calcium sulfate subhydrate.

Calcium sulfate subhydrates are generally metastable on the Earth due to high relative humidity; several studies show that gypsum readily dehydrates to calcium subhydrates under Mars like pressure and relative humidity [4, 8]. One might expect from these studies that any gypsum present at the surface is either recently created, recently exposed or has access to a continuing supply of water (such as ice or vapor from the polar caps – this may explain the persistence of gypsum in the north polar dunes [e.g., 2]). The mesa-like layered deposits in near equatorial Iani Chaos may maintain gypsum at the surface via exposure due to mass wasting. The presence of bassanite and gypsum together has been documented on Earth in Egypt, where alternating wet and dry conditions result in formation and dehydration of gypsum [9]. Calcium sulfate subhydrate, if present at Iani, could be due to three scenarios: 1) the dehydration of primary gypsum due to dessication [3, 4, 8], or 2) elevated temperature, or 3) or direct precipitation from the late stage evaporation of brines [4].

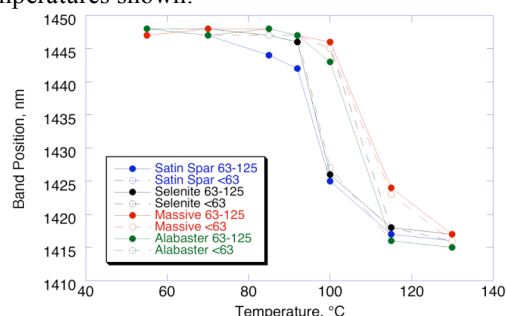
**Conclusion:** Changes in VNIR spectra indicate the gypsum dehydrates to calcium subhydrate (presumably bassanite) at temperatures of 92°- 115° C. Degradation of the resulting spectra to OMEGA resolution shows these minerals should be readily distinguished in OMEGA data. Averaged spectra from Iani Chaos are most consistent with the presence of gypsum in the outcrops there, perhaps requiring a mechanism to prevent dehydration at the surface. Calcium subhydrate features are also present in the spectrum at Iani, consistent with dehydration of primary gypsum via dessication or heating or precipitation from a late stage brine.

**References:** [1] Gendrin, A. et al. (2005) *Science*, 307, 1587–1591. [2] Fishbaugh, K. et al. (2007) *Jour. Geo. Res. Planets*, 112, E07002. [3] Peckmann, J. et al. (2003). *Facies*, 48, 241-254. [4] Vaniman, D.T. & Chipera, S.J. (2006) *Amer. Min.*, 91, 1628-1642. [5] Crowley, J.K. (1991) *JGR*, 96, 16231-16240. [6] Bibring, J.P. et al. *Nature*, 341, 591-593. [7] Cloutis, E. et al. (2006) *Icarus*, 184, 121-157. [8] Cloutis, E. et al. (2007) *Geo. Res. Let.* 34, L20202. [9] Mees, F. & De Dapper, M. (2005) *Sed. Geol.* 181, 225-229.

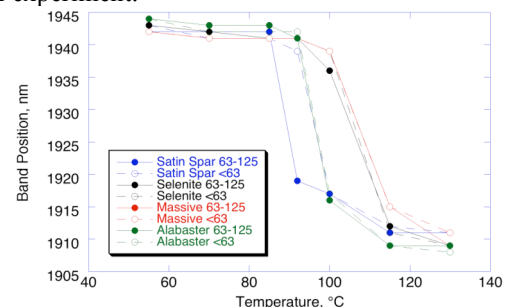
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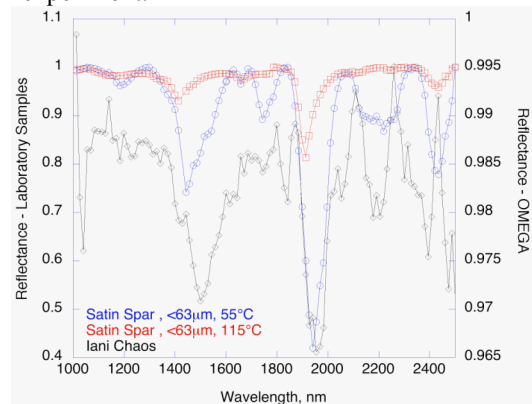
**Fig. 1:** Satin spar <63  $\mu\text{m}$  dehydration experiment. Temperatures shown.



**Fig. 2:** Behavior of 1.4  $\mu\text{m}$  band during the dehydration experiment.



**Fig. 3:** Behavior of 1.9  $\mu\text{m}$  band during the dehydration experiment.



**Fig. 4:** Comparison of laboratory spectra and OMEGA spectrum of the average of 30 pixels in Iani Chaos.