STABILITY OF PHASES IN THE $CaSO_4 \cdot nH_2O$ SYSTEM AND IMPLICATIONS FOR THEIR OCCURRENCE ON MARS. K. M. Robertson[1] and D. L. Bish[2], [1]Department of Civil Engineering and Geological Sciences, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA. [2]Department of Geological Sciences, Indiana University, 1001 E. 10th St., Bloomington, IN 47405, USA.

Introduction: Measurement and interpretation of orbital remote sensing data have been crucial in providing a global picture of the distribution of hydrated minerals on the Martian surface [1]. These data are fundamental to understanding mineralogical associations on the surface and potential H_2O fluxes between the regolith and atmosphere over diurnal and seasonal cycles. In addition, some hydrated phases may be useful paleoclimate indicators [2] and their identification could help to constrain our understanding of Martian climate history.

Calcium sulfate ($CaSO_4 \cdot nH_2O$) is a chemically simple system and serves as an example of how the presence of specific hydrated phases can be used to help constrain the local and regional distribution of water and ice under present and past conditions.

Gypsum has been inferred to exist in some Meridiani Planum and Gusev crater deposits [3] as suggested from chemical data acquired by the Spirit and Opportunity rovers. In addition, orbital data have detected large dunes in Olympia Planitia that exhibit strong gypsum spectral signatures [4]. Recently, a Ca-sulfate vein, possibly hydrothermal in origin, was identified in Endurance crater, which is of great interest as it provides definitive proof of *in situ* liquid H_2O and Ca-sulfate crystallization.

Although several occurrences of gypsum have been identified, the dehydrated forms (bassanite and anhydrite) are more elusive. It can be difficult to identify bassanite from orbital near-infrared spectral data due to the similarity of spectral features to gypsum. Recently however, bassanite was identified on the floor of the Mawrth Vallis outflow channel [5]. Bassanite is rare on Earth due to the tendency for the material to rehydrate to gypsum under conditions of 100% RH, however it may be more prevalent and persistent on Mars due to the arid and cold conditions. Such characteristics of the calcium sulfate system can be exploited and used as indicators of specific dehydration/hydration conditions on a local scale.

Experimental results are presented here that provide a clearer picture of phase stabilities in the $CaSO_4 \cdot nH_2O$ system under martian conditions that help constrain the association between observable hydrous phases and current and past climates.

Methods: X-ray diffraction (XRD) can be used to explore phase transitions and stability fields of selected sulfates through the variation of their crystal structure under specific conditions (T and %RH). A Bruker D8 diffractometer with a VANTEC-1 position-sensitive detector (Cu radiation) and Anton-Paar TTK 450 heating stage was used for all experiments. A low-temperature chiller was used with the heater to attain a wide range of temperatures (-40 - 400C). An environmental cell was placed over the stage and retrofitted with an InstruQuest V-Gen relative humidity (RH) generator to control RH from 0.1% to 95%. Control of temperature and RH allowed for the dehydration and rehydration behavior of $CaSO_4 \cdot nH_2O$ to be investigated over a wide range of P_{H2O} values (250 to 2250 Pa) under vacuum (0.15mbar) and atmospheric pressure. Dynamic heating experiments were performed at various RH conditions to observe the dehydration behavior, and dynamic hydration experiments were performed at low temperatures to observe the hydration behavior.

Results: Dehydration results (Fig. 1) show that the hydrated phases studied here are resistant to changes in hydration state driven solely by temperature-induced changes in %RH over diurnal cycles. Extrapolation of gypsum dehydration data to Mars-relevant surface conditions indicates that even under the most favorable conditions at the equator, dehydration would require ~400 days to begin. The sluggish dehydration behavior of gypsum suggests that, under the current obliquity cycle, it will act as an H_2O sink as opposed to contributing to the flux of H_2O between the regolith and atmosphere.

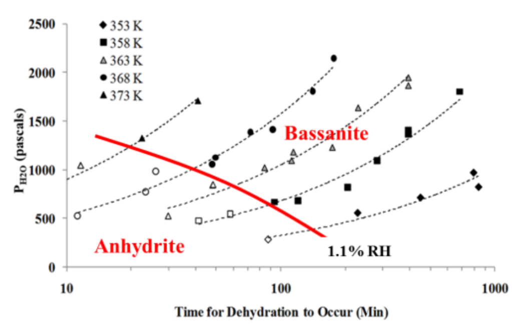

Figure 1. Dehydration results for gypsum under wide range of P_{H2O}. Bassanite (solid) is observed when dehydration occurs above 1.1%RH, and anhydrite (white) forms when dehydration occurs below 1.1%RH.

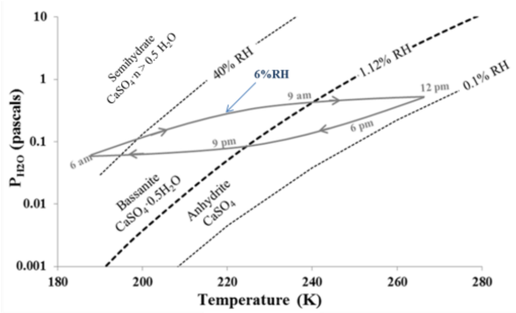

Figure 2. Diurnal T-RH cycle from the Viking 1 landing site is superimposed on the stability fields of bassanite and anhydrite.

Although unlikely under current conditions, dehydration of gypsum could have occurred during different obliquity cycles corresponding to warmer surface temperatures. Formation of bassanite or anhydrite phases could also have been associated with past impact/volcanic events, and it is not unreasonable to assume that gypsum units in and around impact craters could be dehydrated as a result of the impact process [6]. Anhydrite would be the most stable phase in areas of increased temperature, but bassanite could be metastable if RH were greater than 1.1% (Fig. 1).

Extrapolation of the bassanite-anhydrite boundary at 1.1%RH to Mars-relevant conditions (Fig. 2) indicates that bassanite would be metastable (average %RH = 6%) on the surface and would be observable at the Viking 1 lander site. In addition, excursions to both low and high %RH could result in hydration and/or dehydration of bassanite over a diurnal cycle.

Rehydration studies on the soluble anhydrite phase (Fig. 3) show that rapid hydration to bassanite hemihydrate (*n*=0.5) occurs above 1%RH and an additional transition to the bassanite semihydrate phase (*n*>0.5) occurs at ~40%RH. Subsequent dehydration at low %RH results in a stable bassanite (*n*=0.5) phase with no indication of anhydrite formation, suggesting that a diurnal cycle between bassanite and anhydrite is unlikely.

Therefore, if gypsum has dehydrated, then bassanite would be the most likely product. A bassanite phase actively cycling between the *n*=0.5 and *n*=0.67 hydration states represents a flux of 1.78 wt% H_2O between the atmosphere and the regolith (for a 100% bassanite regolith). However, the total impact of this flux is dependent on the size of the deposit, particle size, and permeability of the rock/regolith.

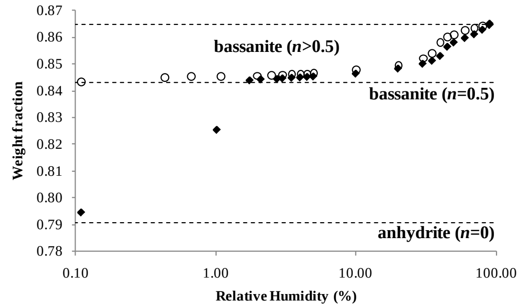

Figure 3. Gravimetric hydration results for anhydrite from 0.1%RH to 95%RH at 5°C. Anhydrite converts to bassanite above 1%RH, and then the hydration state of bassanite changes rapidly in response to %RH. Bassanite does not dehydrate to anhydrite under desiccating conditions.

Conclusions: These results show that the presence of bassanite can constrain the degree of Hydrating or dehydrating conditions of the surrounding area. Areas that experienced prolonged exposure to 100% RH (water or ice) would result in the rehydration of bassanite to gypsum, therefore the presence of a bassanite phase on the surface suggests the area did not experience such conditions for prolonged periods. In the case of dehydration from external influences (impacts/volcanism), bassanite would likely be present on exposed areas in craters, as rehydration of buried units would be restricted by diffusion rates of H_2O through rock, impact breccia, and regolith. Therefore, impact ejecta blankets could potentially display remnants of gypsum dehydration in the form of bassanite.

The upcoming MSL mission to Gale Crater will provide detailed mineralogical analysis of the martian regolith with the CheMin instrument. Although $CaSO_4 \cdot nH_2O$ phases have not been identified in Gale crater, it is not unreasonable to assume that they will be present based on the recent laboratory evidence of gypsum precipitation from hydration reactions of Ca-bearing smectite clays and sulfates [7]. Thus MSL may be able to assess paleoclimatic conditions as they relate to hydration and dehydration reactions in the $CaSO_4 \cdot nH_2O$ system.

References:[1] Bibring et al. (2005) *Science*, *307*, 1576-1581. [2] Bibring et al. (2006) *Science*, *312*, 400-404. [3] Clark et al. (2005) *Earth and Plan. Sci. Let.*, *240*, 73-94. [4] Langevin et al. (2005) *Science*, *307*, 1584-1586. [5] Wray et al. (2010) *Icarus*, *209*, 416–42. [6] Zhang and Sekine (2007) *Geo. Cosmo. Acta*, *71*, 4125-413. Wilson and Bish (2011) *Jour. Geophys. Res. 116*, E09010.