

THERMAL BEHAVIOR OF THE CALCIUM-SULFATE-H₂O SYSTEM. K. M. Robertson and D. L. Bish, Department of Geological Sciences, Indiana University, 1001 E. 10th St., Bloomington, IN 47405-1405, USA email: kevrober@indiana.edu.

Introduction: Sulfate species were verified by Pathfinder in 1997 and more recently by the Mars Exploration Rovers (MER). The best evidence for sulfates on Mars came from the Opportunity rover in Meridiani Planum, where data supporting the existence of Ca and Mg-sulfates were collected from alpha-proton X-ray spectroscopy and thermal emission spectroscopy [1,2].

Hyperspectral VNIR OMEGA images also revealed the presence of monohydrated and polyhydrated sulfates in canyon walls and mounds near Valles Marineris [3] and gypsum in northern polar regions [4]. Recent CRISM data provided much greater resolution of these alternating mono/polyhydrated layers in Valles Marineris as well as in Juventae Chasma [5]. There is, however, considerable debate as to whether or not these represent separate conditions of deposition or subsequent hydration/dehydration reactions.

In order to infer conditions of deposition and subsequent water cycles from the presence of specific phases, it is necessary to understand the kinetics of hydration and dehydration of these hydrated minerals. For example, gypsum has shown a sluggish response to desiccation in previous studies [6]. Kinetic information should allow us to determine whether specific phases were deposited in their present form or are products of subsequent dehydration/rehydration reactions. The dehydrated forms of gypsum (bassanite and anhydrite) have not been definitively identified on the surface of Mars. However, the spectral resolution of CRISM and OMEGA is not optimized to detect these dehydrated phases, which suggests that their presence cannot be ruled out.

Experimental results are presented here that provide a more thorough picture of dehydration rates in the calcium-sulfate-H₂O system. Our results suggest that gypsum desiccation will not occur over a diurnal or seasonal cycle under current martian conditions.

Methods: X-ray diffraction (XRD) allows crystallographic information to be used to explore phase transitions and stability fields of selected sulfates. The dehydration behavior of gypsum (CaSO₄•2H₂O) to bassanite (CaSO₄•0.5H₂O) and anhydrite (CaSO₄) was investigated over a pH₂O range of 250 to 2250 Pa using an Anton-Paar TTK 450 heating stage on a Bruker D8 diffractometer with a VANTEC-1 position-sensitive detector (Cu radiation). An environmental cell was placed over

the stage to control the partial pressure of H₂O (pH₂O) using an InstruQuest V-Gen relative humidity generator. Precise control of temperature and relative humidity allows the pH₂O to be varied *in-situ*, leading to greater precision in analysis of the thermal behavior of this sulfate system.

Time-dependent experiments were performed at various temperatures (70°C, 80°C, 85°C, and 90°C) and relative humidities (20% to 50%). XRD data were measured from 10-55° 2θ to encompass the strongest peaks, with data collection times of 30 minutes and 60 minutes between pattern collections. Measurements were also performed using the detector in fixed-position mode (no detector movement) to measure very short-term changes (10s-120s) as a function of temperature over a small angular range. Measurement parameters for these experiments were chosen between 28° and 34° 2θ because clear transitions between gypsum, bassanite, and anhydrite can be observed in this range. d-spacing measurements used the gypsum 041, bassanite 400, and anhydrite 200 peaks (Figure 1). These peaks were chosen as they were all in close proximity to one another to allow fixed detector scanning and had high peak-to-background ratios.

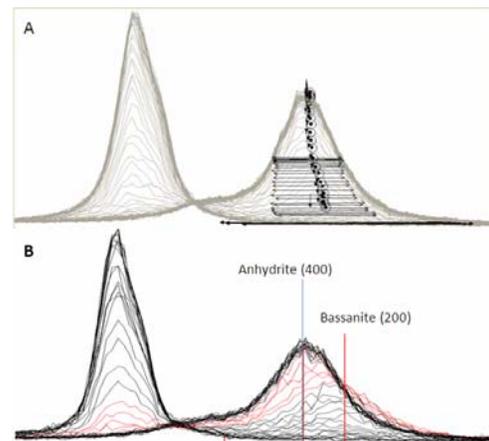


Figure 1. Effect of dehydration on the gypsum 041 peak. Significant thermal expansion was observed prior to dehydration. As dehydration began, bassanite formed and the bassanite peak slowly shifted towards anhydrite.

Results: Figure 2 shows a typical suite of patterns spanning the entire dehydration reaction over a range of 10° to 55° 2θ. The phases are labeled on the pattern with G, B, A representing gypsum, bassanite, and anhydrite, respectively.

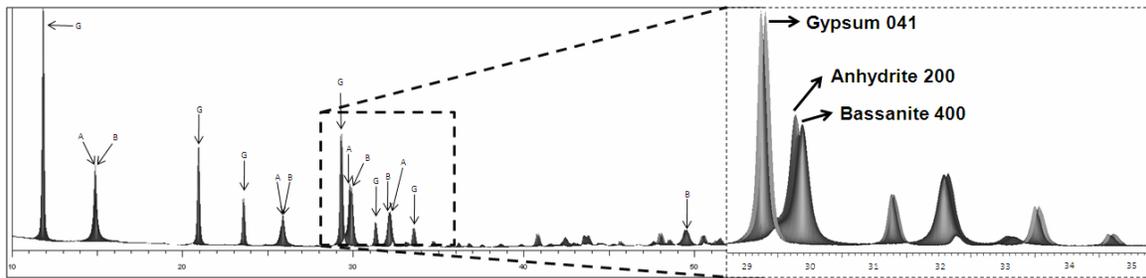


Figure 2. Example of a typical XRD pattern for gypsum, bassanite and anhydrite, with the major peaks labeled. The expanded region (stippled box) covers a 2θ range from 28° to 34° . This region was chosen for d-spacing and area measurements because peaks from all three phases are present.

Figure 3 presents the observed time in hours required to initiate dehydration of gypsum to either bassanite or anhydrite. These data do not, however, indicate the time required for dehydration to go to completion. As expected, initiation of gypsum dehydration takes longer at higher $p\text{H}_2\text{O}$. The thermal stability of gypsum increases with $p\text{H}_2\text{O}$, leading to a decrease in reactivity. With an increase in temperature, the dehydration reaction was initiated sooner, however, as lower $p\text{H}_2\text{O}$ (<500 Pa) values were approached, the differences became less significant. This is likely due to an overall decrease in the activation energy required to remove H_2O molecules from the structure.

There is an order of magnitude difference in dehydration times between 100°C and 80°C . It is possible to extrapolate to lower temperatures and $p\text{H}_2\text{O}$ to compare with the water cycle observed on Mars. Using the slopes from Figure 3, $p\text{H}_2\text{O}$ values were calculated for times of dehydration up to 4000 days. Plotting temperature as a function of $p\text{H}_2\text{O}$, it is possible to extrapolate to martian-relevant temperatures.

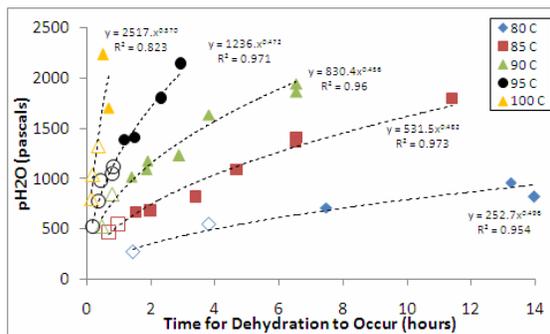


Figure 3. Dehydration time as a function of $p\text{H}_2\text{O}$ for various temperatures. Closed symbols indicate where bassanite formed, and open symbols indicate where the reaction appears to have gone straight to anhydrite.

Figure 4 shows this calibrated $p\text{H}_2\text{O}$ -T space for Mars-relevant conditions. The shaded area shows the general diurnal variations observed by the Viking lander, overlain on the P-T curves

associated with specific times for gypsum dehydration. This figure illustrates that under martian conditions, the time for initiation of gypsum dehydration ranges between 4 and 4000 days. Using average $p\text{H}_2\text{O}$ -T ranges over a diurnal cycle, it is apparent that ~ 400 days are required for gypsum dehydration to begin. This estimate does *not* include the time required for dehydration to go to completion.

As the Viking data were measured during late summer, it is reasonable to assume that dehydration times would increase over the winter season. The summer season is $\ll 400$ days so it is highly unlikely that gypsum dehydration would occur over a seasonal cycle, let alone over a diurnal cycle.

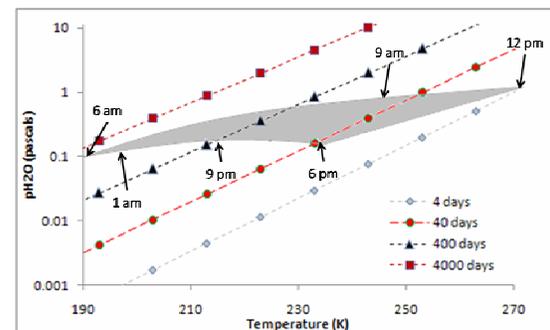


Figure 4. Temperature as a function of $p\text{H}_2\text{O}$ for various rates of dehydration. The shaded region shows the diurnal variation at the Viking landing site. Times for dehydration range from 4 to 4000 days, with an average of ~ 400 days.

References: [1] Rieder et al. (2004) *Science*, 306, 1746-1749. [2] Clark et al. (2005) *Earth and Plan. Sci. Lett.*, 240, 73-94. [3] Gendrin et al. (2005) *Science*, 307, 1587-1591. [4] Langevin et al. (2005) *Science*, 307, 1584-1586. [5] Bishop et al. (2008) *Geo. Cosmo. Acta*, 72, A86-A86. [6] Vaniman et al. (2006) *Am. Min.*, 91, 1628-1642.

Acknowledgements: This research was partially supported by a Mars Fundamental Research Program grant to DLB.