CALCIUM SULFATE HYDRATION, STABILITY AND TRANSFORMATION ON MARS. D. T. Vaniman[1], D. L. Bish[2], and S. J. Chipera[3], [1]Group EES-6, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 (vaniman@lanl.gov), [2]Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405, [3]Chesapeake Energy Corp., 6100 N. Western Ave., Oklahoma City, OK 73118.

Introduction: Hydration states of the calcium sulfate minerals have been studied extensively because of their critical applications in plasters, drywall manufacturing, slip-casting molds, medical, dental and other uses. The common forms of $CaSO_4 \cdot nH_2O$ on Earth are gypsum (n=2) and anhydrite (n=0), with rarer occurrences of bassanite ($n \cong 0.5$). This apparent simplicity belies a complex hydration system that is still poorly understood despite much study. Gypsum (monoclinic) has a layer structure with perfect cleavage parallel to (010), the plane in which H_2O molecules are coordinated between sheets of SO_4 tetrahedra. Bassanite, in contrast, is generally found to be trigonal or pseudo-trigonal/monoclinic and has chains of SO_4 tetrahedra arrayed around channels of ~4 Å diameter that contain H_2O molecules. By careful dehydration of bassanite the H_2O can be removed almost entirely, producing a hexagonal phase described in many studies as "soluble anhydrite" (AII or γ-$CaSO_4$) [1]. More aggressive and complete dehydration produces thermodynamically stable AIII "insoluble" anhydrite with Ca-SO_4-Ca chains in an orthorhombic structure.

The description above is based on extensive research that focused on studies at elevated temperatures relevant to commercial processing methods. Relevance to cold, low-pH_2O transformations that may occur near-surface on Mars is less evident. Exposure of gypsum to very low pH_2O (~0.7 Pa) at room temperature can result in >90% dehydration and formation of a water-poor bassanite with n~0.06 [2]. These conditions are similar to those that could occur on dark surfaces at the martian equator on an exceptionally warm summer day. Experiments at such conditions are not common in the literature because they have little relevance to industrial processing of gypsum to produce reduced hydrates with practical applications. Similarly, for studies of rehydration from desiccated forms, most of the literature focuses on hydration kinetics in solution because that is the method of setting plasters or cements (there is some interest in hydration from water vapor because the commercial dehydrated forms will deteriorate on exposure to high humidity, but this process has not been characterized as well). In our earlier studies of hydration from a desiccated bassanite we found that hydration from n=0.06 was rapid at vapor saturation over H_2O ice at 271 K. In this abstract we expand on these results to provide a more complete picture of how the $CaSO_4 \cdot nH_2O$ system may vary on Mars.

Methods: Samples of natural gypsum were obtained from Bingham, NM (veins of coarse selenite crystals), and from White Sands, NM (gypsum dunes). Additional studies have been done with gypsum from the Todilto Formation evaporite near Echo Amphitheater, NM, and with synthetic gypsum (<10 μm diameter and several hundred μm long) grown from saturated solutions of reagent $CaSO_4$ in deionized water. Dehydration was examined in a vacuum oven at 297 K and 323 K with pH_2O at ~0.7 Pa. Rehydration was examined with pH_2O controlled by vapor over H_2O ice at temperatures of 271 K, 243 K, and 223 K.

Results: Figure 1 shows dehydration data for the White Sands gypsum at 297 K and 323 K. Further data are being collected at lower temperature but are not yet available. Terminal H_2O content in both cases is n~0.06. A 25 K decrease in temperature resulted in an order of magnitude increase in the time required to reach terminal H_2O content. The dehydration curves in Figure 1 illustrate the effect of grain size observed with most samples. Loss of H_2O is more rapid in finer size fractions, but this effect is more pronounced at lower than at higher temperatures.
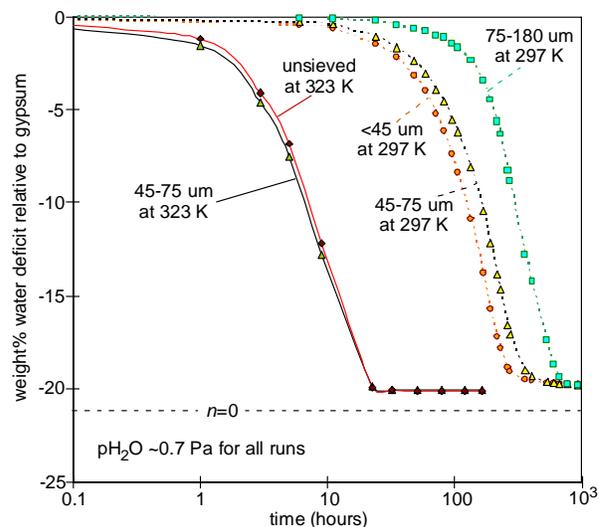

Figure 1: Dehydration of White Sands gypsum at 323 K (unsieved and 45-75 μm fraction – solid curves) and 297 K (three grain sizes – dashed curves). Dashed horizontal line represents full dehydration (n=0).

Figure 2 shows rehydration curves for several different gypsum samples at three different temperatures over H_2O ice (271 K, 243 K, and 223 K). Experiments at the two lower temperatures are ongoing and have not yet attained full rehydration to gypsum. At the two higher temperatures there is a pronounced inflection in hydration rate at a value near n~0.8; at 243 K (black curves) the hydrating samples remain near this value of n for about 1500 hours before hydrating to higher values of n. At the lowest temperature (red curves) accurate results and reproducibility were difficult because frost accumulation on sample containers was problematic, even when container blanks were used to track and correct for this problem. Thus the results shown here for hydration at 223 K are preliminary. In general, as with dehydration at low temperature, the finer size fractions change hydration state more rapidly than coarser size fractions. However, this is not true in all cases and there are some systematic differences between samples from different sources (e.g., for a given size fraction Bingham samples dehydrate and rehydrate more rapidly than White Sands samples).
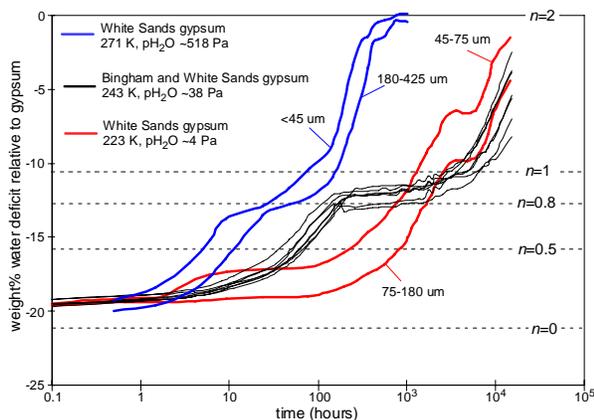

Figure 2: Rehydration of bassanite samples generated from White Sands and Bingham gypsum by desiccation at 297 K with pH_2O at ~0.7 Pa. Curves show hydration at 271 K (blue curves), 243 K (black curves), and 223 K (red curves) in vapor communication with H_2O ice. Dashed horizontal lines mark full dehydration (n=0) and various other values of n below full gypsum hydration (n=2).

Discussion: In earlier work [2] we suggested that gypsum exposed on the surface of Mars may resist desiccation even at equatorial summer conditions. Figure 1 shows that at Mars-like pH_2O, a very warm surface (24 C) will require several hours to initiate desiccation and well over 100 hours to reach terminal low H_2O content in a bassanite form. Such high tempera-

tures might be reached near dark basaltic boulders at high summer conditions but will not persist for more than a few hours. For these reasons we still consider it unlikely that surface-exposed gypsum would be desiccated to bassanite forms by such a mechanism. However, there are other ways to derive bassanite from gypsum. Possible pathways include dehydration from gypsum under other heat sources (volcanic, impact, or burial), direct precipitation in fumaroles that distribute sulfur species from volcanic or impact thermal systems, and, particularly relevant to Mars, reaction of primary calcium carbonate with sulfuric acid. The latter process has been invoked to explain occurrence of bassanite zones in the Lyme Regis area of England [3]. Given multiple potential origins and the prevalence of both acidic conditions and low pH_2O on Mars, it is possible that bassanite may be common on Mars along with both gypsum and, as a product of higher heating, anhydrite.

Figure 2 indicates relatively aggressive first-stage rehydration of dehydrated bassanite forms, even at temperatures as low as 223 K if in vapor communication with H_2O ice. If bassanite is common on Mars, hydration at various latitudes and at various soil or outcrop depths could lead to highly variable water content of $CaSO_4$-bearing occurrences. Also from figure 2, the common decrease of hydration rate at n~0.8 may indicate formation of a transitional phase unlike the commonly assumed bassanite composition of n=0.5. Computer simulations show that binding energy for H_2O in bassanite is maximized at n=0.5 [4], but there is some support in the research literature for a distinct bassanite hydration phase with n=0.8 [5]. Our observations may lend support to the validity of such a distinct form, but further work is needed.

Detection of bassanite on Mars may have implications for exobiology, for it occurs in microbial communities [6] and as a structural biomineral in deep sea medusae [7]. However, the potentially most significant occurrence of $CaSO_4$ subhydrate on Mars may be as an acid sulfate alteration product [3], marking whether and where calcium carbonate deposits once existed on the planet and providing insight into the environmental shifts that may have destroyed such deposits.

References: [1] Freyer D. and Voigt W. (2003) *Monatshefte für Chemie* 134, 693-719. [2] Vaniman D. and Chipera S. (2006) *Am. Min.* 91, 1628-1642. [3] Worku T. and Parker A. *Min. Mag.* 56, 258-260. [4] Adam C. D. (2003) *J. Solid State Chem.* 174, 141-151. [5] Abriel W. (1983) *Acta Cryst.* C39, 956-958. [6] Douglas. S. (2004) *Planet. Space Sci.* 52, 223-227. [7] Tiemann H. et al. (2002) *J. Chem. Soc., Dalton Trans.*, no. 7, 1266-1268.