

BASSANITE ON MARS. D. T. Vaniman¹, D. L. Bish², and S. J. Chipera³, ¹Group EES-14, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 (vaniman@lanl.gov), ²Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405, ³Chesapeake Energy Corp., 6100 N. Western Ave., Oklahoma City, OK 73118.

Introduction: Spectral data from orbit indicate widespread occurrence of gypsum on Mars, particularly in northern latitudes [1] and in layered deposits near the equator [2]. In prior work [3,4] we examined hydration of Mg- and Ca-sulfates ($M^{2+}SO_4 \cdot nH_2O$ where n =water content). Whereas dehydration of more hydrous Mg-sulfates may be common on Mars, the most hydrous of the Ca-sulfates (gypsum, $CaSO_4 \cdot 2H_2O$) is likely to be relatively stable even under near-equatorial surface heating at summer. Nevertheless, we have noted [4] that there are several ways to form bassanite ($CaSO_4 \cdot \sim 0.5H_2O$) on Mars. Possible pathways include dehydration from gypsum by igneous, impact, or burial processes, direct precipitation in fumaroles, and acid-sulfate alteration of primary calcium carbonate as suggested for some terrestrial occurrences [5]. Moreover, although gypsum may be stable at the surface in most occurrences, local heating in low-albedo occurrences such as basaltic sands could raise surface temperatures to a point where primary gypsum can dehydrate to form bassanite. In such situations bassanite occurrence may be an indicator of warm paleoclimates, but only if the bassanite is preserved, i.e., if it has not rehydrated to gypsum. Here we extend our previous work to address two questions: (1) once formed, is bassanite likely to remain bassanite on Mars and (2) if bassanite rehydrates to gypsum via water vapor from H_2O ice at cold martian conditions, is that gypsum identical to primary gypsum formed from solution or does it carry vestiges of its previous bassanite form?

Methods: Samples of natural gypsum were obtained from Bingham, NM (coarse selenite crystals). These samples were crushed into several size fractions and desiccated in a vacuum oven at 297 K with P_{H_2O} at ~ 0.7 Pa. Rehydration was examined with P_{H_2O} controlled by vapor over H_2O ice at temperatures of 243 K and 220 K. Products of rehydration were analyzed by X-ray diffraction (XRD) to determine phases present and by thermogravimetric analysis (TGA) to determine amount and retention parameters of water present.

Results: As noted in previous studies [3], dehydration at low P_{H_2O} and 297 K produces a desiccated bassanite rather than anhydrite or an amorphous product. The bassanite has exceptionally low water content, with ~ 0.06 waters of hydration rather than ~ 0.5 .

Figure 1 shows rates of weight increase in desiccated bassanite with P_{H_2O} controlled by H_2O ice at 243

K and 220 K. At both temperatures weight increase is rapid to $n \sim 0.8$, which is the highest water content recorded for homogeneous bassanite [6,7], but hydration rates are significantly slower beyond that point.

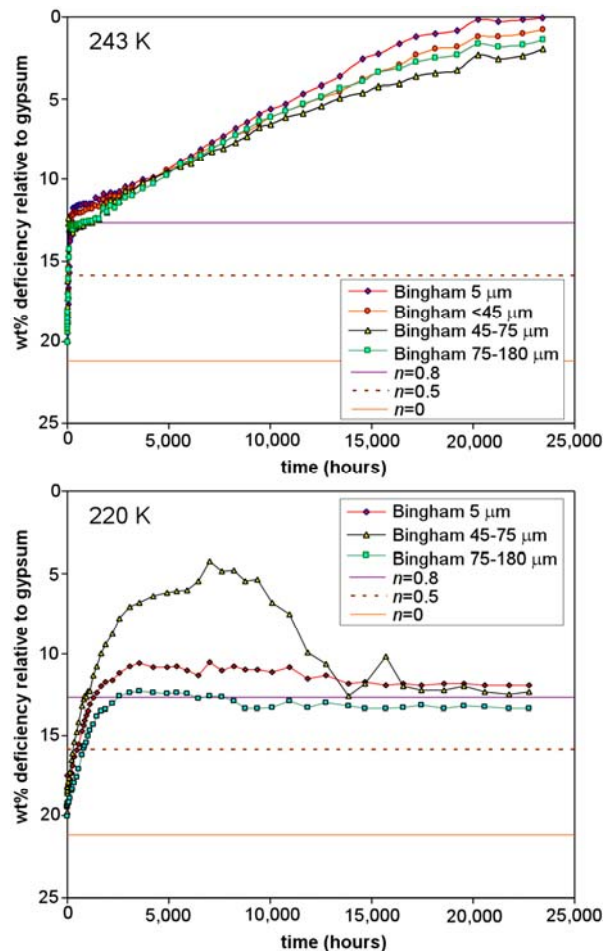


Figure 1: Rehydration of desiccated bassanite over H_2O ice at 243 K and 220 K.

Frost accumulation was insignificant at 243 K, but at 220 K initial stages of weight accumulation included frost on the sample container as well as on the sample; at later times (beyond 10,000 hours) monitored blanks showed that the frost diminishes. Major differences in rehydration between 243 K and 220 K are (1) longer time required to reach $n \sim 0.8$ at lower temperature (in fine-grained samples, 190 hrs at 243 K vs. 1000 hrs at 220 K), and (2) at 243 K the samples formed gypsum beyond $n \sim 0.8$, whereas at 220 K no gypsum formed.

Figure 2 shows differences in mineralogy for some of the terminal samples in Figure 1. No gypsum formed at 220 K (Bingham 5 μm sample in the lower panel of Figure 1) but gypsum did form in samples at 243 K. However, at 243 K even the Bingham 5 μm sample that appears to be “100% rehydrated” to gypsum (upper panel of Figure 1) retained some bassanite.

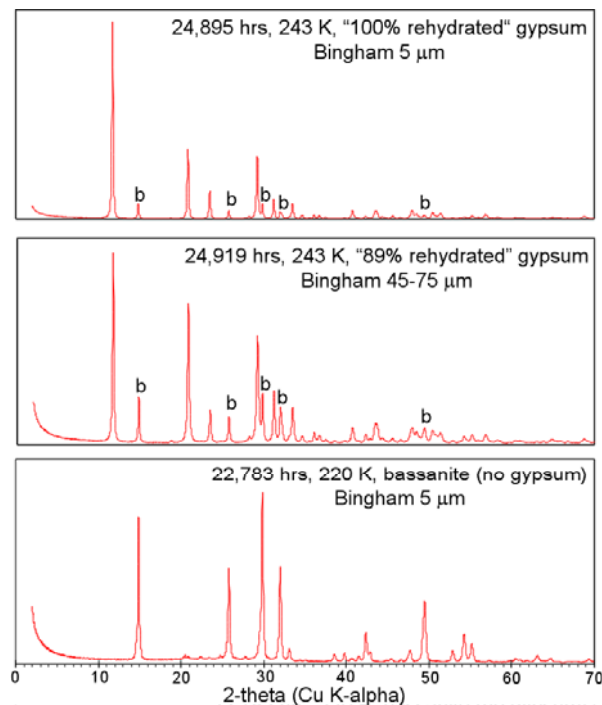


Figure 2: XRD analyses of rehydration products from desiccated bassanite. Sample at 220 K is entirely bassanite, but samples at 243 K rehydrated to gypsum plus bassanite (bassanite peaks at 243 K labeled ‘b’).

Figure 3 shows TGA analyses of the samples in Figure 2, with replicate analyses of the 220 K rehydrated sample (bassanite without gypsum) collected immediately after removal from the freezer and again after 24 hours at room conditions (295 K, 15% RH). Water content of the 243 K gypsum/bassanite samples ranged from 19.5% in the “100% rehydrated” sample to 18.4% in the “89% rehydrated” sample, below ideal gypsum (21.16% water) due to retention of bassanite.

TGA analyses of bassanite rehydrated at 220 K should indicate 9.7% water if the water content were at $n=0.8$; actual water content soon after removal from the freezer was 8.6% to 700 °C, but weight loss appeared to persist beyond this temperature. Weight loss profiles for the 220 K bassanite indicated three different structural types of water. Interestingly, water lost after 24 hours at room conditions appears to be primarily from sites where water is most strongly held. This may indicate that the structurally stronger retention at

low temperature relaxes at higher temperature. These are preliminary results; water sites in cold-hydrated bassanite are a subject of ongoing study.

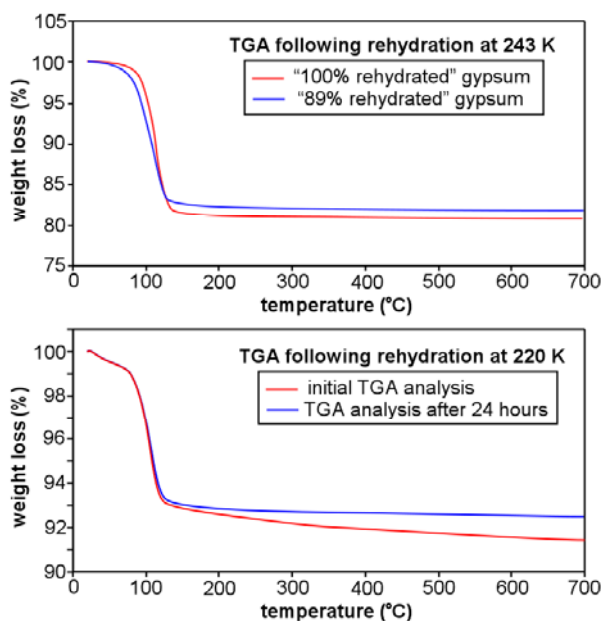


Figure 3: TGA analyses of samples from Figure 2.

Discussion: Results reported here suggest that if gypsum were desiccated on Mars, rehydration via water vapor from H₂O ice at higher temperatures may produce gypsum, but at colder temperatures more typical of Mars the product is likely to be bassanite. Even if rehydrated to values of n near 2, preservation of minor bassanite may be a clue that the gypsum is not primary and may have gone through a paleoclimate or geothermal desiccation cycle. Finally, there are several ways to form bassanite on Mars but rehydration at cold, dry conditions is more likely to retain bassanite than to form gypsum. Thus bassanite may be more common on Mars than on Earth. As one example, dark gypsum dunes at Olympia Undae provide a site where bassanite could be forming currently on Mars, for here in summer bright seasonal patches appear that are low in gypsum [8]. Summer heating of low-albedo gypsum to form local patches of bassanite may be the cause.

References: [1] Langevin Y. et al. (2005) *Science* 307, 1584-1586. [2] Gendrin A. et al. (2005) *Science* 307, 1587-1591. [3] Vaniman D. and Chipera S. (2006) *Am. Min.* 91, 1628-1642. [4] Vaniman D. et al. (2008) *LPS XXXIX*, Abstract #1816. [5] Worku T. and Parker A. *Min. Mag.* 56, 258-260. [6] Oetzel M. et al. (2000) *ZKG Int.* 53, 354-361. [7] Abriel W. (1983) *Acta Cryst.* C39, 956-958. [8] Fishbaugh K. E. et al. (2007) *JGR* 112, doi:10.1029/2006JE002862.