

**CALCIUM SULFATES AT GALE CRATER AND LIMITATIONS ON GYPSUM STABILITY.** D.T. Vaniman<sup>1</sup>, G.M. Martínez<sup>2</sup>, E.B. Rampe<sup>3</sup>, T.F. Bristow<sup>4</sup>, D.F. Blake<sup>4</sup>, A.H. Yen<sup>5</sup>, D.W. Ming<sup>3</sup>, W. Rapin<sup>6</sup>, P.-Y. Meslin<sup>6</sup>, J.M. Morookian<sup>5</sup>, R.T. Downs<sup>7</sup>, S.J. Chipera<sup>8</sup>, R.V. Morris<sup>3</sup>, S.M. Morrison<sup>9</sup>, A.H. Treiman<sup>10</sup>, C.N. Achilles<sup>7</sup>, J.P. Grotzinger<sup>11</sup>, R.M. Hazen<sup>9</sup>, J.A. Crisp<sup>5</sup>. <sup>1</sup>([dvaniman@psi.edu](mailto:dvaniman@psi.edu)) Planetary Science Institute, Tucson AZ, <sup>2</sup>U. Mich., Ann Arbor MI, <sup>3</sup>NASA JSC, Houston TX, <sup>4</sup>NASA Ames, Moffett Field CA, <sup>5</sup>JPL-Caltech, Pasadena CA, <sup>6</sup>Institut de Recherche en Astrophysique et Planétologie, Toulouse France, <sup>7</sup>Univ. Ariz., Tucson AZ, <sup>8</sup>Chesapeake Energy, Oklahoma City OK, <sup>9</sup>Carnegie Inst., Washington DC, <sup>10</sup>LPI, Houston TX, <sup>11</sup>Caltech, Pasadena CA.

**Calcium sulfates at Gale Crater:** The Mars Science Laboratory rover has been exploring sedimentary rocks of the Bradbury group and overlying Murray formation, as well as the unconformably overlying Stimson formation. Early in exploration, and continuing to present, there have been observations of many Ca-sulfate veins that cut all three stratigraphic units. The CheMin XRD instrument on Curiosity [1] provides complete mineralogy for drilled or scooped samples, with explicit identification of gypsum, bassanite, and anhydrite (crystal structure of so-called “soluble anhydrite,” or  $\gamma$ -CaSO<sub>4</sub>, is so similar to bassanite [2] that it can’t be distinguished at CheMin 2-theta resolution; here we refer to these similar dehydrated forms simply as bassanite).

Figure 1 shows gypsum, bassanite, and anhydrite abundances for all CheMin samples. Most are drill samples of sedimentary rocks, but included are scoop samples of two eolian sands and drill samples of two fracture-associated haloes in the Stimson formation. The latter samples provide information on fracture-associated mineralogy not usually obtained with CheMin, since drilling avoids fractures for engineering considerations.

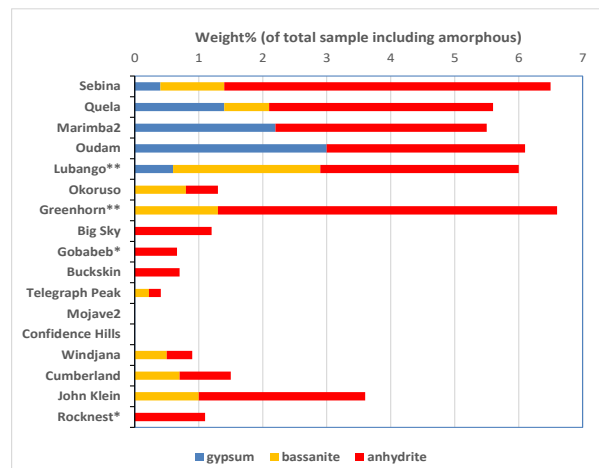


Figure 1: Ca-sulfate analyses by CheMin. Samples are of sedimentary rocks except for eolian sands (\*) and alteration haloes adjacent to open fractures (\*\*). Lubango represents an alteration halo in Okoruso, and Greenhorn a halo in Big Sky.

Samples in Figure 1 are in relative sample sequence, from the basal Bradbury group at Yellowknife Bay (John Klein, Cumberland) to a more recent sample ~160 m higher in the section (Sebina), in the Murray formation.

There are notable differences in Ca-sulfate abundances and phase associations, but interpreting these differences requires some consideration of phase stability.

**Phase transitions within the CheMin diffractometer:** CheMin is in the warm body of the rover, suspended from the rover deck. Heat from the radioisotope thermoelectric generator that charges the rover batteries is dissipated in part through the rover deck, which in summer can reach 50 °C at the warmest time of day (early afternoon). Maximum temperatures in CheMin are typically 30 °C and never less than 5 °C. Figure 2 shows thermal cycles in CheMin when the sample Oudam was analyzed.

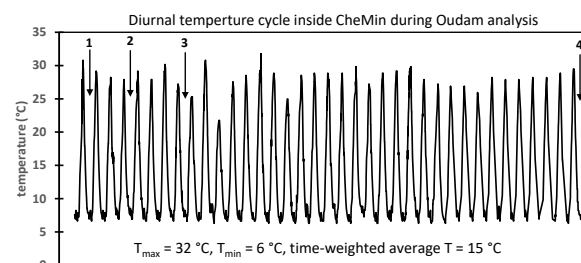


Figure 2: Analyses of Oudam (numbered 1-4) and diurnal temperature cycles in CheMin, from sol 1362 to sol 1399.

During the analysis of Oudam there was a marked loss of gypsum, with formation of bassanite, over the period that the sample was held inside CheMin (Figure 3).

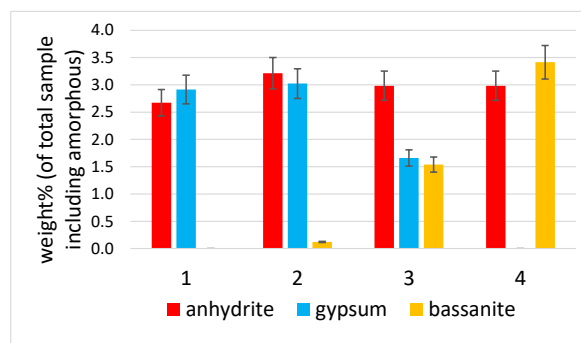


Figure 3: Gypsum, bassanite and anhydrite abundances in Oudam while held inside CheMin. Error bars are  $\pm 1$ -sigma.

Figure 3 shows that gypsum converts to bassanite at warm conditions inside CheMin. This conversion is expected from laboratory data [3]. Because gypsum is destabilized over several sols in CheMin, for samples containing gypsum we use data prior to significant gypsum

loss to determine *in situ* gypsum and bassanite abundances (Figure 1). Samples prior to Lubango did not contain gypsum, so there was no conversion of gypsum to bassanite in these.

**Maximum environmental temperatures *in situ* compared to temperatures in CheMin:** Drill samples that are delivered to CheMin come from depths of 2-6 cm (the drill bit must advance to 2 cm before cuttings enter the auger). Figure 4 shows differences in maximum summer temperature between the surface and CheMin sample depth; the surface has maximum summer temperatures ~18-40 °C warmer than the sample depth. The difference in maximum temperature between a sample *in situ* and inside CheMin is even greater ( $\Delta$  ~45-65 °C).

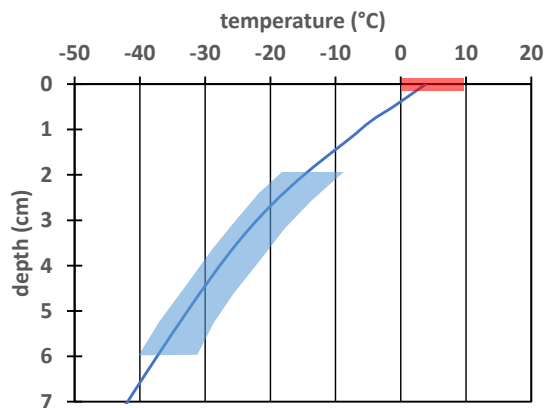


Figure 4: Model of maximum diurnal summer temperatures versus depth at Yellowknife Bay ( $L_s=234$ , blue line); maximum sedimentary rock surface temperatures observed by the MSL REMS ground temperature sensor ( $L_s=170-245$ , red); and range of maximum summer temperatures at borehole depths (2-6 cm) of CheMin samples (blue field).

Atmosphere relative humidity (RH) at midday temperatures of ~0 °C is close to 0% and must be even lower at 30 °C inside CheMin, which communicates with atmosphere through a HEPA filter. From Figures 3 and 4 it is evident that gypsum is preserved below ~2 cm and destabilized within a few sols inside CheMin. In contrast, ChemCam has collected many H analyses from Ca-sulfate veins to show that at the surface, bassanite predominates and gypsum is not observed [4]. This suggests that with extended exposure over many summers, gypsum transforms to bassanite at the surface. Perhaps gypsum was never present in the fractures, despite its occurrence in the host rock, but we consider this less likely since minor amounts of gypsum were identified in some veins by Mastcam [5], and desiccation of gypsum is the likely process that led to bassanite in fractures [4]. It has been suggested that anhydrite in the mudstone matrix represents an earlier episode, or a lower  $a_{H_2O}$  environment, relative to fractures that appear to lack anhydrite [4].

**Gypsum stability and mixed Ca-sulfate associations:** The association gypsum + bassanite + anhydrite at

Gale crater is clearly in disequilibrium, but petrogenesis of this association is uncertain. On Earth it is rare to find all three of these phases associated. However, the rare occurrences are quite varied, including fumaroles [6], cave walls [7], saline environments such as endorheic basins [8], playas [9], gypcrete [10], and possible cryoprecipitation [11]. Variability in the settings of this 3-phase assemblage does not constrain a single petrogenetic model. However, these settings are either water-starved or limited in  $a_{H_2O}$ , conditions that may guide interpretation.

*The 3-phase Ca-sulfate association may be a simple result of gypsum dehydration.* Although it's possible that the 3-phase association is a result of multiple events, such as high-temperature or high-salinity precipitation of anhydrite followed by lower temperature precipitation of gypsum that partially dehydrated to bassanite, a simpler origin is possible. In the terrestrial settings cited above, the 3-phase association can result from incomplete gypsum dehydration to anhydrite through a bassanite intermediate [e.g., 7,9]. Although bassanite can occur as an intermediate in the dehydration of gypsum to anhydrite it does not occur as an intermediate in hydration of anhydrite to gypsum [4]. The 3-phase association at Gale crater may represent slow kinetics and incomplete reaction in dehydration of original vein and matrix gypsum.

*Ca-sulfate abundances and species in the sedimentary rocks have stratigraphic significance.* CheMin did not detect gypsum until the fracture halo Lubango. Mudstone samples since Lubango have abundant Ca-sulfate and some have all three phases, similar to Lubango (Figure 1). It is possible that Ca-sulfate solutions penetrating the walls of larger fractures are related to solutions that penetrated smaller fractures and matrix in mudstones.

Lower mudstone at Confidence Hills and Mojave2 has no Ca-sulfate and may represent a relatively acidic episode in Gale crater lake(s) [12]. Here the mudstone alteration history involves Mg- rather than Ca-sulfate, even though penetrative fractures contain Ca-sulfate [13].

*Eolian sands have only anhydrite.* Eolian sands contain only anhydrite. Gypsum and bassanite are lost in eolian processing. REMS surface temperatures of dark eolian sands at Gale reach 15 °C and long exposure at this temperature may destabilize gypsum and bassanite. Anhydrite in eolian deposits may be both eroded from local sedimentary rocks and a product of gypsum and bassanite dehydration during eolian processing.

**References:** [1] Blake D. et al. (2012) *Space Sci. Rev.* 170, 341. [2] Robertson K. and Bish D. (2013) *Icarus* 223, 407. [3] Vaniman D. and Chipera S. (2006) *Am. Min.* 91, 1628. [4] Rapin W. et al. (2016) *EPSL* 452, 197. [5] Vaniman D. et al. [6] Jacobsson S. et al. (2008) *Fjölrit Náttúrufræðistofnunar* 52, 65 pp. [7] Hill C. (1979) *Nat. Spel. Soc. Bull.* 42, 126. [8] Schütt B. (1998) *Geomorph.* 23, 273. [9] Moiola R. and Glover E. (1965) *Am. Min.* 50, 2063. [10] Khalaf F. (2014) *Geoderma* 226-227, 223. [11] Englert P. et al. (2015) *46<sup>th</sup> LPSC*, Abstract #2297. [12] Rampe E. (in press) *EPSL*. [13] Nachon M. et al. (2017) *Icarus* 281, 121-136.