

**MARTIAN RELEVANCE OF DEHYDRATION AND REHYDRATION IN THE Mg-SULFATE SYSTEM.**

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**Introduction:** Evidence for sulfate salts in soils on Mars has persisted from the initial recognition of an Mg-S correlation in 1976 X-ray fluorescence data collected by Viking [1] through detection of similar Mg-S correlations at the Pathfinder landing site [2]. Results from the Mars Exploration Rover MER-B (Opportunity) at Meridiani Planum provide compelling evidence that sediments rich in Ca- and Mg-sulfate salts [3] formed on Mars by precipitation from water. Whether present within soils or sediments, sulfate salts include many hydrated species that may be significant reservoirs of water near the martian equatorial surface.

The Mg-sulfate system includes the common terrestrial minerals epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 51 wt% water), hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , 47 wt% water), and kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , 13 wt% water). Rare minerals of the series include pentahydrate ( $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , 43 wt% water), starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , 37 wt% water), and sanderite ( $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ , 23 wt% water). Other hydration states are not recognized as minerals but can be synthesized [e.g., 4]. In a companion abstract for this conference, Chipera et al. summarize data delimiting the stability field for starkeyite.

In previous work [5] we have found that hydration in the Mg-sulfate system is affected by sluggish transformations and pathway dependence. Those studies also recognized possible formation of an X-ray amorphous form of  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ , where  $n$  has persistent values slightly greater than 1. At 298 K the amorphous form can be generated within a few hours from hexahydrate at very low relative humidity (<1% RH), similar to RH at the martian equatorial surface at mid-day in summer [6]. Higher RH, up to 100%, can be attained at equatorial regions in the colder temperatures of early morning and for prolonged periods ( $\sim 2 \times 10^4$  yrs) during episodes of high obliquity [7]. The extreme range of RH variation over several timescales at the martian equatorial surface makes the hydration state of Mg-sulfate phases a matter of some interest, particularly since these minerals may hold a considerable amount of water in accessible near-surface areas where water ice should not be stable.

**Methods:** Crushed powders of hexahydrate were prepared in five size ranges (850-425  $\mu\text{m}$ , 425-180  $\mu\text{m}$ , 180-75  $\mu\text{m}$ , 75-45  $\mu\text{m}$ , and <45  $\mu\text{m}$ ). A larger split of crushed hexahydrate representing all of these size fractions was reserved and exposed to identical

conditions in order to provide portions for periodically determining mineralogy by X-ray diffraction (XRD) and for subsequent rehydration measurements. The sieved powders were weighed into thin-walled plastic containers with perforated lids, in amounts of  $\sim 0.5$  g per sample. All samples were then exposed in a vacuum chamber at  $\sim 1$  torr, 298 K, and 0.3-0.4% RH; duration of exposure was >3800 hrs (to date). The sieved splits were removed periodically to monitor weight loss; precision during weighing was within 1 mg. Portions of the reserved split were removed for XRD analysis at 8, 24, and 33 hrs.

Weight records at 3000 hrs show that the amorphous sample retains 14.5 wt% water ( $n \sim 1.2$ ). At 3000 hrs the remainder of the reserved split was removed and divided into four aliquots of  $\sim 0.2$  g weighed into thin-walled plastic containers with perforated lids; these were sealed into Teflon threaded vessels, with internal exposure to water in two vessels and to water ice in the other two vessels. These samples were held at temperatures of 297, 275, 271, and 243 K. The samples were removed periodically to monitor weight gain; precision during this weighing was within 10 mg.

**Results:** Dessiccation of hexahydrate at  $\sim 1$  torr and 0.3-0.4% RH is summarized in Figure 1. The water-loss data are shown as both wt% and as equivalent stages of water loss from  $n=6$  to  $n=0$ , where  $n$  represents the number of water molecules in the formula  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ . XRD analysis showed that the hexahydrate starting material became X-ray amorphous between 24 and 33 hrs. Weight-loss curves show little difference between the five size fractions. After rapid weight loss within the first  $\sim 10$  hours the rate of loss diminished markedly. Even after >3800 hours at 0.3-0.4% RH the value of  $n$  remains >1.

Progress of rehydration of amorphous material at 100% RH and four different temperatures is summarized in Figure 2. Rehydration is plotted as both wt% gain relative to  $n=1.2$  (hydration state of the dehydrated amorphous sample) and as equivalent stages of water gain from  $n=2$  to  $n=7$ . The samples at 297 K and 275 K, exposed to 100% RH over water, rapidly reached  $n=7$  and then began to gain surplus water as the Mg-sulfate went into solution (deliquescence). The sample at 271 K approached  $n=7$  without going into solution; at 243 K the solid sample was still rehydrating at 1100 hrs. XRD analysis of these samples will be done following completion of rehydration.

**Preliminary conclusions:** Cycling of RH from ~1% to 100% occurs presently at martian equatorial regions on a timescale of one martian day. Noon to early-afternoon temperatures are highest and correspond with lowest RH [6]; this combination of conditions favors dehydration to an amorphous state. Figure 1 shows that dehydration of highly hydrated Mg-sulfate forms can occur to at least the  $n=3$  form within 10 hours at 298 K; this loss rate will be slower at martian noonday equatorial summer temperatures of ~270 K but formation of the amorphous form is still likely to be favored over crystalline forms, because rehydration will be extremely sluggish at night-time temperatures of ~180 K when RH rises to ~100%. However, periods of high obliquity may redistribute polar ice to equatorial regions and generate prolonged episodes (~ $10^4$  yrs) of temperatures at ~220 K and 100% RH [7]. Un-

der these conditions rehydration to  $n=7$  is likely (Figure 2; conclusions dependent on further experiments at other temperatures and of longer duration). If highly hydrated Mg-sulfate minerals (epsomite, hexahydrate) formed near the equator at high obliquity, they may be preserved today if either (1) water vapor diffusion within shallow soil is diminished by low-permeability horizons or (2) depth is sufficient to maintain little deviation from the diurnal average of ~50% RH.

**References:** [1] Clark B. C. et al. (1976) *Science* 194, 1283-1288. [2] Foley C. N. et al. (2003) *JGR* 108, doi:10.1029/2002je002019. [3] Christensen P. R. et al. (2004) *Science* 306, 1733-1739. [4] Chipera S. et al. (2004) *GSA Annual Mtg. Abst.* [5] Vaniman D. T. et al. (2004) *Nature* 431, 663-665. [6] Savijarvi H. (1995) *Icarus* 117, 120-127. [7] Mellon M. T. and Jakosky B. M. (1995) *JGR* 100, 11781-11799.

