

**MAGNESIUM SULFATE PHASE EQUILIBRIA IN SIMULATED MARTIAN CONDITIONS.** L. A. Podratz<sup>1</sup>, D. L. Bish<sup>1</sup> and J. Schieber<sup>1</sup>, <sup>1</sup>Department of Geological Sciences, Indiana University, 1001 E. 10<sup>th</sup> St. Bloomington, IN 47405, lpodratz@indiana.edu, bish@indiana.edu, jschiebe@indiana.edu.

**Introduction:** Recent investigations from the Alpha-Particle X-ray Spectrometers (APXS) on board the Mars Exploration Rovers (MER) have shown that martian sedimentary rocks and surface materials can contain up to 40 wt% sulfate and up to 15 wt% Mg, with possible correlations between Mg and S [1]. OMEGA on board the ESA Mars Express mission has also detected the presence of hydrated sulfate minerals. Although these minerals cannot be identified unambiguously because many hydrated sulfates have very similar NIR spectral signals [2], they may be present in the form of evaporite minerals including those of the  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  series [3]. Minerals in the  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  series may be important in understanding the climate and hydrologic history on Mars because their hydration state is closely linked with the temperature and pressure conditions under which the minerals formed.

At  $\sim 23^\circ\text{C}$ , the mineral epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) dehydrates to form hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ) at approximately 50% relative humidity (RH) [3]. Kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) is the most stable form under very low RH [3], even under martian temperatures. Figure 1 (modified from [3]) shows the temperature dependence of this relationship. It can be seen that the reaction between epsomite and hexahydrate occurs at lower relative humidities as temperature increases.

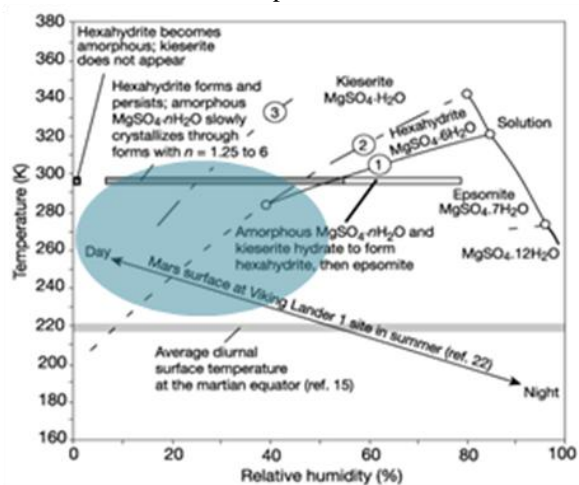


Figure 1: Magnesium sulfate phase diagram showing the stability fields of epsomite, hexahydrate and kieserite [3]. The shaded blue oval shows the region of most interest to this study. Although relative humidities can reach 100% on the martian surface, low-humidity and low-temperature conditions predominate on the surface of Mars today.

**Methodology:** In order to better understand the behavior of magnesium sulfates under simulated martian conditions, we are conducting two main types of experiments. The first set of experiment consists of X-ray diffraction (XRD) analyses conducted under controlled-temperature and RH conditions in an environmental cell. By conducting multiple analyses while keeping temperature constant and varying RH, the epsomite-hexahydrate reaction can be determined at various temperatures. Of greatest interest is the behavior of the reaction at temperatures below  $0^\circ\text{C}$ , and we are evaluating this reaction using an environmental stage on our X-ray powder diffraction instrument. The diffraction patterns of epsomite and hexahydrate are distinctly different, facilitating detection of the phase transformation. By using a very thin sample mount (so-called slurry mount), problems with diffusion of  $\text{H}_2\text{O}$  vapor can be minimized.

We are also evaluating the epsomite-to-hexahydrate reaction using a scanning electron microscope (SEM) in environmental mode (ESEM), in which the temperature is held constant and the RH is varied by changing the pressure in the chamber. As epsomite dehydrates to hexahydrate, a  $\sim 10\%$  volume loss occurs, thereby degrading the surface of the crystal. By continuously observing the appearance of the epsomite crystal, the point where dehydration occurs can be seen. Single-crystal samples were allowed to equilibrate after each decrease in humidity to account for diffusion into or out of the interior of the crystal.

The presence of the gas atmosphere in ESEM mode somewhat degrades the resolution of SEM images but the changes in crystal appearance are still clearly visible. Surface irregularities of the crystals become more apparent with decreasing humidity, after the epsomite dehydrates to hexahydrate. To see this change more clearly, videos of the dehydration process were taken and viewed at a higher speed.

Figure 2 shows SEM images taken during the epsomite-hexahydrate transition. The first image, taken under 80% RH shows relatively little etching on the crystal surface. The second image was taken under 30% RH, after the epsomite had dehydrated to hexahydrate. This etching is the result of the diffusion of  $\text{H}_2\text{O}$  out of the crystal. Further etching would occur as the mineral dehydrates to form kieserite, a low-RH phase, but the kinetics of this reaction are very slow [3].

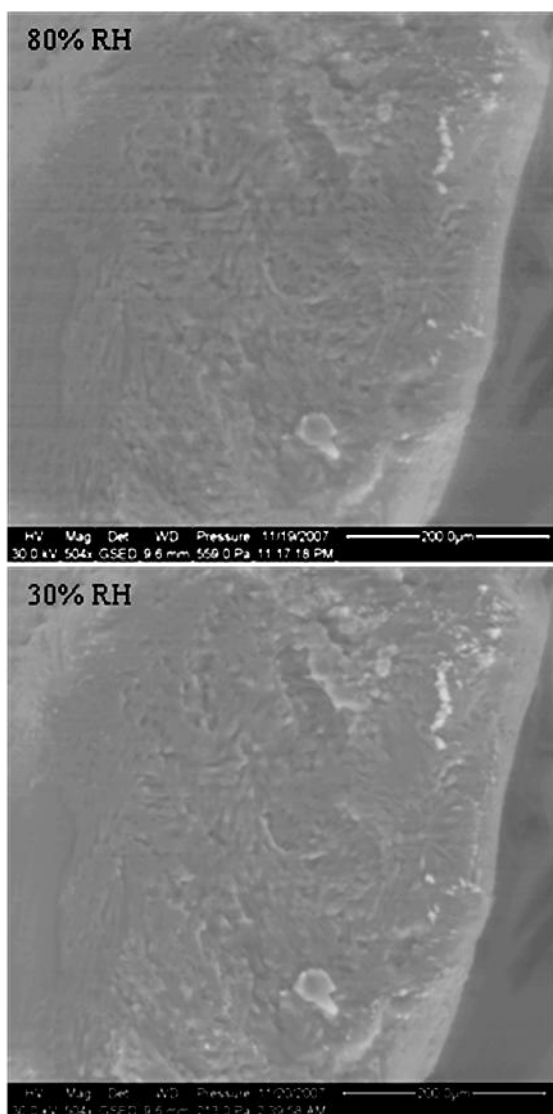


Figure 2: SEM photomicrographs taken at 2°C, 80% relative humidity (559 Pa) and 30% relative humidity (213 Pa), respectively

**Conclusions:** The results of the low-temperature XRD experiments, coupled with ESEM measurements, will further clarify the relationship between RH and the hydration state of minerals in the  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  series. In particular, these experiments will extend to lower temperatures our information on the temperature dependence of the epsomite-hexahydrate reaction.

The ESEM measurements are valuable for understanding the physical effects of dehydration reactions, and our results show degradation in the surface texture of crystals with decreasing humidity. These observations may have relevance for the interpretation of NIR spectral data measured from Martian orbiters. The empirical data from the XRD and SEM analyses, coupled with thermodynamic calculations [4, 5], can be power-

ful tools for understanding the behavior of magnesium sulfates on the surface of Mars.

The scale of surface textures seen under the SEM is partially within the resolution range of the Mars Hand Lens Imager (MAHLI) on Mars Science Lab (MSL). Thus, textural observations from the martian surface could provide evidence for a history of changing RH. Such observations could thereby yield information about the climatic and hydrologic past on Mars.

**References:** [1] Brückner J. L. et al. (2007) *7th Int. Conf. Mars*, Abstract #3120. [2] Bibring J-P. et al. (2007) *7th Int. Conf. Mars*, Abstract #3234. [3] Vaniman D. T. et al. (2004) *Nature*, 431, 663-665. [4] Zolotov M. Y. and Moronenko M. V. (2007) *JGR-Planets* 112, E07007. [5] McAdam A. C. et al. *Geochimica et Cosmochimica Acta* 70(18) A406-A406 Suppl. S.