

**EXPERIMENTAL STABILITY AND TRANSFORMATION KINETICS OF MAGNESIUM SULFATE HYDRATES THAT MAY BE PRESENT ON MARS.** S. J. Chipera<sup>1</sup>, D. T. Vaniman<sup>1</sup>, D. L. Bish<sup>2</sup>, J. W. Carey<sup>1</sup>, and W. C. Feldman<sup>3</sup>, <sup>1</sup>Group EES-6, Los Alamos National Laboratory, MS D469, Los Alamos, NM 87545 ([chipera@lanl.gov](mailto:chipera@lanl.gov)), <sup>2</sup>Department of Geological Sciences, Indiana University, 1001 E 10<sup>th</sup> St., Bloomington, IN 47405, <sup>3</sup>Group ISR-1, Los Alamos National Laboratory, MS D466, Los Alamos, NM 87545.

**Introduction:** The dominant naturally-occurring members of the  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  series on Earth are epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), and kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ). In addition, other magnesium sulfate hydrates (sanderite -  $2\text{H}_2\text{O}$ , starkeyite -  $4\text{H}_2\text{O}$ , pentahydrate -  $5\text{H}_2\text{O}$ ) have been identified as efflorescent salts in limited localities in the United States, Chile, and Germany.

Significant attention has been given to Mg-sulfate salts on Mars as they are believed to be a widespread cementing agent in martian soils and a possible contributor to near-equatorial H detected by the Odyssey spacecraft [1]. Most studies examine only the possible occurrences of epsomite, hexahydrate, and kieserite at the martian surface, on the assumption that the other  $\text{MgSO}_4$  hydrates are unstable or metastable [2]. However, other Mg-sulfates do have distinct stability fields [3]. In particular, starkeyite shows a pronounced stability field between hexahydrate and kieserite.

**Methods:** To study the stability relationships between the different Mg-sulfate hydrates, various forms of  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$  were placed over saturated salt solutions (to control humidity) at temperatures of 3, 23, 50 and 75°C. Samples chosen for this study include anhydrous  $\text{MgSO}_4$ , reagent monohydrate  $\text{MgSO}_4$  (non-kieserite structure), synthetic kieserite, synthetic starkeyite, and reagent hexahydrate. Equilibration times varied from 20 to 99 days. Initially, short runs were conducted before the significant control that kinetics exerted on the Mg-sulfate hydrate system became apparent. Longer runs are currently being conducted to further explore reaction kinetics.

To better characterize the stability field boundaries and kinetics of the reactions, in particular for the starkeyite-hexahydrate-amorphous phases, kinetic experiments were conducted using X-ray powder diffraction (XRD) and a controlled humidity system at 28°C to monitor reaction progress and rates. To conduct these experiments, a Siemens D500 utilizing Cu-K $\alpha$  radiation, incident beam Soller slits, a Kevex solid-state PSi detector and a controlled-environment cell was used. Humidity was regulated with an automated humidity-control system [4] that mixes wet and dry  $\text{N}_2$  gas using mass-flow controllers, monitored in the sample cell with a Vaisala capacitance film hygrometer for computer automation and control. Repeated XRD scans were collected from 2-70°2 $\theta$ , with-0.02° steps,

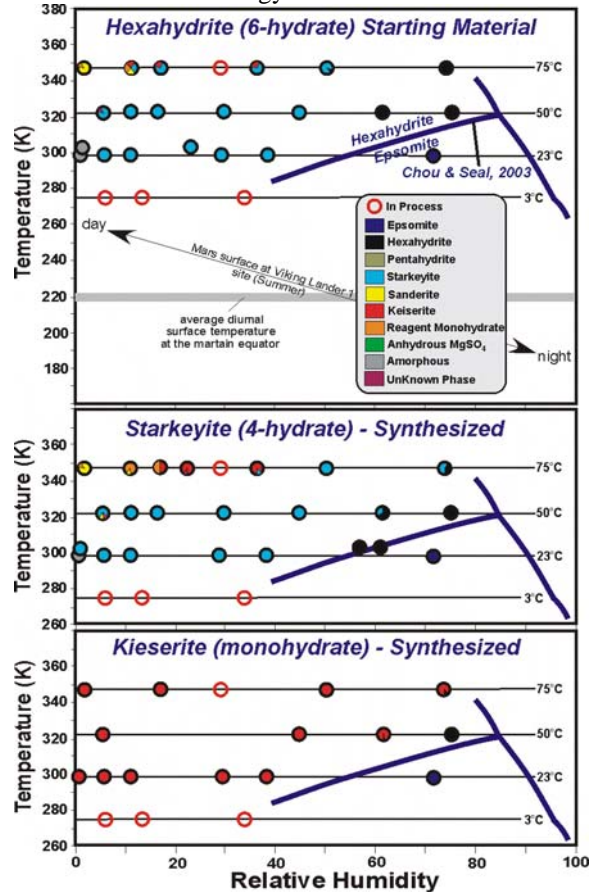
counting for 4s/step (4 hour runs) for durations of up to 11 days.

**Results:** Transformations occurring within the Mg-sulfate hydrate system are plagued by metastability, sluggish kinetics, and path dependence. With the exception of hexahydrate-epsomite, the transformation between the various species involves more than simple removal of water, requiring significant crystal structure rearrangement and consequently, activation energy barriers for reactions exist. Close to stability field boundaries, the reactions are extremely sluggish. As conditions are changed further from the stability boundaries, increased metastability can overcome the activation energy. Certain path-dependent reactions are also encountered. Mg-sulfates subjected to conditions that place them in the epsomite field first react to form hexahydrate before they transform to epsomite.

Hexahydrate and epsomite are common hydrates on the Earth's surface that occur at ambient temperatures and elevated RH. However, significant stability fields were determined in this study for starkeyite at lower relative humidities and for kieserite at elevated temperatures. Figure 1 shows the controlled humidity results using reagent hexahydrate, synthetic starkeyite, and synthetic kieserite as starting materials at various RH and temperatures. Superimposed are the hexahydrate-epsomite experimental data from Chou and Seal [2] and the summer day-night temperatures and relative humidities measured at the Viking Lander 1 site [5], to indicate where the data need to be extrapolated for Mars-like conditions. Although sanderite formed in several experiments, its stability field, if thermodynamically stable, appears to be rather limited. To date, we were only able to form pentahydrate as a metastable phase during rehydration of amorphous  $\text{MgSO}_4$  hydrate. In addition, we were able to form several  $\text{MgSO}_4$ -hydrates whose identities in X-ray diffraction analysis are uncertain, as there were no matching phases in the International Centre for Diffraction Data database.

Decreasing relative humidity or increasing temperature out of the stability field of hexahydrate produced starkeyite. Further increases of temperature resulted in the formation of kieserite. Likewise, it was found that at elevated temperatures, starkeyite also produced kieserite. Reversing the reaction with kieserite as a starting material, however, did not form

starkeyite but only formed hexahydrate when the RH and T conditions were changed to well within the hexahydrate stability region. This is a common trait seen in the Mg-sulfate system where metastable conditions overstep a stability field before they can overcome an activation energy barrier.

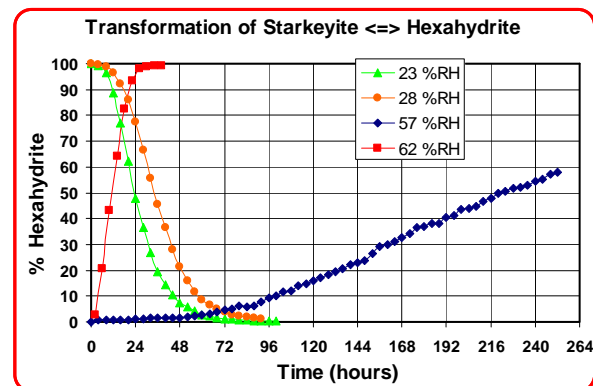


**Figure 1:** Experimental results at various %RH and temperatures for hexahydrate, starkeyite, and kieserite starting materials.

Vaniman et al. 2004 [6] found that subjecting hexahydrate to low RH (<1% RH) causes transformation to an amorphous phase within ~32 hours at 28°C. When starkeyite was subjected to low RH (<0.4% RH) for 9 days, it showed no evidence of transformation to the amorphous Mg-sulfate phase even though it did transform when placed under vacuum.

A preliminary estimate of the stability field boundary between starkeyite and hexahydrate at 23°C is approximately 45% RH. Kinetic experiments are currently being conducted to better constrain this boundary. Figure 2 shows the transformation rates between starkeyite and hexahydrate at 28°C as a function of RH. The complete transformation of hexahydrate to starkeyite at 23% RH took just over 72 hours and at 28% RH, ~another 24 hours longer. The reverse trans-

formation of starkeyite to hexahydrate at 57% RH was rather sluggish and it is projected that the transformation would take approximately 16 days. Repeating the experiment but raising the relative humidity to 62% RH (5% RH increase), the transformation took only 24 hours. By conducting these experiments at different temperatures and at numerous relative humidities, we hope to constrain the nature and position of the stability boundary between hexahydrate and starkeyite.



**Figure 2:** Rates of reaction between hexahydrate and starkeyite at 28°C and at various RH.

**Conclusions:** Results of this study show that MgSO<sub>4</sub> hydrates other than epsomite, hexahydrate, and kieserite can be stable (especially starkeyite) but under conditions not normally encountered on the Earth's surface. Unlike the sharp hexahydrate/epsomite transition, the occurrence of the other MgSO<sub>4</sub> hydrates shows considerable overlap, probably indicative of both metastability and kinetic limitations. As expected, the stable form of the MgSO<sub>4</sub>·nH<sub>2</sub>O series is significantly dependent on both RH and temperature.

Starkeyite has a pronounced stability field in the Mg-sulfate system and should not be overlooked when assessing possible Mg-sulfate minerals that can occur on Mars. It is interesting that given the extent of the starkeyite stability field, especially when forming from hexahydrate, starkeyite is not more prevalent on Earth. However, with natural terrestrial precipitation cycles, it is likely that starkeyite, when it does form, would readily dissolve into solution to precipitate as epsomite and hexahydrate.

**References:** [1] Feldman W. C. et al. (2004) *GRL* 31, doi:10.1029/2004GL020181. [2] Chou I.-M. and Seal R. R. II (2003) *Astrobiology* 3, 619-630. [3] Chipera, S. J. et al. (2004) *GSA Annual Mtg. Abst.* [4] Chipera, S. J. et al. (1997) *Advances in X-Ray Analysis*, 39, 719-721. [5] Savijarvi H. (1995) *Icarus* 117, 120-127. [6] Vaniman, D. T. et al. (2004) *Nature* 431, 663-665.