

PATHWAYS TO FORM KIESERITE FROM EPSOMITE AT MID TO LOW TEMPERATURES, WITH RELEVANCE TO MARS, John J. Freeman, Alian Wang, Bradley L. Jolliff, Department of Earth & Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 (john@levee.wustl.edu)

Kieserite on Mars: The hydrous Mg-sulfate that has been identified definitively on Mars by OMEGA (Mars Express orbiter) is kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) [1]. An additional class of OMEGA spectra has been attributed to “polyhydrated sulfate.” This class has spectral features that match Mg-sulfates of higher hydration or multi-cation sulfates [2,3]. Ca-sulfates, especially gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), are also identified in polar regions on Mars [4], but anhydrite (CaSO_4) does not possess an absorption in the OMEGA spectral region. Of interest is an apparent systematic trend in the geomorphic siting of different types of sulfates at regional and global scales on Mars [5,6,7]. Kieserite has been found mostly on steep slopes or on plateaus, whereas “polyhydrated sulfates” occur on shallow slopes or on valley floors. This trend indicates a potential commonality in the geological processes that is responsible for transitions (hydration state, etc.) between these two phases, and also between these and other co-existing phases that would be invisible to OMEGA, e.g., anhydrite. The new findings from missions demonstrate that the study of potential martian sulfates, their composition, hydration states, crystallinity, and phase transition pathways are very important to understanding the early history, hydrologic evolution, and present-day surface of Mars.

Laboratory study of Mg-sulfate: Laboratory experiments [8-16] on hydrous sulfates under well-controlled conditions provide fundamental knowledge of phase boundaries, reaction pathways, and conditions of phase transitions, which will help to interpret surface and orbital observations. The limitations of laboratory experiments include difficulties in simulating real, complex geologic processes and the extremely long durations needed for low-temperature experiments.

We have studied the stability field and phase-transition pathways of hydrous Mg-sulfates using humidity-buffer techniques and vacuum desiccation. Laser Raman spectroscopy is used

as the major analytical tool, accompanied by mass-loss measurements, XRD, and IR spectroscopy. We have done 126 experiments between 800-2500 hrs duration at three temperatures (50°C , 21°C , and 5°C) and using ten relative humidity (RH) buffers covering a RH range from 5.5% to 100%. The powdered pure samples epsomite, starkeyite, kieserite and amorphous Mg-sulfate (with two structural waters) were used as starting phases. Six samples of powdered epsomite mixed with powdered anhydrite, bassanite, and gypsum with molar ratios of Mg:Ca at $\sim 8:2$ and $\sim 4:6$ were studied at 30% RH and 50°C .

Can kieserite form by dehydration of higher hydrates? Although kieserite has been identified at many locations on Mars by orbital remote sensing, it *cannot* be formed in our experiments from the direct dehydration of epsomite, hexahydrate, or starkeyite at $5^\circ\text{C} \leq T \leq 50^\circ\text{C}$ (kieserite can be produced from dehydration of epsomite at $T \geq 75^\circ\text{C}$). Figure 1a & b shows the hydrous Mg-sulfate phases identified in the latest reaction products of our experiments based on their Raman spectra. Except for a few cases that will be discussed in later section, starkeyite is the apparent stable phase of Mg-sulfate at $5^\circ\text{C} \leq T \leq 50^\circ\text{C}$ and mid-low relative humidity $5.5\% \leq \text{RH} \leq 50\%$ (or 35% depending on T).

Starkeyite has a very stable four-member-ring substructure [17], thus additional activation energy is needed to break the ring and to form a tighter framework in the kieserite structure where all SO_4 tetrahedra and MgO_5O_w octahedra share their coordinating oxygen. It appears unlikely that temperatures high enough to provide these activation energies exist at the surface of Mars today. Therefore if the primary hydrous Mg-sulfates precipitated from aqueous solution on Mars were epsomite (or $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ at low T [18,19]), are there dehydration pathways that could produce abundant kieserite detected by OMEGA today?

1st Pathway for kieserite formation at mid to low T: Amorphous Mg-sulfate is the first pathway to form kieserite from epsomite in our experiments ($5^\circ\text{C} \leq T \leq 50^\circ\text{C}$). During the two experiments shown in

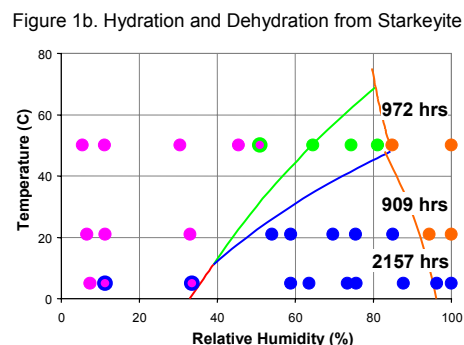
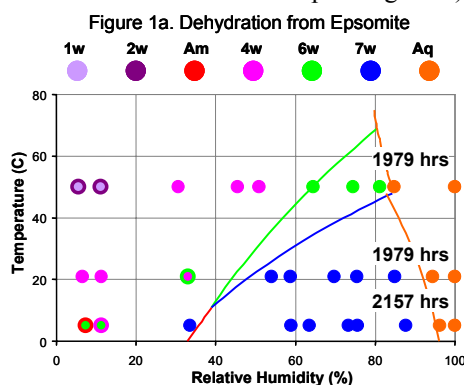
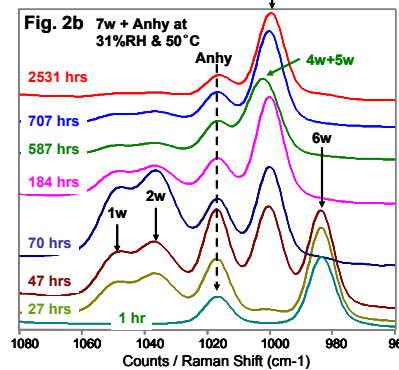
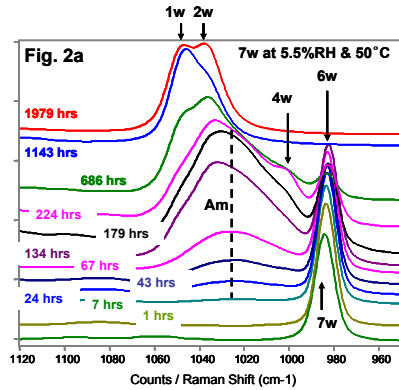


Fig. 1a at 50°C and an RH range of 5.5-11.1%, the epsomite samples first convert to amorphous Mg-sulfate, then a mixture of kieserite and sanderite appeared, and finally the entire sample converted to crystalline kieserite and sanderite. Fig. 2a shows a set of Raman spectra obtained during the entire experiment. A similar set of hydration experiments using amorphous Mg-sulfate ($\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) as the starting phase shows the same phenomenon: at 50°C and 30.5% RH after 20 hrs with samples in the humidity buffer, the amorphous Mg-sulfate gradually converted to a mixture of kieserite and sanderite (not shown). We did not observe a similar conversion in the experiments done at $T < 50^\circ\text{C}$, possibly owing to the slow reaction rates at lower temperature. For example at 5°C, we see a trace amorphous phase

formed from epsomite at low RH (7.4%) after 2157 hrs, whereas it appeared quickly after 7 hrs in the buffer at 50°C. With experiments done at 5°C and starting with amorphous Mg-sulfate, the samples converted to a mixture of starkeyite and hexahydrite at 33.6% RH or remained as the amorphous phase at lower RH. We consider that the irregular structure of an amorphous Mg-sulfate must have provided a lower energy threshold for the formation of kieserite.

2nd Pathway for kieserite formation at mid to low T: A second potential pathway to form kieserite from epsomite occurs in physical mixtures with anhydrite (CaSO_4). A set of Raman spectra in Figure 2b shows that epsomite first converts to hexahydrite, then starkeyite, sanderite, and kieserite appear together after 27.3 hrs in RH buffered samples. The increase of Raman peak intensities of kieserite and sanderite continues until 91 hrs, then decreases. Because we used a mid-RH (30.5%) for these experiments, starkeyite became the major Mg-sulfate in the mixture after 2531 hrs, and only trace amounts of kieserite, sanderite, and hexahydrite are still present. We postulate that kieserite and sanderite could become the major stable Mg-sulfates in this type of mixture if the experiments were done in a lower RH range (e.g., 5.5-11.1%, similar conditions as the two points in Fig. 1a). No Raman peak position shifts in both Mg- and Ca-sulfates, as would indicate cation substitutions (at least to a detectable level), were observed. The conditions to form stable starkeyite from epsomite are 30.5% RH at 50°C



when using pure Mg-sulfates as starting phases. In our experiments, the formation of kieserite and sanderite was not observed when epsomite and anhydrite powder samples in separate vials were placed within the same humidity buffer, or when epsomite was mixed with basanite or with gypsum powder samples. It appears that the physical contact of epsomite grains ($< 75 \mu\text{m}$ in our experiments) with those of anhydrous Ca-sulfate is required for this reaction, i.e., the surrounding anhydrite grains may provide a favorable microenvironment for the dehydration reaction.

Implications for remote sensing observations:

Amorphous Mg-sulfates can be formed from the direct dehydration of epsomite and hexahydrite, readily at $T > 0^\circ\text{C}$ or at a much slower rate when $T < 0^\circ\text{C}$ [20]. The coexistence of Ca- and Mg-sulfates is anticipated on Mars because (1) Mg^{2+} and Ca^{2+} are released from igneous minerals (especially clinopyroxene) as

a result of chemical weathering e.g., through reaction with acidic aqueous fluid; (2) Mg- and Ca-sulfates likely coexist in evaporite sequences, and their coexistence on Mars is implied by modal mineral analyses based on MER results [21,22]. Thus the essential phases for both pathways would be available on Mars, and could be involved in the origin of kieserite as a dehydration product of epsomite and $\text{MgSO}_4 \cdot 1\text{H}_2\text{O}$. It is also possible that martian kieserite was formed as part of primary evaporite deposits similar to those that occur on Earth.

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