

**PHASE STABILITIES IN THE  $\text{Na}_2\text{Mg}(\text{SO}_4)_2\text{-H}_2\text{O}$  SYSTEM AND HYDRATION/DEHYDRATION BEHAVIOR OF A NEW 16-HYDRATE PHASE UNDER MARS-RELEVANT CONDITIONS.** K. M.

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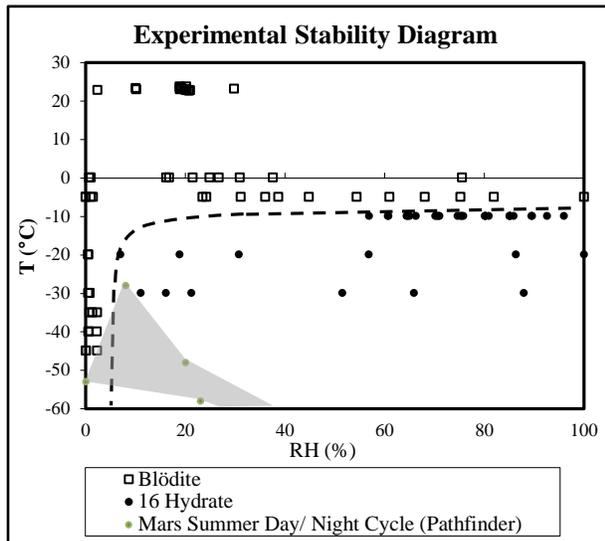
**Introduction:** With limited liquid water stability on the martian surface, hydration and dehydration of minerals with changes in temperature (T) and relative humidity (RH) during a Mars sol have the potential to influence the bioavailability of water and potentially affect the atmospheric  $\text{H}_2\text{O}$  concentration. An increasing inventory of hydrous evaporite and silicate minerals has been identified from orbital and lander data on Mars [1]. Hydrous sulfate minerals are known to be present on Mars, based on spectral, chemical, and geomorphic observations (e.g., CRISM, OMEGA, and Mars Exploration Rover results) [2]. Sulfate minerals are of particular interest on Mars due to the ability of many phases to hydrate reversibly, e.g., those in the Mg-sulfate system. Meridianiite,  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ , occurs only below  $2^\circ\text{C}$  [3] and readily dehydrates above that temperature to a less-hydrated  $\text{MgSO}_4$  phase. This study examines the hydration behavior of phases in the sodium magnesium sulfate system, predicted to occur on Mars by Clark *et al.* (1981) based on the concentration of Mg observed through X-ray fluorescence (XRF) analyses on the Viking lander [4]. King *et al.* also predicted phases in this system based on groundwater compositions of igneous rocks on Earth [5]. We examined this system under Mars-relevant T and RH conditions to determine the potential for phases in the system to participate in the martian  $\text{H}_2\text{O}$  cycle. Our experiments represent the first to describe this system's behavior under Mars-relevant conditions and are the first to describe the low-temperature 16-hydrate phase.

**Methods:** All experiments began with a natural sample of blödite from Soda Lake, CA. Blödite ( $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) is the stable hydrate at room temperature. Experiments at low temperatures ( $T < -10^\circ\text{C}$ ), gave evidence for a new  $\text{Na}_2\text{Mg}(\text{SO}_4)_2$  phase, which was investigated further via powder X-ray diffraction (XRD). The resulting data were used to define experimental stability conditions for blödite and the new phase. The structure of the low-temperature phase was subsequently solved by single-crystal XRD methods [6].

*Powder Diffraction.* Hydration/dehydration reactions were investigated using XRD under controlled RH/T conditions. These data were obtained at Indiana University in the Department of Geological Sciences using a Bruker D8 Advance diffractometer with a Vantec position-sensitive detector (Cu radiation:  $\lambda = 1.5406 \text{ \AA}$ ). This instrument is equipped with an Anton-Paar TTK 450 temperature-control stage that was utilized for measurement of non-ambient, RH- and T-controlled data to produce the experimental stability diagrams. Cooling was achieved by circulation of chilled methanol through the base of the stage, and sample temperature was held constant using the heater of the TTK stage. The stage is contained within an environmental cell that can be open to air, put under vacuum, or exposed to controlled RH. Controlled-RH conditions were generated using an InstruQuest V-Gen dew point/RH generator. Roughing-pump vacuum conditions were also used for generating low-RH conditions for low-temperature experiments. The RH for these experiments was calculated using the room  $P_{\text{H}_2\text{O}}$  (determined using room RH and T). The V-Gen RH generator is designed to be operated to RH values as low as 1%RH, although we successfully operated down to  $\sim 0.5\%$  RH. Controlled-RH conditions  $\leq 0.5\%$  at room temperature were required for experiments below  $-30^\circ\text{C}$ ; vacuum was used on both dry and humid days for these measurements.

**Results:** New diffraction peaks were first observed when blödite was exposed to  $-10^\circ\text{C}$ , and the new phase was analyzed at this temperature over a range of RH values (47-78% RH). These new peaks formed within minutes and persisted at temperatures as low as  $-123^\circ\text{C}$  (as evidenced by the single-crystal diffraction measurements [6]). As we were unable to identify any existing phase that matched these new diffraction peaks, the new peaks were interpreted to represent a new, low-temperature phase. This presumed new phase was observed under the RH/T conditions represented as black dots in Figure 1. Reaction from blödite to the new phase did not proceed to complete

transformation in any of our experiments, and the black dots in Figure 1 represent those experiments in which we observed *any* new phase. The empty boxes represent conditions under which only blödite peaks were observed. The shaded area represents RH/T conditions observed by Pathfinder [6].



**Figure 1. RH/T experimental stability fields determined with XRD.**

Time-resolved XRD measurements were also used to evaluate reaction kinetics. These measurements were conducted under fixed- $P_{\text{H}_2\text{O}}$  conditions, while decreasing T at a controlled rate. These data were used to determine the rate of reaction in much the same manner as kinetics are determined through thermogravimetric analysis (TGA). The relative concentration of blödite and the new phase used in kinetics calculations were determined with Rietveld refinement using Bruker TOPAS [7].

**Discussion:** The RH/T cycle over a Mars late-summer day as observed by the Phoenix lander in the martian north polar region [8] is represented by the shaded area on Figure 1. This area lies within the projected experimental stability field for the new 16-hydrate phase, suggesting that the 16-hydrate would be stable under martian polar conditions. Curiosity's REMS (Rover Environmental Monitoring Station) instrument has revealed diurnal ground temperature variations of 3°C to -91°C [9], a range that diurnally crosses the hydration/dehydration reaction line in Figure 1. The kinetics of these reactions are sufficiently rapid that this hydration/dehydration cycle

would occur at the equator on the time scale of a Mars sol. The reaction would be expected to occur wherever the daytime T exceeded -10°C. If phases in the  $\text{Na}_2\text{Mg}(\text{SO}_4)_2\text{-H}_2\text{O}$  system occur on Mars, as suggested by Clark *et al.* [4] and King *et al.* [5], our results show that hydration/dehydration reactions between the 4- and 16-hydrate will occur over much of the martian surface.

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