

**FORMATION OF GYPSUM AND BASSANITE BY SOLID-STATE MINERAL REACTIONS: IMPLICATIONS FOR THE BIOAVAILABILITY OF WATER ON MARS.** S. A. Wilson<sup>1</sup> and D. L. Bish<sup>1</sup>,  
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**Introduction:** Water ice is unstable at the low water-vapor pressures that prevail at near-equatorial latitudes on Mars [1, 2]. However, some of the near-surface H<sub>2</sub>O inferred from an orbital survey of H [3] is suspected to reside within hydrated minerals [2–6]. The hydrated sulfate minerals kieserite [MgSO<sub>4</sub>·H<sub>2</sub>O] and gypsum [CaSO<sub>4</sub>·2H<sub>2</sub>O] have been detected [7], and other hydrated MgSO<sub>4</sub> minerals including meridianiite [MgSO<sub>4</sub>·11H<sub>2</sub>O] and epsomite [MgSO<sub>4</sub>·7H<sub>2</sub>O] are expected to be common near the martian surface.

The hydration states of sulfates, clay minerals, and zeolites are temperature dependent and may exert significant control on cycling and bioavailability of H<sub>2</sub>O [5, 8–9]. Under water-limited conditions, these materials represent a potential source of bioavailable water and nutrients for microbial life. On Earth, saline lakes, evaporite deposits, and smectite-rich soils are inhabited by a wide variety of microorganisms. Analogous deposits on Mars may represent viable habitats for possible (extant or extinct) microbial life. However, H<sub>2</sub>O, metals, and organic molecules trapped within the crystal structure of a mineral would not necessarily be accessible to microorganisms near the martian surface.

Using experiments that employ X-ray powder diffraction (XRD), we demonstrate that solid-state reactions can occur within mixtures of hydrous sulfate minerals and smectite clays under conditions of varying relative humidity (RH) similar to those that operate at or just beneath the martian surface. Our results suggest that cycling of H<sub>2</sub>O between the atmosphere and minerals within the martian regolith could provide an unexpectedly accessible – and detectable – source of water and nutrients for possible microbial life.

**Methods:** The behavior of smectite clays, hydrated MgSO<sub>4</sub> minerals, and mixtures of these phases was investigated under variable conditions of atmospheric water activity using a Bruker D8 X-ray diffractometer equipped with a SolX energy-dispersive detector. An ambient-temperature environmental cell surrounding the sample stage was used to maintain relative humidity (RH) from 10% to 90% with an InstruQuest V-Gen RH generator. Mineral phases were identified from XRD patterns with reference to the ICDD PDF-4 database using the program DIFFRAC<sup>plus</sup> EVA 16 [Bruker AXS, Germany]. Rietveld refinements were done using the program Topas 4.1 [Bruker AXS, Germany].

*Cavity mount experiments.* Three-day long (66 h) experiments were run on powdered specimens of

montmorillonite, hydrated MgSO<sub>4</sub> minerals, and mixtures thereof contained in 1 mm depth cavity mounts. Most experiments used mixtures of 50 wt.% montmorillonite (either Clay Minerals Society source clay SAz-1 or SWy-1) and 50 wt.% MgSO<sub>4</sub>·nH<sub>2</sub>O (either kieserite or epsomite). Two specimens contained 10 wt.% synthetic kieserite (prepared according to [10]) and 90 wt.% of montmorillonite. By adding a known amount of a well-ordered internal standard material (annealed synthetic CaF<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) with known unit-cell parameters, the linear displacement of the specimen surface could be measured. This strategy permitted changes in sample volume that accompanied mineral transformations to be monitored using XRD data. Humidity-dependent changes in specimen volume, changes in mineralogy, and interlayer spacings in montmorillonite were monitored for all experiments.

XRD patterns were collected in 10% RH increments, beginning at 40% RH (near ambient), declining to 10% RH, then increasing to 90% RH, and finally returning to near-ambient conditions of 50% RH. Variability of atmospheric water activity in these experiments was similar to conditions at the Viking Lander 1 site in summer [11].

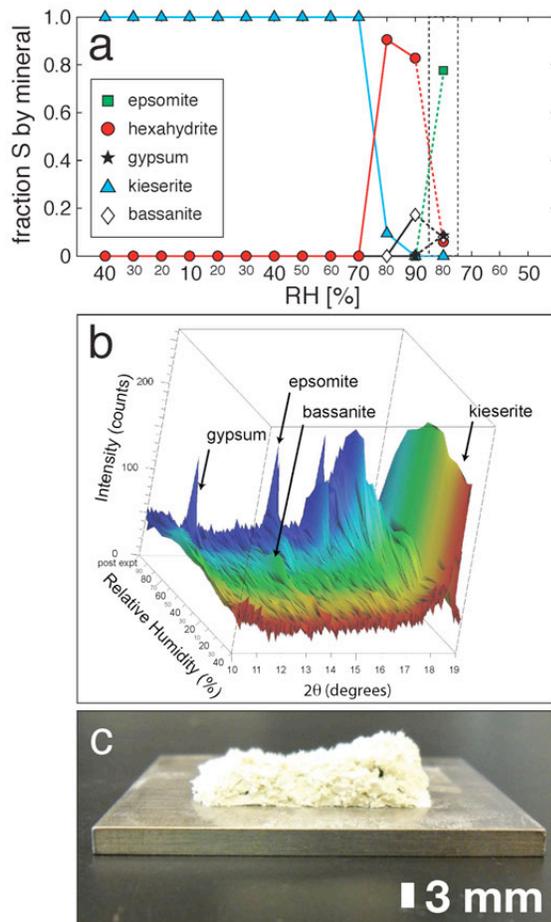
*Slurry mount experiments.* Shorter desorption-desorption experiments were done using thin slurry-mounted specimens of smectites and MgSO<sub>4</sub> minerals. Three one-day cycles (74.5 h) of desorption-desorption (instead of one three-day cycle used for cavity mounted samples) were used to reflect the length of the martian sidereal day (~24 h, 40 min).

**Results:** At high RH (>70%), gypsum formed from air-dry mixtures of Ca-montmorillonite (SAz-1) and epsomite. At 90% RH, ~10% of the epsomite in a 1:1 mixture of Ca-montmorillonite and epsomite reacted to produce gypsum within hours.

In mixtures of 90 wt.% Ca-montmorillonite (SAz-1) and 10 wt.% kieserite, bassanite [CaSO<sub>4</sub>·0.5H<sub>2</sub>O] and hexahydrate [MgSO<sub>4</sub>·6H<sub>2</sub>O] formed at the expense of kieserite at RH > 70%. Gypsum began to form at the expense of bassanite at RH ~80%. More than half of the kieserite was consumed by this reaction and sample volume increased as higher hydrates formed. The final sample height was ~130% of the initial value.

In a mixture of 90 wt.% Na-montmorillonite (SWy-1) and 10 wt.% kieserite, reactions proceeded similarly to those observed for mixtures using Ca-montmorillonite, but a dramatic increase in sample volume occurred at ~90% RH as epsomite and gypsum

began to form at the expense of hexahydrate and bassanite (Figs. 1a and b). A relative linear displacement of up to 800% was observed (Fig. 1c).



**Fig. 1.** (a) Weight-percent of total S in each mineral from Rietveld refinements. (b) XRD patterns collected during the experiment. (c) Side-view of the 9:1 mixture of Na-montmorillonite and kieserite after a three-day desorption-sorption-desorption experiment. Sample surface was originally flush with the surface of the mount.

Throughout these experiments, no significant differences were observed in the positions of the 001 and 002 reflections of montmorillonite in the mineral mixtures relative to the positions measured in a pure sample of montmorillonite. Pure samples of montmorillonite did not exhibit considerable specimen displacement due to volume increase; however, large volume increases were coincident with (1) hydration of kieserite to hexahydrate, which was accompanied by formation of bassanite, and (2) hydration of hexahydrate to epsomite, accompanied by the formation of gypsum.

Experiments that employed three one-day cycles (74.5 h) of desorption-sorption-desorption produced an increasing amount of gypsum after each day.

**Discussion:** Our experiments demonstrate the capacity of two possible components of the martian regolith, hydrated  $\text{MgSO}_4$  minerals and smectites, to react under water-limited conditions to produce hydrated  $\text{CaSO}_4$  minerals on the timescale of the martian day. The observed increase in specimen volume, which accompanies these reactions, appears to be controlled primarily by the hydration of sulfate minerals rather than smectite. Formation of  $\text{CaSO}_4$  minerals began above the deliquescence humidity of kieserite, suggesting that thin films of liquid water could be present at the grain scale [12]. Similarly, cryobrine is expected to form within pores in the regolith near the surface of Mars. This process is expected to occur by deliquescence of evaporite minerals by atmospheric  $\text{H}_2\text{O}$  vapor [13]. In our experiments, the formation of  $\text{CaSO}_4$  minerals began below the deliquescence humidity of epsomite, which is  $>90\%$  RH at  $25^\circ\text{C}$  [9–10]. At higher humidities, mixtures that initially contained kieserite are subject to considerable stresses, volume increase, and fracturing [12, 14], which should be detectable on Mars if they are a daily occurrence.

Our experimental results suggest that solid-state reactions between hydrated minerals could provide a source of bioavailable water and nutrients at or near the surface of Mars. The presence of  $\text{CaSO}_4$  minerals in association with  $\text{MgSO}_4$  minerals and smectites in the martian regolith (detectable by orbital spectroscopy) could be used to identify regions where  $\text{H}_2\text{O}$  was once or is actively being cycled between minerals. Furthermore, these reactions should be detectable using LIDAR from changes in regolith volume that would occur on the timescale of the martian day.

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