

THE DEHYDRATION KINETICS OF GYPSUM: THE EFFECT OF RELATIVE HUMIDITY ON ITS STABILITY AND IMPLICATIONS IN THE MARTIAN ENVIRONMENT. K. Robertson and D. Bish, Dept. of Geological Sciences, Indiana Univ., 1001 E. 10th St., Bloomington, IN 47405-1405, USA email: kevrober@indiana.edu.

Introduction: Increasing evidence for sulfate salts in near-surface soils on Mars has led to renewed interest in their hydration-dehydration behavior under Mars-like conditions. Hydrated sulfate salts can serve as indicators of past aqueous alteration events on Mars, as well as help understand the present water cycle.

Sulfate-bearing minerals were verified by Pathfinder in 1997 and by the Mars Exploration Rovers (MER). The most compelling evidence for sulfates on Mars has come from the MER rover Opportunity in the Meridiani Planum, where strong chemical evidence for the existence of Ca- and Mg-sulfates was provided by alpha-proton X-ray spectroscopy and by thermal emission spectroscopy [1, 2]. OMEGA orbital spectrometry has recently shown the widespread existence of gypsum in high-latitude surface soils [3] as well as in equatorial regions (Valles Marineris) [4].

The discovery by Mars Odyssey [5] of high levels of H₂O-equivalent hydrogen in the equatorial region has led to various analyses of the potential exchange of water between the martian atmosphere and hydrated salts and clays [6, 7, 8, 9]. Evidence from studies on clinoptilolite dehydration showed that zeolites maintain up to 90% hydration (20 wt% H₂O) under Mars surface conditions [9]. Ca and Na smectites were also suggested to exchange water on a diurnal cycle [8]. Calculations show that surface soils would require 30-70% hydrated silicate minerals to account for the high levels of H₂O-equivalent hydrogen. This conclusion and the apparent abundance of sulfates on the Mars surface make it likely that sulfate salts are involved in the cycling of water [5]. Although the dehydration kinetics of MgSO₄•nH₂O salts is rapid, their hydration kinetics may be too slow to allow rehydration on a diurnal cycle [6, 7]. Conditions of 100% RH on Mars during a daily cycle are fleeting and therefore conditions of desiccation may be persistent under the present level of obliquity [7]. In contrast, gypsum has shown sluggish response to desiccation, most likely due to its greater thermal stability relative to epsomite [7].

Gypsum has two confirmed dehydration products, bassanite (CaSO₄•0.5H₂O) and anhydrite (CaSO₄), but there remains debate as to the number of semihydrates that exist in the system. There have been reports of hydrates with 0.6 and 0.8

H₂O, although these hydrates are still unconfirmed [10, 11, 12].

Experimental results are presented here that revise the dehydration behavior of gypsum under varying relative humidity. Our results suggest that diurnal variations in relative humidity will have a strong control on the dehydration of Ca-sulfate minerals.

Methods: Powder X-ray diffraction (XRD) measurements of gypsum (alabaster) samples were performed using an Anton-Paar TTK 450 heating stage on a Bruker D8 diffractometer with a VANTEC-1 position-sensitive detector (Cu radiation). Time-dependent experiments were performed at various temperatures (70°C, 80°C, 85°C and 90°C) using cavity mounts as well as thin slurry mounts. Data were measured from 10° - 55° 2θ to encompass the strongest peaks, with collection times of 30 minutes and 60 minutes between pattern collections. Measurements were also performed using the detector in fixed mode (no detector movement) to measure very short-term changes (1-2 min) as a function of temperature.

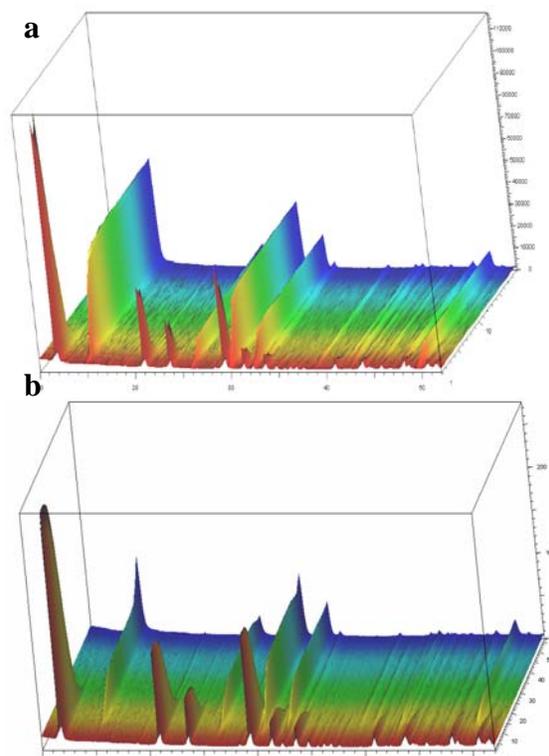


Figure 1. a) Dehydration of gypsum at 85 °C and 17.6% RH. Reaction starts in <1 hr and is complete after 5.6 hr. b) Dehydration of gypsum at 85 °C and 47% RH. Reaction starts after 6.6 hr and is close to completion after 50 hr.

Measurement parameters for the fixed-scan experiments were chosen between 28° and 34° 2θ because clear transitions between gypsum, bassanite, and anhydrite can be observed in this angular range. Experimental temperatures ranged from 23°C to 115°C , with an increment of 2°C . Relative humidities for all experiments varied from 20% to 50%, measured at 22.5°C .

Results: Figure 1 compares two time-dependent dehydration reactions of gypsum under different relative humidities at atmospheric pressure. As expected, the initiation of dehydration for gypsum takes longer at higher relative humidities. The thermal stability of gypsum increases with relative humidity, leading to a decrease in reactivity. Interestingly, the higher relative humidity run shown in Fig. 1b shows that the bassanite phase plateaued after 20 hr and then continued to dehydrate to anhydrite after 40 hr.

Figure 2 shows the same pattern as in Fig. 2b but from 28° to 35° 2θ . The bassanite phase

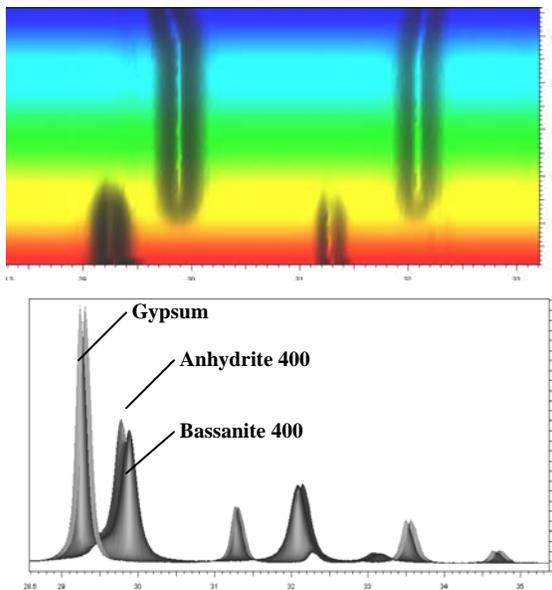


Figure 2. Dehydration of gypsum at 85°C and 47% RH, pattern is between 28° and 35° 2θ . Dehydration to bassanite occurs initially and then completely dehydrates to anhydrite.

remained stable under these conditions for another 20 hr before dehydration continued to anhydrite.

The kinetics of dehydration at 47% RH were considerably slower, to the point where intermediate phases such as bassanite were observed. However, formation of bassanite was not observed in the experiments at lower relative humidities as a consequence of slower reaction kinetics.

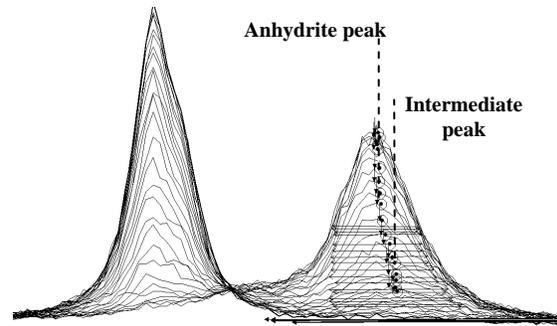


Figure 3. Dehydration of gypsum at 32.5% RH from 25°C to 115°C . The measured peak positions (circles) indicate a mixture of bassanite and anhydrite phases.

The temperature-dependent experiments in fixed-detector mode revealed that a bassanite phase may form even in low relative humidity environments. Ramping the temperature from 23°C to 115°C while making 10-sec fixed scans every 2°C increases the temporal resolution for rapid phase changes. In the case of bassanite, phase formation was initiated, but continued dehydration to anhydrite masked its presence.

An intermediate peak exists between the bassanite 400 peak and anhydrite 400 peak shown in Figs. 2 and 3, most likely representing a mixture of the two phases. The bassanite phase forms shortly before the occurrence of the anhydrite transition, creating the coexistence of both phases. The position of this intermediate peak shifts towards the anhydrite 400 peak as bassanite continues to dehydrate to anhydrite. This will be evaluated through the use of Rietveld methods.

There is a strong humidity dependence of the dehydration of gypsum, and effect on the dehydration kinetics has direct implications in a Martian like atmosphere. The sluggish dehydration behavior of gypsum at high relative humidities indicates that it may resist desiccation in the present diurnal relative humidity cycle on Mars.

References: [1] Rieder et al. (2004) *Science*, 306, 3, 1746-1749. [2] Clark et al. (2005) *Earth and Plan. Sci. Let.*, 240, 73-94. [3] Langevin et al. (2005) *Science*, 307, 1584-1586. [4] Gendrin et al. (2005) *Science*, 307, 1587-1591. [5] Feldman et al. (2004) *Jour. Geophys. Res.*, 101, E09006. [6] Vaniman et al. (2004) *Nature*, 431, 663-665. [7] Vaniman et al. (2006) *Am. Min.*, 91, 1628-1642. [8] Bish et al. (2003) *Icarus*, 164, 96-103. [9] Fialips (2005) *Geochim. et Cosmochim. Acta*, 69, 2293-2308. [10] Putnis et al. (1990) *Min. Mag.*, 54, 123-128. [11] Lager et al. (1984) *Am. Min.*, 69, 910-919. [12] Bezou et al. (1995) *Jour. Sol. State Phys.*, 117, (1), 165-176.