

HYDRATION EXPERIMENTS AND PHYSICAL OBSERVATIONS AT 193 K AND 243 K FOR Mg-SULFATES RELEVANT TO MARS. D. T. Vaniman, S. J. Chipera, and J. W. Carey, Group EES-6, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 (vaniman@lanl.gov) LA-UR-06-0127

Introduction: In a companion abstract [1] Chipera et al. discuss dehydration in the Mg-sulfate system and the likely occurrence of complex metastable hydrates in this system on Mars. The Mg-sulfate system can have highly variable values of n in the formula $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$, with common terrestrial values of 7 (epsomite), 6 (hexahydrate), and 1 (kieserite). Chipera et al. [1] point out the propensity for multiple metastable forms under dehydration (at least 10 species with different values of n , including polymorphs of $n=1$). In addition, at low pH_2O , amorphous forms appear with low values of n dependent at least in part on temperature of desiccation, with higher n at lower temperature for a given pH_2O [2]. In this abstract we consider hydration pathways for two forms with low n values, amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ and kieserite.

Methods: Amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ was prepared from Alfa Aesar Puratronic reagent by exposing synthesized epsomite to ~ 0.5 torr at ~ 0.7 Pa pH_2O for 1 month at 37°C ($n=1.1$) or for 4 months at 24°C ($n=1.25$). Kieserite ($n=1$) was synthesized from Fisher Scientific magnesium sulfate anhydrous reagent by placing aliquots in a sealed Teflon vessel over a saturated salt solution of SrCl_2 at 75°C for 1 month. Purity of kieserite or amorphous products was confirmed by X-ray diffraction (XRD). Hydration of kieserite and the $n=1.1$ amorphous form was tracked by weight gain over pH_2O vapors fixed at 100% RH by water ice at 193 K ($\text{pH}_2\text{O} \sim 0.1$ Pa) and 243 K ($\text{pH}_2\text{O} \sim 38$ Pa) in two ScienTemp research freezers. Container blanks were monitored to evaluate weight gains attributable to frost accumulation on the containers. Multiple aliquots of ~ 150 mg were exposed to hydration at both temperatures; aliquots were removed periodically for analysis by XRD. At the time this abstract was prepared, rehydration had been monitored for over 4000 hours.

In a separate experiment, hydration rates for size fractions of the amorphous form with $n=1.25$ were monitored at the 243 K, $\text{pH}_2\text{O} \sim 38$ Pa conditions.

Results: Amorphous and kieserite samples exposed to hydration at 193 K showed small weight gains of $\sim 2\%$ (corrected for weight gain due to frost accumulation on the containers), reaching a maximum at ~ 1000 hours with little weight gain beyond that time. XRD analysis showed no production of more hydrous crystalline forms in either the amorphous or kieserite starting materials. Blank containers at these conditions

gained $\sim 5\%$ weight; all weight gain at 193 K can be attributed to frost accumulation alone.

In contrast, amorphous and kieserite forms hydrated at 243 K showed much more rapid weight gain, with the amorphous form hydrating more rapidly than the kieserite. Rapid hydration of amorphous forms relative to kieserite is in accord with prior experiments [2,3]. Figure 1 summarizes hydration weight gains for the amorphous form (black curve) and kieserite (red curve). Tick marks along the weight-gain curves indicate the increase in integral waters of hydration (n) beginning with a starting hydration of $n=1.1$ (amorphous) and $n=1$ (kieserite). If stepwise crystallization from one crystalline hydrous form to another were occurring, XRD analyses of periodically analyzed aliquots would show a transition from either the amorphous form or the kieserite to sanderite ($n=2$), starkeyite ($n=4$), pentahydrate ($n=5$), hexahydrate ($n=6$), and finally epsomite ($n=7$) (note that there is no documented crystalline form with $n=3$).

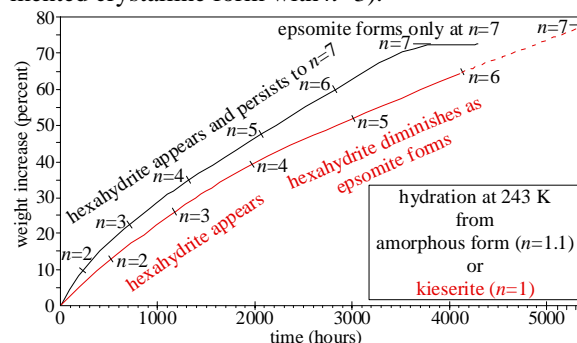


Figure 1: Hydration curves for amorphous Mg-sulfate hydrate (black curve) and kieserite (red curve) at 243 K. Hydration is from vapor at $\text{pH}_2\text{O} \sim 38$ Pa. Mineral forms determined by periodic XRD analysis are indicated for both curves. Dotted line indicates anticipated change projected to experiment completion.

The XRD data collected for the hydration pathways in Figure 1 show that none of the crystalline forms with $n < 6$ appear. Instead, the first crystalline form to appear even at $n \ll 6$ is hexahydrate, both in incipient crystallization of the amorphous form and in recrystallization of kieserite. This contrasts with the complex appearance of many intermediate hydrates seen on dehydration of hexahydrate at low pH_2O [1].

Following the first appearance of hexahydrate, crystallization pathways of kieserite and amorphous samples differ. The amorphous material changes by gradual reaction of the amorphous form to hexahydrate; only at $n=7$ does epsomite appear as the hexahydrate transforms to this more hydrous phase. Kieserite, on

the other hand, transforms to hexahydrate initially but the hexahydrate is joined by epsomite early on; at mid-hydration both kieserite and hexahydrate diminish as epsomite appears and increases. In hydration-recrystallization of kieserite the sample is converted largely to epsomite well before the $n=7$ stage is attained.

Elsewhere we reported that cementation and expansion occurs on hydration of desiccated clay – Mg-sulfate mixtures [4]. Here we find that pure forms of amorphous hydrate and kieserite differ physically during hydration at 243 K (at 193 K, powders of both show no change). Figure 2 shows amorphous (A) and kieserite (B) samples after 4000 hours of rehydration over water ice at 243 K. Kieserite forms cemented crusts that expand against the walls of their containers and push up their lids. Linear expansion in the kieserite samples, at almost complete hydration to epsomite, is ~12%. This mode of cementation and expansion differs from that observed in the amorphous precursors of comparably low initial n ; in those samples the amount of linear expansion is greater (~19% [2]) but the individual grains do not adhere to form a crust.

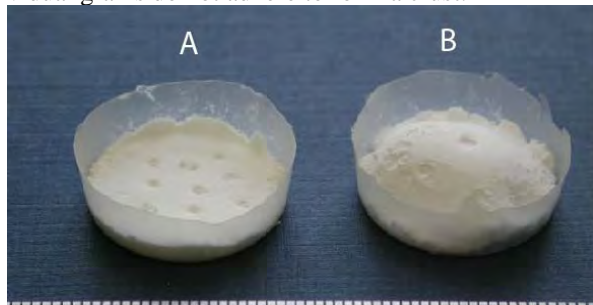


Figure 2: Amorphous Mg-sulfate (A) and kieserite (B) rehydrated for 4000 hours at 243 K. The amorphous precursor, now largely hexahydrate, remains a loose powder. The kieserite precursor has recrystallized to a mixture of hexahydrate and epsomite with minor remnant kieserite; this mixture has cemented into a friable crust that has expanded to push up the lid of the container (removed for photography). The dimpling on the samples is due to perforations in the container lids. Scale is in mm.

Implications: Kieserite resists desiccation at Mars surface temperatures [2,3], but at temperatures at least as low as 243 K it will hydrate to epsomite if water ice is present. Should kieserite be eroded from sediments at lower latitudes where ice is rare and transported to higher latitudes, its survival is unlikely and epsomite will be the likely product. Conversely, if epsomite or hexahydrate is transported from higher to lower latitudes, a dehydrated amorphous product will form – reversion to kieserite will not occur [3]. The effective mode of transport at present on Mars is eolian, where particles of silt size and finer are particularly mobile [5]. Figure 3 shows hydration rate curves for four different size fractions of amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ with initial $n=1.25$. This figure shows that there is little difference in hydration rate for grain sizes above 75 μm , but at 45-75 μm the rate is about three times as fast.

The fine particles most susceptible to global redistribution are thus also most susceptible to transformation.

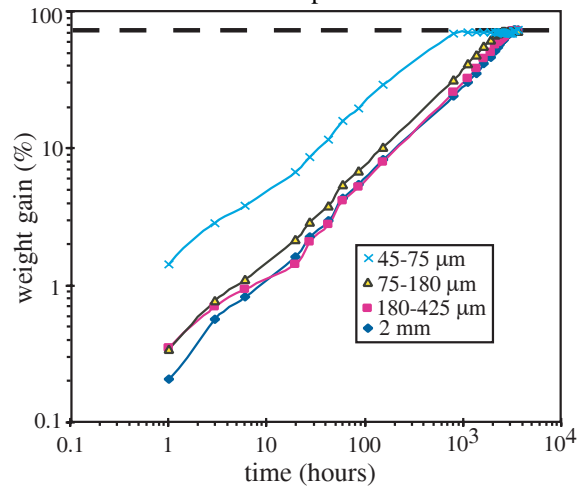


Figure 3: Rehydration of four size fractions of amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ ($n_0=1.25$) to epsomite (dashed line) at 243 K & 100% RH

As noted in our companion abstract [1], desiccation in the $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ system can lead to a variety of intermediate or metastable forms with $n < 6$. In contrast, hydration at temperatures at least as low as 243 K tends to bypass the intermediate hydrates to produce hexahydrate or epsomite. Hydration destroys kieserite (and possibly all other hydrates of $n < 6$) as well as amorphous forms, producing hexahydrate and ultimately epsomite. Whether this results in a duricrust may depend on (1) whether kieserite or an amorphous form is the precursor and (2) whether other hydrous minerals, particularly clays, are present.

Phase variability in the $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ system is reduced by hydration. Kieserite may be present at latitudes lower than those where surface ice is stable, but if present it indicates that the surface is unlikely to have seen water ice accumulation during episodes of higher obliquity. However, as suggested by durability of kieserite for $>4,000$ hours at 193 K, it is possible that kieserite exposed to very cold ice (~200 K?) will not hydrate due to (1) pH_2O too low to drive hydration and (2) sluggish reaction rates at such low temperatures. Such conditions may occur at present in Martian polar regions, but are unlikely to persist through high obliquity cycles [6]. As a consequence, long-term refugia for kieserite at any latitude on Mars are likely to be rare.

References: [1] Chipera S. J. et al. (2006) *this volume*. [2] Vaniman D. T. et al. (2006) *Am. Min.*, in press. [3] Vaniman D. T. et al. (2004) *Nature*, 431, 663-665. [4] Vaniman D. T. et al. (2004) *Eos Trans. AGU*, 85(47), P21A-0207. [5] Edgett K. S. and Christensen P. R. (1994) *JGR*, 99, 1997-2018. [6] Mischna M. A. et al. (2003) *JGR*, 108, 10.1029/2003JE002051.