DEHYDRATION AND METASTABLE STATES OF Mg-SULFATE HYDRATES THAT MAY BE PRESENT ON MARS.

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Introduction: The dominant naturally-occurring members of the $MgSO_4 \cdot nH_2O$ series on Earth are epsomite ($MgSO_4 \cdot 7H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$), and kieserite ($MgSO_4 \cdot H_2O$). In addition, other magnesium sulfate hydrates (sanderite - $2H_2O$, starkeyite - $4H_2O$, pentahydrite - $5H_2O$) have been identified as efflorescent salts in limited localities in the United States, Chile, and Germany. Chipera et al., [1,2] conducted an extensive study of the relative stability among the various Mg-sulfate hydrates. They, observed Mg-sulfate hydrates outside of their predicted stability field, and for some phases found in nature, were not able to establish that there was a stability field at all. One of the conclusions from the earlier studies was that the Mg-sulfate hydrate system is dominated by kinetics, metastability, and what was believed to be reaction path dependence. They initially conducted short experimental runs (2-3 weeks) before the significant control that kinetics exerted on the Mg-sulfate hydrate system became apparent. Subsequently, longer experiments were conducted (2-4 months) in an attempt to attain equilibrium conditions. Longer runs at the same conditions produced more complete reactions although even some of the longer experiments produced polyphase mixtures, indicating that they also may not have gone to completion.

This raised the question of how the Mg-sulfates dehydrate and whether they dehydrated in a stepwise fashion with intermediate phases as suggested by the limited available data. The present study was carried out to examine the possibility that Mg-sulfate hydrates dehydrate along established reaction paths. We also explored the behavior of sanderite which appears to violate the expected dehydration trend, forming after a 1-H_2O stage with decreasing RH and increasing temperature (i.e., $7 \rightarrow 6 \rightarrow 4 \rightarrow 1$, then the sanderite 2-hydrate). It is currently believed that sanderite is a metastable intermediate form.

Methods: To study whether hydrous Mg-sulfates dehydrate incrementally, Alfa Aesar Puratronic hexahydrite reagent was chosen as the starting material. The experiments were conducted at 75°C to allow comparison with the equilibration data of Chipera et al [1,2] and to help overcome the sluggish kinetics that are known to occur in this system. Approximately 1 gram of hexahydrite was placed into an open Teflon vessel, which was then placed into a second sealed Teflon vessel containing saturated salt solutions (to control humidity). Saturated salt solutions chosen were NaOH, LiCl, $CaCl_2$, and $MgCl_2$ which at 75°C produce relative humidities of approximately 2, 11, 17, and 27% RH respectively [3]. These reaction cells were then placed into a 75°C oven (calibrated to NIST standards). Samples were periodically removed, analyzed via X-ray powder diffraction, and then returned to the oven for further equilibration. Analyses were conducted at 1, 2, 6, 10, 14, 21, 28, 38, 58, and 84 days.

To conduct the XRD analyses, a Siemens D500 diffractometer utilizing Cu-Kα radiation, incident-beam Soller slits, and a Kevex solid-state PSi detector was used. Samples were analyzed from 2-70°2θ, with 0.02° steps, counting for 2s/step (2 hour runs).

Results: The results of this study show the dehydration process for hexahydrite (6 H_2O) at 75°C (Figure 1). Reaction products observed include starkeyite (4 H_2O), sanderite (2 H_2O), kieserite (1 H_2O), a second monohydrate polytype as described by Chipera et al. [1,2], the "unknown phase" described by Chipera et al. [1,2] (2.4 H_2O), and yet another unknown phase (#2) that has not been previously described and which is yet to have its water content determined.

In all cases, the hexahydrite (6 H_2O) was gone by the time the samples were analyzed after 24 hours of reaction, with the products dominated by starkeyite (4 H_2O). The starkeyite product in turn was destroyed within an additional 24 hours in the 11% and 17% RH experiments, although it persisted a bit longer in the 2% and 27% RH experiments. The products of the starkeyite reaction were typically the unknown phase #1, measured to have (~2.4 H_2O) or sanderite (2 H_2O), but the second unknown phase was observed in the 27% RH data. With additional time (2 to 4 weeks) the two "unknown phases" completely reacted to form the monohydrate polymorph structure at the low relative humidity, and kieserite, whose proportion increased with increasing relative humidity of the experiments.

It is interesting that the sanderite was again so prevalent at the lowest relative humidity and persists longer at the lower RH. However, trends in the data suggest that the sanderite will eventually fully react to the monohydrate if given sufficient time. The final ratio between kieserite and the second monohydrate polymorph, however, appears to change only slightly

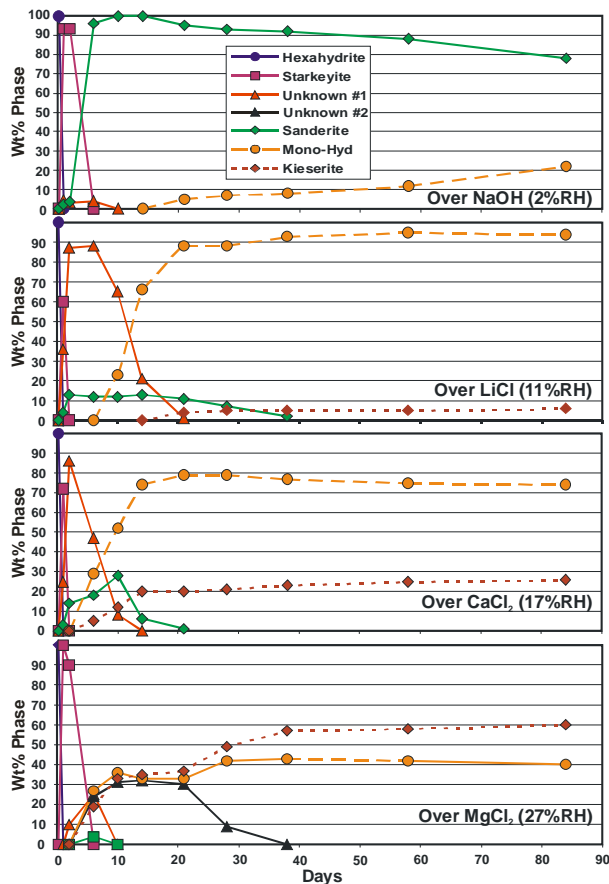or insignificantly with time and may reflect final stable/metastable ratios.

Figure 1: Reaction progress of hexahydrite placed at 75°C over four different low-RH salt solutions (NaOH, LiCl, CaCl₂ and MgCl₂) as a function of time.

Figure 2 shows the results for the long equilibration times for hexahydrite at various temperatures and relative humidity from Chipera et al. [1,2]. Superimposed are hexahydrite-epsomite-solution experimental data [4] and the late summer day-night temperatures and relative humidities measured at the Viking Lander 1 site [5] as a reference for Mars conditions. Some of the lower RH and elevated temperature data points show polyphase mixtures containing sanderite and the unknown phase, suggesting that these runs have not yet fully reacted, even with the long (several month) equilibration times used. One phase not addressed in these experiments is the amorphous Mg-sulfate phase observed by rapid dehydration of hexahydrite at lower temperatures [6]. In this case, it is suspected that the amorphous phase is a metastable phase resulting from the direct dehydration of hydrous Mg-sulfates without the ability to form the intermediate hydrates. For ex-

ample, subjecting hexahydrite to low RH (<1% RH) causes transformation to an amorphous phase within ~32 hours at 28°C.
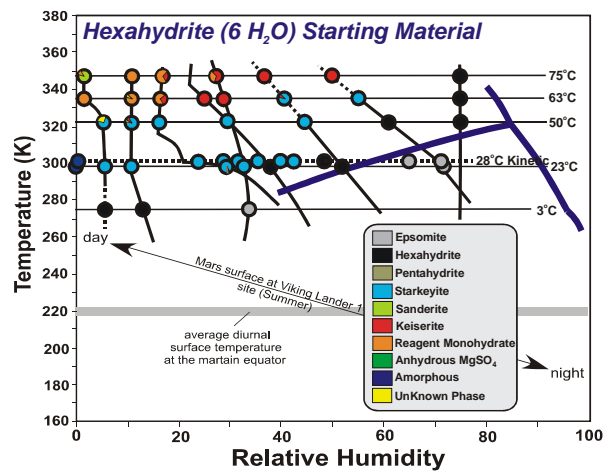

Figure 2: Experimental results for the equilibration of hexahydrite at different temperatures and RH (Chipera et al. [1,2]).

Conclusions: As determined from this and earlier studies [1,2], both temperature and time have significant effects on reaction kinetics. Hexahydrite dehydrated in these 75°C experiments by recrystallizing in a step-wise fashion to progressively lower-water-content species. The exact path and the species formed are dependent on the relative humidity of the system and presumably the amount of driving force required to get the reactions to go.

In the earlier studies [1,2], it was found that experimental reaction times had to be extended from several weeks to several months in an attempt to attain equilibrium, even at elevated temperatures. Kinetics to attain equilibrium at the colder temperatures of the Martian surface could be extremely sluggish and metastable intermediate Mg-sulfate hydrates are likely to be encountered at lower, drier latitudes if the material starts out in a more hydrous form such as hexahydrite or epsomite.

References: [1] Chipera, S.J., Vaniman, D.T., Bish, D.L., Carey, J.W., and Feldman, W.C. (2005) Lunar and Planetary Science Conference, XXXVI, #1497. [2] Chipera, S.J. and Vaniman, D.T, submitted to Geochimica et Cosmochimica Acta. [3] Greenspan L. (1977) J. Res. Natl. Bureau Standards A. Phys. Chem. B1A, 89:96. [4] Chou I.-M. and Seal R. R. II (2003) *Astrobiology 3*, 619-630. [5] Savijarvi H. (1995) *Icaras 117*, 120-127. [6] Vaniman, D. T. et al. (2004) *Nature 431*, 663-665.