

SULFATE SALTS, REGOLITH INTERACTIONS, AND WATER STORAGE IN EQUATORIAL MARTIAN REGOLITH. D. T. Vaniman¹, S. J. Chipera¹, D. L. Bish², J. W. Carey¹, C. I. Fialips¹, and W. C. Feldman³, ¹Group EES-6, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 (vaniman@lanl.gov), ²Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405, and ³Group ISR-1, Los Alamos National Laboratory, MS D466, Los Alamos, NM 87545.

Introduction: Neutron spectrometer data from the Odyssey Mars Orbiter provide evidence of water abundances up to ~10 wt% in regolith to a depth of ~1 m in some near-equatorial locations on Mars [1]. Water ice is unstable in these locations, suggesting that some of this water may be present in hydrous silicates (clays or zeolites) or hydrated salts [2,3]. Viking chemical analyses of excavated duricrust indicate that Mg and S are correlated and ~10% MgSO₄ (anhydrous weight) is a likely cementing agent [4]. Pathfinder chemical data support a similar abundance of MgSO₄ in the most altered materials [5]. However, there are many possible Mg-sulfates with widely varying hydration states. On Earth, the only common members of this series are epsomite (7-hydrate; 51 wt% water), hexahydrate (6-hydrate; 47 wt% water), and kieserite (monohydrate; 13 wt% water). Occurrences on Mars may be very different; intermediate hydrates such as pentahydrate (5-hydrate, 43 wt% water), starkeyite (4-hydrate; 37 wt% water), a possible 3-hydrate (no mineral name; 31 wt% water), and sanderite (2-hydrate; 23 wt% water) could be present. Important to this study as well is gypsum (CaSO₄·2H₂O; 21 wt% water). Complexity in martian salts is suggested by lesser but significant amounts of Cl. In addition the Mg-S correlation in Viking and especially Pathfinder data is weak, and other cations (Mn, Fe, Co, Ni, Cu, Zn) that readily substitute for Mg in the MgSO₄ series could be present in the sulfate salts. These are important points to consider, but here we focus on other complicating factors, particularly potential regolith-salt interactions that may influence sulfate mineralogy in martian regolith.

Methods: Solutions of MgSO₄ saturated with respect to epsomite were mixed with a martian soil simulant (JSC-1), hydrous silicates (smectites and zeolites), or inert media (alumina and quartz powders). Clays used were chosen to represent a range of compositions (smectite from Succor Creek, Oregon, and two Clay Minerals Society source clays, ferruginous smectite SWa-1 and nontronite NG-1); the zeolites were chabazite from Christmas, Arizona, and clinoptilolites from the Fish Creek Mountains, Nevada, and from Castle Creek, Idaho. Compositions of representative clay, zeolite, and JSC-1 are listed in Table 1. Samples were prepared as thick slurries with MgSO₄ solutions; crystallization of salts was achieved within a few minutes by evaporation under vacuum (2 torr) at 297 K.

Table 1: Clay, Zeolite, and JSC-1 Compositions (wt%)

	SWa-1	Castle Ck.	JSC-1*
SiO ₂	43.8	62.8	34.5
TiO ₂	0.54	0.32	3.0
Al ₂ O ₃	7.95	12.6	18.5
Fe ₂ O ₃	25.3	2.35	12.4
MgO	1.75	1.57	2.7
CaO	2.05	1.38	4.9
Na ₂ O	0.00	2.86	1.9
K ₂ O	0.03	1.52	0.5
LOI**	19.4	14.4	21.8

*JSC-1 data from [6]

**LOI is loss on ignition at 1000°C, a close approximation of total water content

Results: Salts formed included hexahydrate, gypsum, and starkeyite. Hexahydrate and starkeyite can precipitate from MgSO₄ solution without chemical interaction with host media, but formation of gypsum requires Ca leaching or Mg-Ca exchange with the host.

Figure 1 shows the X-ray diffraction (XRD) pattern of Mg-sulfate solution evaporated from a slurry made with fine alumina powder (0.1 μm corundum). In this sample there is no possibility of Ca extraction from the host; thus no gypsum is formed but the salts crystallized include both hexahydrate and starkeyite.

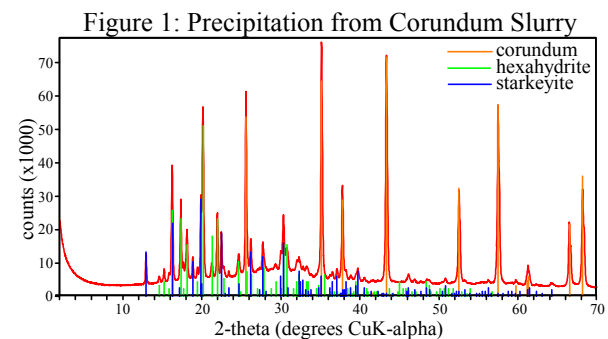


Figure 2 shows the XRD pattern of products from evaporation of a slurry made with martian simulant JSC-1 (for simplification, diffraction lines are only labeled for sulfate salts in this and subsequent figures). In this sample Ca was leached from the the host, and gypsum formed along with hexahydrate on evaporation. No other Mg-sulfate salts are present. Figure 3 shows comparable data for Mg-sulfate solution evaporated from a slurry with smectite SWa-1, forming gyp-

sum and hexahydrate as in the JSC-1 sample. Figure 4 shows data for slurry with Castle Creek clinoptilolite; here hexahydrate formed but gypsum isn't detected.

Figure 2: Precipitation from Palagonite (JSC-1) Slurry

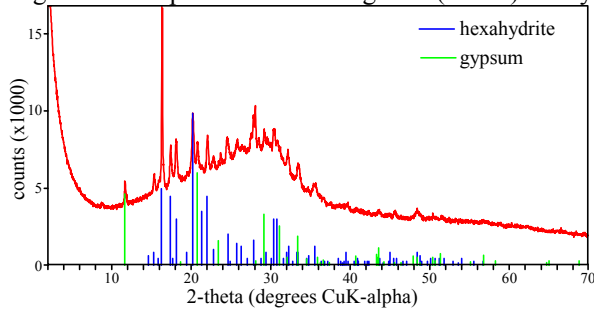


Figure 3: Precipitation from Clay (SWa-1) Slurry

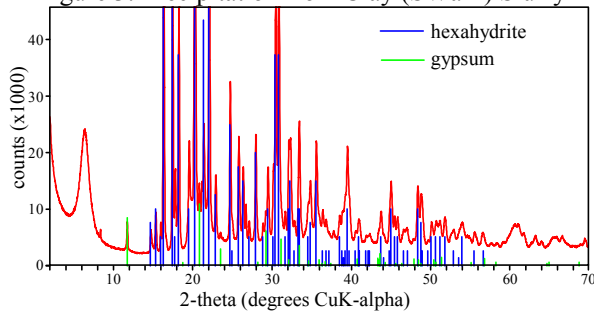
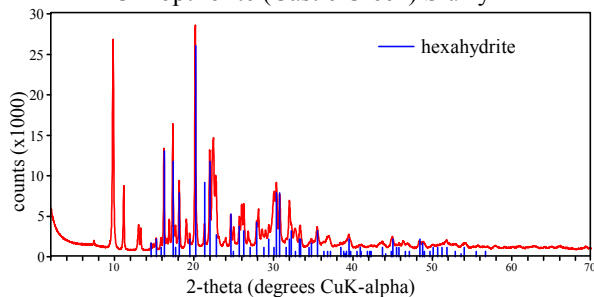


Figure 4: Precipitation from Clinoptilolite (Castle Creek) Slurry



The results for Mg-sulfate solution evaporation with different solid media provide data that support almost ubiquitous occurrence of hexahydrate, aggressive extraction of Ca from solids to produce gypsum, and precipitation of hydrates lower than hexahydrate (starkeyite) with chemically inert corundum powder.

Persistence of metastable hexahydrate. Hexahydrate was formed in all experiments at 2 torr and 297 K. At these conditions kieserite, not hexahydrate, is the stable phase [7]. Calculated evaporation pathways for most terrestrial saline waters show that epsomite and hexahydrate precede kieserite in the crystallization sequence [8]. It is evident that hexahydrate can persist metastably well into the field of kieserite stability, par-

ticularly in conditions of rapid crystallization at low RH in systems with a low water/solid ratio.

Common reaction of $MgSO_4$ solutions with admixed materials to form gypsum. In most experiments with Ca-bearing materials, saturated $MgSO_4$ solution reacted to form gypsum as well as hexahydrate. This is expected for smectites with exchangeable interlayer cations (Ca, Na, K) but was not anticipated with palagonite JSC-1 that lacks crystalline clay. Gypsum was not detected in the experiment with Castle Creek clinoptilolite and formed in very small amounts with Fish Creek clinoptilolite and Christmas chabazite. It was expected that more of the Ca in zeolites would have exchanged for Mg in solution to form gypsum. We suspect that rapid evaporation did not allow time for this process in the zeolite slurries.

Formation of other hydrous sulfates influenced by admixed media. All experiments formed hexahydrate, but starkeyite also formed in the experiment with alumina powder (starkeyite did not form with quartz powder). These results suggest that admixed solids can influence the hydration state of Mg-sulfate salts.

Conclusions: Results of these experiments indicate that sulfate mineralogy of crystallized $MgSO_4$ solutions is greatly influenced by host media. These influences include both chemical exchange (formation of gypsum by extraction of Ca from the host) and probable structural influence (specific formation of starkeyite with a host of fine corundum powder). These results have implications for considering hydrous minerals as water reservoirs in near-surface martian soils. Clays, zeolites and hydrated salts have all been implicated as water reservoirs in this environment, but the results presented here indicate that admixtures of these minerals will not be accurately represented by simple mixing models that do not allow for chemical interaction. Most importantly, the results indicate that water contents can be greater than nonreactive equilibrium calculations might suggest, because both gypsum (21 wt% water) and metastable hexahydrate (47 wt% water) may occur where kieserite (13 wt% water) would otherwise be expected. A separate question is whether water-rich salts remain hydrated over long timespans at martian conditions [3]; we are pursuing this question in further studies.

References: [1] Feldman W. C. et al. (in press) *JGR*. [2] Bish D. L. et al. (2003) *Icarus* 164, 96-103. [3] Bish D. L. et al. (2003) *6th Int. Conf. on Mars, Abstract #3066*. [4] Toulmin P., III, et al. (1977) *JGR* 82, 4625-4634. [5] Wänke H., et al. (2001) *Space Sci. Rev.* 96, 317-330. [6] Allen C. C. et al. (1998) *LPS XXIX, Abstract #1690*. [7] Chou I. M. and Seal R. R. (2003) *Astrobiology* 3, 619-630. [8] Spencer R. J. (2000) in *Min. Soc. Amer. Reviews in Mineralogy* 40, 173-192.