

**CAN SULFATES BESIDES THOSE OF Mg FORM LOW-TEMPERATURE HYPER-HYDRATES?**

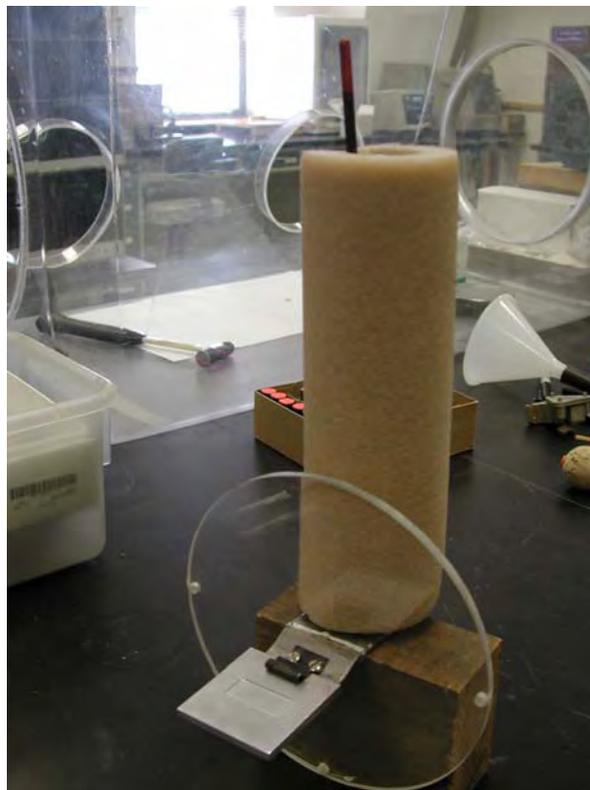
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**Introduction:** It has been known for some time that at low temperatures, Mg-sulfates can form hyper-hydrates (crystalline forms with more waters of hydration than commonly observed [1,2]). Mg-sulfate hyper-hydrate has been postulated as a dominant phase for the surface of Europa [3]. In earlier work, it was believed that the low-T Mg-sulfate hydrate possessed 12 waters of hydration (64 wt% water). More recently, Peterson and Wang [4] studied this low temperature hydrate, both solving its crystal structure and determining that it actually contains only 11 waters of hydration (62 wt% water). The present study was carried out to determine if other sulfates form hyper-hydrates at lower temperature and to see if there are other, even more hydrated forms of MgSO<sub>4</sub>-hydrates.

**Methods:** Sulfates analyzed include those of Na, K, Fe<sup>+2</sup>, Mg, Mn, and Zn. Approximately saturated solutions of the various sulfates (Table 1) were placed into laboratory freezers set at -30 and -50°C for periods of over 2 weeks. Samples were extracted, lightly ground, pressed into an aluminum sample mount, placed onto a liquid nitrogen cooled cold-finger sample stage (Figure 1), and analyzed for structure using X-ray powder diffraction (XRD; Figure 2). Care was taken to pre-chill all the sample preparation equipment to the freezer temperatures and to work in the freezers as much as possible to ensure that the samples remained cold. Even minor amounts of heat and pressure were found to be enough to transform or melt the solids before the analysis could be conducted. Scan parameters were 3-60 degrees 2θ, with 0.1 degree steps, counting 1 second per step. A sequence of 9 runs was set up but rarely did we let them go to completion as even with the cold-finger, the samples tended to warm up and turn back into solution during the analyses.

**Table 1: Amount of sulfate added to 20 ml deionized water to produce the solutions.**

Sulfate	Grams sulfate per 20 ml H <sub>2</sub> O
Na <sub>2</sub> SO <sub>4</sub>	~1
K <sub>2</sub> SO <sub>4</sub>	2.4
FeSO <sub>4</sub> • 4H <sub>2</sub> O	3.2
MgSO <sub>4</sub>	5.2
MnSO <sub>4</sub> • 1H <sub>2</sub> O	17
ZnSO <sub>4</sub> • 4H <sub>2</sub> O	20



**Figure 1: LN cold-finger sample stage with aluminum sample mount attached.**



**Figure 2: LN cold-finger sample stage fitted onto an environmental cell on the diffractometer to prevent ice from forming on the sample during analysis. Note the ice forming where the cold-finger sits outside of the cell.**

One of the driving forces to fabricate the cold stage was to analyze a sample of  $\text{MgSO}_4$ -hydrate which was made by dissolving 5g of anhydrous  $\text{MgSO}_4$  into 12 ml  $\text{H}_2\text{O}$ , then placed into a  $-30^\circ\text{C}$  freezer on 10/28/04 and allowed to sit for 2 years. Previous attempts to X-ray this sample before the fabrication of the cold-finger resulted in almost immediate transformation into a liquid. Peterson and Wang [4] also encountered difficulty in analyzing this phase and found that it is only stable below  $2^\circ\text{C}$  and had an extremely low heat of fusion, readily transforming to epsomite and water.

**Results:** Table 2 shows results for the various sulfates analyzed. In all cases, there was excess water in the solution to ensure enough water was present to form a hyper-hydrate. Water-ice is readily apparent in all the XRD analyses. It is interesting that the only hyper-hydrate observed is that of Mg-sulfate. The rest of the sulfates only formed the hydrated phases that are readily found in nature. Fe, Mn, and Zn formed the common 7-hydrates, melanterite, mallardite, and goslarite, respectively. Na formed the 11 hydrate, mirabilite, and K did not form a hydrate at all and remained anhydrous arcanite. It appears that arcanite is rather stable and helps to explain why there are so few  $\text{K}_2\text{SO}_4$  phases known to occur.

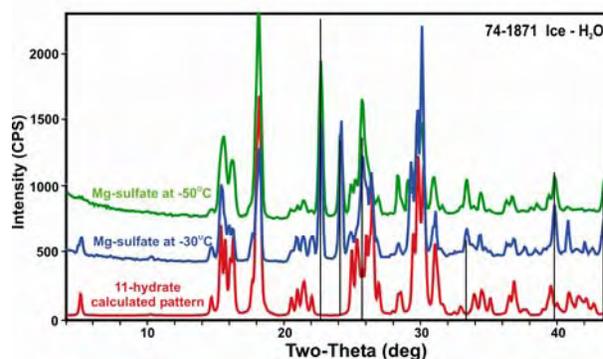
**Table 2: Results of frozen sulfate solutions.**

Sulfate	$-30^\circ\text{C}$	$-50^\circ\text{C}$
$\text{Na}_2\text{SO}_4$	not analyzed	11 hydrate
$\text{K}_2\text{SO}_4$	anhydrous	anhydrous
$\text{FeSO}_4$	7 hydrate	7 hydrate
$\text{MgSO}_4$	11 hydrate	11 hydrate
$\text{MnSO}_4$	7 hydrate	7 hydrate
$\text{ZnSO}_4$	7 hydrate	7 hydrate

Figure 3 shows the calculated pattern for the Mg-sulfate 11-hydrate phase compared with the results of the  $-30^\circ\text{C}$  and  $-50^\circ\text{C}$  frozen saturated Mg-sulfate solutions. Excess water is clearly present in the  $-30^\circ\text{C}$  and  $-50^\circ\text{C}$  patterns as water-ice. Due to the nature of the samples, grinding was minimized to prevent alteration of the frozen samples, resulting in significant preferred orientation in the XRD data. In order to compensate for the preferred orientation effects, data from several different sample mounts were added together; the  $-30^\circ\text{C}$  data is the compilation of data runs conducted on 4 different sample mounts and the  $-50^\circ\text{C}$  data, the compilation of 5 different sample mounts.

The  $-50^\circ\text{C}$  runs lack most of the low angle peaks of the 11-hydrate and the  $-30^\circ\text{C}$  samples. However, enough of the pattern is the same to suggest that it is either the 11-hydrate or a similar phase. It could be a

slightly greater hydrate as the pattern for ice is slightly weaker, although this hypothesis assumes that the ice distribution is homogeneous in the samples. Further studies will be conducted to confirm the nature of the  $-50^\circ\text{C}$  Mg-sulfate hydrate.



**Figure 3 Comparison of the calculated 11-hydrate pattern (red) with the Mg-sulfate solution that was frozen at  $-30^\circ\text{C}$  (blue) and at  $-50^\circ\text{C}$  (green). Reflections for ice are shown as black vertical lines.**

The Mg-sulfate hydrate that was in the freezer for 2 years was made with 5g anhydrous  $\text{MgSO}_4$  in 12 ml deionized water, which would make it a 15.5 hydrate if all the water went into the crystal structure. The XRD data for this sample show it to be the Mg-sulfate 11-hydrate phase. The sample was not as solid as the recently frozen samples and very little ice was apparent in the pattern, suggesting that excess water as ice probably sublimated over the two years that the sample was in the  $-30^\circ\text{C}$  freezer.

If Mg-sulfate was originally in solution on the surface of Mars, it appears that the 11-hydrate phase would be a viable form if ambient temperatures were less than  $0^\circ\text{C}$ , even as low as  $-50^\circ\text{C}$ . However, confirmation of the existence of an 11-hydrate will require that the sample be kept below  $2^\circ\text{C}$ , a constraint not currently being planned for the scientific instrumentation that will reside in the interior of the upcoming 2009 Mars Science Laboratory (MSL) rover where an 11-hydrate could readily convert to epsomite and water.

**References:** [1] Fritzsche J. (1837) *Annalen der Physik und Chemie* 42, 577-580. [2] Hogenboom, D.L., Kargel, J.S., Ganasan, J.P. and Lee, L. (1995) *Icarus* 115, 258-277. [3] Kargel, J.S. (1998) *Science* 280, 1211-1212. [4] Peterson, R.C. and Wang, R. (2007) *Geology* 34, 957-960.

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