

**RATES OF Al-, Fe-, Mg-, Ca-SULFATES DEHYDRATION UNDER MARS RELEVANT CONDITIONS.**

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**Introduction:** Hydrated sulfates are one of the two major types of secondary minerals (the other type is phyllosilicates) that have been found on the surface of Mars, in large quantities and with wide spreading. Among them, Ca-, Mg-, Fe-sulfates, and recently Al-sulfates, have all been identified. The degrees of hydration of these sulfates at the surface and subsurface on Mars would be heavily influenced by environmental conditions, which would be subjective to the diurnal and seasonal cycles, and in the long term, to the cycles of Mars obliquity. During MER, MSL, and Mars 2020 missions, to determine the hydration degrees of sulfates and other salts will shed light on the current water reservoir and the hydrologic evolution of Mars. Both of these aspects also relate to the potential generation of Martian life (if that ever happened) and the preservation of biosignatures.

This study reports two sets of dehydration experiments conducted on crystalline alunogen  $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$  and melanterite  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  under Mars relevant pressure (P) and partial  $\text{H}_2\text{O}$  pressure ( $P_{\text{H}_2\text{O}}$ ) at three temperatures (T). These results are compared with those obtained from a similar set of experiments on crystalline epsomite  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  [1], and with published data of Ca-sulfate [2] and  $\text{Fe}^{3+}$ -sulfate [3]. These comparisons revealed the differences in the phase transition pathways, and especially in the dehydration rates, of these hydrated sulfates under Mars relevant conditions.

Laser Raman Spectroscopy (LRS) has been the major tool that we used to monitor the changes of hydration degrees of these five types of major sulfates. Figure 1 shows the finger-print Raman spectra of five sulfates with difference cation but the highest hydration degrees.

We found that the dehydrations of Mg-sulfate and  $\text{Fe}^{2+}$ -sulfate would progress the fastest on Mars.

**Dehydration Experiments under Mars relevant conditions:**

Both starting sulfates,  $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , are in the

same grain size range (90-150  $\mu\text{m}$ ), whose ID and homogeneities were checked by XRD and multi-spot laser Raman spectroscopy measurements.

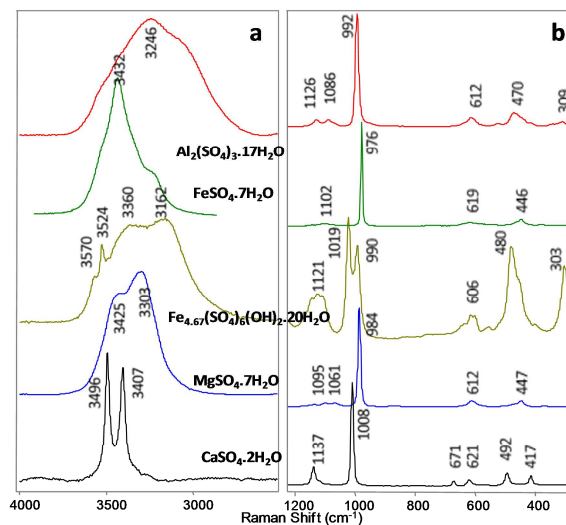
The dehydration experiments were conducted by placing the reaction vials in a vacuumed desiccator. The atmospheric pressure was maintained by a vacuum pump and monitored by a gas-pressure meter. Pressure from 0.26 to 0.16 mbar was reached during the progress of dehydration experiments which are lower than the average atmospheric pressure on Mars (~ 7 mbar). The partial  $\text{H}_2\text{O}$  pressure ( $P_{\text{H}_2\text{O}}$ ) in vacuum desiccator was in the range of 0.25 – 0.14 Pa, near the reported  $P_{\text{H}_2\text{O}}$  on Mars ~ 0.04 – 0.15 Pa [4]. The dehydration experiments were conducted at three temperatures:  $21 \pm 1^\circ\text{C}$ ,  $0 \pm 0.5^\circ\text{C}$ , and at  $-12 \pm 2^\circ\text{C}$ . The temperatures during the experimental periods are recorded by a T-RH-data logger.

Depending on the selected temperature, the total durations of dehydration experiments vary from 26 hours to over 200 hours. During each experiment, 10 reaction vials (among the total of 15) were taken out periodically from the vacuumed desiccator at pre-determined time interval (i.e., 20, 40, 60 min, then 2 h, 4 h, 8 h, 15 h, 30 h, etc), sealed immediately, then to make gravimetric measurements to monitor the change in hydration degree. The rest of 5 vials were taken out at larger time intervals (i.e. 40 min, 4 h, 15 h, 30 h, etc), sealed immediately, then to make LRS measurements to monitor the structural changes.

**Result#1—T-dependent:** Comparison among the dehydration processes of alunogen, melanterite, and

epsomite under Mars relevant conditions, revealed that they are all strongly dependents on temperature.

**Result#2 – dehydration pathways:** the dehydration pathways and the ending hydration degrees of three sulfates are very different, which obviously reflect the differences in fundamental compositional and structural properties of these three sulfates. These properties would affect the activation energy values for phase transitions. The dehydration of melanterite went through rozenite, then amorphous  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  ( $x > 1$  in this study). The dehydration of



**Figure 1.** Raman spectra of alunogen, melanterite, ferricopiapite, epsomite, and gypsum.

epsomite went through hexahydrite, then amorphous  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  ( $x$  changes from 3 w to 1.8 w, [1]). In comparison, alunogen lost its hydrogen-bonded structural  $\text{H}_2\text{O}$  much faster than epsomite and melanterite, (Fig. 2) suggesting an highly unstable

structure, but. meta-alunogen  $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$  has a much stable structure than hexahydrite and rozenite.

The comparison of dehydration processes of melanterite and epsomite are complicate because both can have two different pathways, involving crystalline-to-crystalline or crystalline-to-amorphous phase transitions. Current experiments revealed following stability orders: (1) ferroxahydrite is much less stable than hexahydrite; (2) rozenite is less stable than starkeyite; (3) amorphous  $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$  is less stable than rozenite.

**Result#3 – dehydration rates:** When comparing the dehydration rates, the dehydration pathways have to be considered. Figure 2 revealed that under the same Mars relevant P,  $P_{\text{H}_2\text{O}}$ , Ts, the dehydration of epsomite (when going through amorphous phases) has the fastest rate. Figure 3 shows when only crystalline-to-crystalline phase transformations involved, melanterite has a faster dehydration rate than epsomite. Furthermore, Robertson and Bish [2] reported a laboratory investigation on the phase transition among three  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  ( $x=2, 0.5, 0$ ). In their experiment, the starting of dehydration from gypsum to bassanite was observed after two weeks into the reaction at 323K in vacuum of 15 Pa. If compare their observation (20160 minutes) with the starting time of alunogen, epsomite, and melanterite (20 - 40 minutes) at similar atmospheric pressure but lower temperature at 294K (Fig. 2), it can be readily concluded that gypsum has the lowest dehydration rate.

**Conclusion:** Among the five major types of hydrous sulfates, Al-,  $\text{Fe}^{2+}$ -,  $\text{Fe}^{3+}$ -, Mg- and Ca-sulfates with the highest hydration degrees, malenterite has the highest dehydration rate through crystalline-to-crystalline path. When amorphization happens, epsomite has the highest dehydration rate.

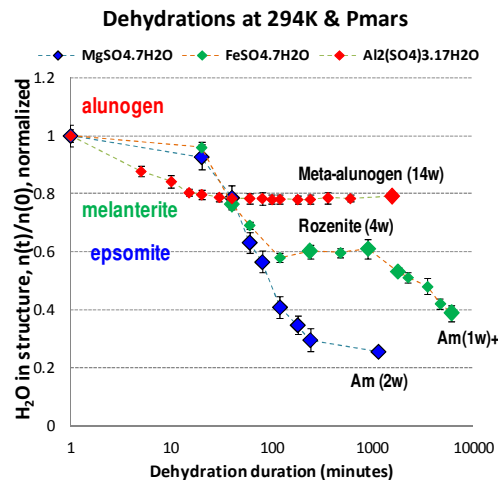


Figure 2. Number of  $\text{H}_2\text{O}$  per sulfate molecule, as  $n(t)/n(0)$  (%) vs. experimental duration in minutes, during their dehydration processes under Mars relevant P and  $P_{\text{H}_2\text{O}}$ . Amorphous species occurred.

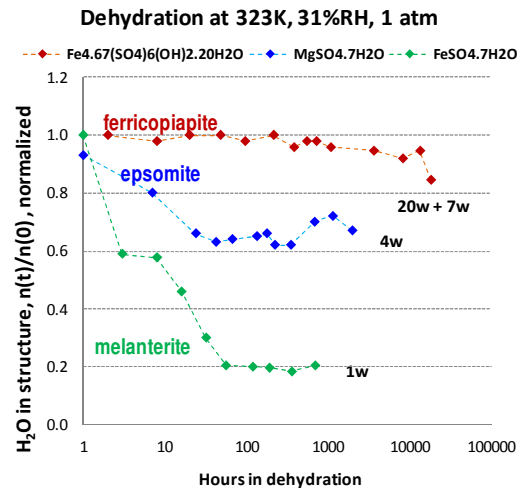


Figure 3. Number of  $\text{H}_2\text{O}$  per sulfate molecule, as  $n(t)/n(0)$  (%) vs. experimental duration in minutes, during the process of dehydration at 1 atm, 31%RH, and 323K. Only crystalline-to-crystalline phase transformation happened.

**Implication to sulfate dehydrations on Mars:** An comparison between recent Mars obliquity cycle and the low T dehydration rate of epsomite made by Wang et al [5] suggests that Mg-sulfates with mid-high hydration degree could remain in subsurface of Mars equatorial regions until today. On the other hand, the experimental results reported here indicating that epsomite has the fastest dehydration rates when compared with other four major type of sulfates. Therefore, if  $\text{Al}^{3+}$ -,  $\text{Fe}^{3+}$ -, and  $\text{Ca}^{2+}$ -sulfates formed during high obliquity periods in sub-surface salt-rich layers, we anticipate an even higher (than in Mg-sulfates) % of structural  $\text{H}_2\text{O}$  in them would remain until today. The existence of ferric sulfates with highest hydration degree at subsurface in Gusev was demonstrated by the color change of  $\text{Fe}^{3+}$ -sulfates-rich subsurface regolith after their exposure by Spirit rover to Mars surface [6,7].

The current experimental study supports the hypothesis that subsurface hydrated sulfates are the major host for the high Water-Equivalent-Hydrogen (WEH) values observed at two equatorial regions on Mars [8,9,10].

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**References:** [1] Wang et al., 2009, JGR, 114, E04010; [2] Robertson and Bish (2013, Icarus, 223, 407-417; [3] Wang et al., 2012, Icarus, 218, 622-643; [4] Smith 2002, JGR, 107, 5115; [5] Wang et al., 2013, Icarus, 226, 980-991; [6] Wang et al., 2008, JGR, 113, E12S40; [7] Wang et al., 2011, JGR, 116, E00F17; [8] Feldman et al., 2004, GRL, doi:10.1029/2004GL020181; [9] Fialips et al., 2005, Icarus, 178, 74-83; [10] Jakosky et al., 2005, Icarus, doi:10.1016/j.icarus.2004.11.014.