**Introduction:** Hydrous 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 Al₂(SO₄)₃·17H₂O and melanterite FeSO₄·7H₂O under Mars relevant pressure (P) and partial H₂O pressure (P_H₂O) at three temperatures (T). These results are compared with those obtained from a similar set of experiments on crystalline epsomite MgSO₄·7H₂O [1], and with published data of Ca-sulfate [2] and Fe³⁺-sulfate [3]. These comparisons revealed the differences in the phase transition pathways, and especially in the dehydration rates, of these hydrous 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 fingerprint Raman spectra of five sulfates with difference cation but the highest hydration degrees.

We found that the dehydration rates of Mg-sulfate and Fe²⁺-sulfate would progress the fastest on Mars.

**Dehydration Experiments under Mars relevant conditions:** Both starting sulfates, Al₂(SO₄)₃·17H₂O and FeSO₄·7H₂O, are in the same grain size range (90-150 µm), 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 H₂O pressure (P_H₂O) in vacuum desiccator was in the range of 0.25 – 0.14 Pa, near the reported P_H₂O on Mars ~ 0.04 – 0.15 Pa [4]. The dehydration experiments were conducted at three temperatures: 21 ± 1°C, 0 ± 0.5 °C, and at -12 ± 2 °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 predetermined 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 FeSO₄·xH₂O (x>1 w in this study). The dehydration of
Dehydration at 294K & Pmars

- Alnogen
- Melanterite
- Epsomite
- Meta-alunogen
- Rozenite

Dehydration at 323K, 31%RH, 1 atm

- Ferricopiapite
- Epsomite
- Melanterite

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 Al\(^{3+}\), Fe\(^{3+}\), and 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 H\(_2\)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 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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