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Experimental comparison of the pathways and rates of the dehydration of Al-, Fe-, Mg- and Ca-sulfates under Mars relevant conditions

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ABSTRACT

This study reports two sets of dehydration experiments conducted on crystalline alunogen $Al_2(SO_4)_3$. 17H₂O and melanterite FeSO₄·7H₂O under Mars relevant pressure (*P*) and partial H₂O pressure (*P*_{H2O}) at three temperatures (*T*). These experimental data are compared with those obtained from a similar set of experiments on crystalline epsomite MgSO₄·7H₂O, and revealed the differences in the phase transition pathways of the dehydrations of these hydrous sulfates, with different cations and the highest hydration degrees, under Mars relevant conditions. Specifically, the differences in the dehydration rates were discussed, and further compared with the dehydration processes of Ca-sulfate and Fe³⁺-sulfate of the highest hydration degrees. We found that the dehydrations of Mg-sulfate and Fe²⁺-sulfate would progress the fastest on Mars.

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1. 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. The determination of hydration degrees of detected sulfates on Mars can shed light on the hydrologic evolution of Mars, and can also provide information about the current water reservoir on the planet. Both of these aspects relate to the potential generation and preservation of martian life (if that ever happened).

Up to now, only incomplete information about the hydration degrees of the identified sulfates were revealed by most missions to Mars. Among the orbital remote sensing observations, OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité on Mars Express orbiter, Bibring et al., 2006) and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars on Mars Reconnaissance Orbiter, Murchie et al., 2009) identified kieserite MgSO₄. H₂O and gypsum CaSO₄·2H₂O. In addition, large quantity of polyhydrated sulfate was observed, with unknown hydration degree, as well as the unknown type of cation. Dehydrated jarosite (Lich-

tenberg et al., 2010) and alunite (Swayze et al., 2008) were also identified.

Among the landed missions, the Spirit and Opportunity rovers have found Mg-, Ca-, Fe³⁺-sulfates within the outcrops and regolith at Gusev crater and Meridiani Planum (Squyres et al., 2006, 2009; Arvidson et al., 2006; Clark et al., 2005; Haskin et al., 2005; Wang et al., 2006a, 2006b, 2008; Wang and Ling, 2011). The MER rovers, however, were not equipped to provide detailed information on the hydration degree of minerals; the definitive identification of jarosite (Klingelhofer et al., 2004) is an exception. Furthermore, hydrous sulfates were implied existing in the regolith at Mars polar region by Phoenix lander (Rennó et al., 2010; Kounaves et al., 2010). Gypsum was suggested to be the mineral filler of the veins found at Endeavour crater and Gale crater explored by Opportunity and Curiosity Rovers (Squyres et al., 2012). Anhydrite CaSO₄ was suggested as a minor component of the surface soil at Gale crater by CheMin instrument on the Curiosity rover (Blake et al., 2013; Bish et al., 2013).

On the other hand, high levels of water-equivalent-hydrogen (WEH) were observed (Feldman et al., 2004a; Maurice et al., 2011) in two large equatorial regions on Mars by Neutron Spectrometer on Mars Odyssey orbiter (NS-ODY). Studies have been proposing that subsurface hydrous sulfates are the most suitable mineral hosts for these WEH (Feldman et al., 2004b; Jakosky et al., 2005; Fialips et al., 2005; Wang et al., 2013), especially at equatorial regions on Mars.

In addition to Mg-, Fe-, and Ca-sulfates, we anticipate Al-sulfates and Al-bearing sulfates would be another major type of sulfates to





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be formed in localized region on Mars. Extensive weathering of basaltic minerals is required for the releasing of Al, i.e., from feldspar (to release Al with Ca, Na, K) that has a higher Gibbs free energy for weathering reactions ($\Delta G_f^0 \sim -1.32$ to -0.32 kcal/atom) than those of olivine (\sim -6.58 to -4.0 kcal/atom) and pyroxene (-2.72 to -2.98 kcal/atom). Alternatively, volcanic glasses are relatively easy to be chemically weathered thus to release Al (with many other cation). The evidence of extensive weathering, as well as the evidence of volcanic activity, were found in localized areas explored by the Spirit rover at Gusev crater (Morris et al., 2006, 2008; Squyres et al., 2007, 2008). Furthermore four groups of evidences were found on Mars that consistent with the release of Al and Ca from extensive weathering. They include the Ca-sulfate observed by OMEGA and MER (Langevin et al., 2005; Wang et al., 2006a); spectral evidence of alunite (KAl₃(SO₄)₂(OH)₆) found in Cross crater by MRO-CRISM data analysis (Swayze et al., 2008): a group of Alenriched rocks identified at West Spur on Columbia Hills at Gusev (Ming et al., 2006; Wang et al., 2006a); and Al-rich clays (kaolinite and montmorillonite) implied by MER data analyses (Clark et al., 2007; Wang et al., 2006a) and by orbital remote sensing (Carter and Poulet, 2012).

On Earth, Al-sulfates and Al-bearing sulfates are commonly formed in natural acidic sulfate-rich environments, such as active crater lakes, fumaroles, and acidic hot springs (Adele et al., 2010; Bigham and Nordstrom, 2000). In brines that contain Al and anionic groups $Cl^-, SO_4^{2-}, NO_3^-, ClO_4^-$, Al-sulfates have the lowest solubility and thus would precipitate first (Lide, 2001). In addition, Al-bearing sulfates can be produced from acidic alteration of clays (Altheide et al., 2010).

Laboratory experimental studies on the stability field and reaction rate of hydrous sulfates under Mars-relevant conditions provide fundamental knowledge that can be used to explain the phenomena observed during the past, the current, and the future exploration missions on the planet, and to link these mission observations to geochemical and hydrological processes that could have happened at martian surface or within the subsurface. Extensive experimental studies have been conducted on thermodynamics and kinetics properties of Mg- and Fe³⁺-sulfates (Bish et al., 2003; Chou et al., 2002, 2013; Chou and Seal, 2003, 2007; Chipera and Vaniman, 2007; Grevel and Majzlan, 2009; Kong et al., 2011a, 2011b; Ling and Wang, 2010; Peterson and Wang, 2006; Peterson et al., 2007; Majzlan et al., 2004, 2005, 2006; Majzlan and Michallik, 2007; Tosca et al., 2007; Vaniman et al., 2004; Vaniman and Chipera, 2006; Wang et al., 2006c, 2009, 2011, 2012, 2013; Wilson and Bish, 2012; Xu et al., 2009).

This manuscript reports two sets of systematic dehydration experiments conducted on crystalline alunogen $[Al_2(SO_4)_3 \cdot 17H_2O]$ and melanterite $[FeSO_4 \cdot 7H_2O]$ under Mars relevant atmospheric pressure (*P*) and partial H₂O pressure (*P*_{H2O}) at three temperatures (*T*). The purpose of this study is to compare the dehydration process of Al- and Fe²⁺-sulfate with that of Mg-sulfate, and especially to compare their dehydration rates under Mars relevant conditions. Furthermore, we will compare our data with the reported dehydration processes of Ca- and Fe³⁺-sulfates of the highest hydration degrees (Robertson and Bish, 2013; Wang et al., 2012), in order to gain understanding on the preservation probability of these hydrous sulfates on Mars today.

2. Samples and experiments

2.1. Al-sulfate and Fe^{2+} -sulfate samples

Among 101 Al-sulfates and Al-bearing sulfates found on Earth (Gaines et al., 1997), there are ten common groups: alunogen, alum, mendozite halotrichite, voltaite, alunite, woodwardite,

felsobanyaite, aubertite and copiapite. Alunogen $Al_2(SO_4)_3 \cdot 17H_2O$ is the one having the highest hydration degree in alunogen group and is widely seen on Earth (240 localities based on mindat.org, the mineral and locality database). We selected it as the starting Al-sulfate phase for this study.

Similarly, melanterite $FeSO_4 \cdot 7H_2O$ has the highest hydration degree in ferrous sulfates, with a very similar structure to that of epsomite $MgSO_4 \cdot 7H_2O$. We select it as the starting Fe^{2+} -sulfate phase for this study.

Pure crystalline grains of alunogen and melanterite were purchased from ACROS (code 400595000, CAS 7784-31-8, lot A0259507) and ACROS (code 201390010, CAS 7782-63-0, lot A0242021). XRD measurements were made on bulk samples to confirm their identity, status of crystallinity, and hydration degrees. 5–10 Raman measurements were made on individual grains to confirm the chemical purity and homogeneity in hydration degree of the samples. The Mid-IR attenuated total reflection (ATR) and Near-IR diffuse reflection (DRF) measurements were then made to get characteristic spectra.

To prepare the starting samples for dehydration experiment, pure crystalline alunogen $[Al_2(SO_4)_3 \cdot 17H_2O]$ and melanterite $[FeSO_4 \cdot 7H_2O]$ grains were hand grounded and sieved, fine powder of 90–150 µm grain size were used in the experiments to ensure sufficient surface area for reaction. Because the dehydration of these hydrous sulfates can happened during grounding and sieving, a Petri dish filled with grounded Al-sulfate powder was placed into a glass jar filled with relative humidity (RH) buffer KNO₃ solution that maintains ~94% RH at room *T*, and was kept for a few days to re-hydrate the sample powder to reach the highest hydration degree (17w). 100-spot Raman measurements were made on the final powder sample of alunogen, and confirmed its homogeneity in hydration degree.

Similarly, a Petri dish filled with grounded Fe²⁺-sulfate powder was placed into a glass jar filled with RH buffer KCl solution (~85% RH at room *T*), and was kept for a few days to re-hydrate the sample powder to reach the highest hydration degree (7w). Specifically, a fast preparation procedure was employed for FeSO₄·7H₂O to avoid the transformation of Fe²⁺-sulfate to Fe³⁺-sulfates. No color change was observed during the whole process. 100-spot Raman measurements were made on the final powder sample of melanterite, no Raman peaks of ferric-sulfates were observed (based on previous study of ferric sulfates by Ling and Wang (2010), Kong et al. (2011a, 2011b), and Wang et al. (2012)). The homogeneity in hydration degree of this powder sample was confirmed as well.

2.2. Dehydration experiments at three temperatures

For both alunogen and melanterite, fifteen reaction vials (~10 mm diameter and 40 mm height) filled with 50–100 mg sample powder (of grain size 90–150 μ m) were prepared. The dehydration experiments were conducted by placing these vials (without caps) in a vacuumed desiccator. The atmospheric pressure in the vacuumed desiccator 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 which are lower than average atmospheric pressure on Mars (~7 mbar). Based on measured laboratory RH during the experiment period, the partial H₂O pressure (*P*_{H2O}) in vacuum desiccator was calculated and found to be in the range of 0.25–0.14 Pa, near the reported *P*_{H2O} on Mars ~0.04–0.15 Pa (Smith, 2002).

The dehydration experiments for alunogen and melanterite were conducted at three temperatures: 21 ± 1 °C by placing the vacuumed desiccator on laboratory bench-top, 0 ± 0.5 °C by placing the vacuumed desiccator in water–ice bath; and at -12 ± 2 °C by placing the vacuumed desiccator in a *T*-controlled freezer. The

Table 1

Dehydration experiments under Mars relevant pressures.

	Sample mass (mg)	Total duration (h)	End products (Raman ID)
Alunogen, $Al_2(SO_4)_3$ ·17 H_2O			
21 ± 1 °C	${\sim}60$	26	Meta alunogen
0 ± 0.5 °C	${\sim}60$	140	Meta alunogen
−12 ± 2 °C	$\sim \! 70$	209	Meta alunogen
Melanterite, FeSO ₄ :7H ₂ O			
21 ± 1 °C	~ 110	102	Razonite + AmFeSO ₄ · <i>x</i> H ₂ O (<i>x</i> > 1)
0 ± 0.5 °C	~135	174	Razonite
−12 ± 2 °C	$\sim \! 110$	238	Razonite
Epsomite, MgSO₄·7H₂O			
21 ± 1 °C	\sim 50	19	Amorphous MgSO ₄ .1.8H ₂ O
0 ± 0.5 °C	\sim 55	178	Amorphous MgSO ₄ ·1.8H ₂ O
−8 ± 2 °C	~ 55	157.5	Amorphous MgSO ₄ :4.1H ₂ O

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 h to over 200 h (Table 1). During each experiment, 10 reaction vials (among the total of 15) were taken out 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. After the mass measurements, they were placed back into the vacuumed desiccator for continuing the dehydration. 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 laser Raman spectroscopic (LRS) measurements through glass wall of reaction vial to monitor the structural changes. These vials after LRS measurements were not put back for continuing the dehydration. These samples are available for further XRD measurement to confirm the structural changes observed by LRS.

2.3. Dehydration experiment of melanterite at 1 atm

Additional 30 dehydration experiments of melanterite were conducted at Earth atmospheric pressure (1 atm), for the purpose of comparing its phase transition pathways and the rates with those of crystalline MgSO₄·7H₂O. The need for conducting these experiments came up during the data analysis of above dehydration experiments under Mars relevant *P*, P_{H2O} (discussed in Section 5.2).

During these experiments, a reaction vials (\sim 10 mm diameter and 40 mm height) containing about 50 mg FeSO₄·7H₂O powder (90–150 µm grain size) was placed into a glass bottle (\sim 25 mm diameter and 50 mm height) half-filled with a RH buffer solution. Ten RH buffers were used. Ten pairs of reaction vial and RH bottle were then placed in an environment with controlled *T*, i.e., $50 \pm 1 \,^{\circ}$ C in an oven, $21 \pm 1 \,^{\circ}$ C on laboratory bench top, and $5 \pm 1 \,^{\circ}$ C in a refrigerator. Gravimetric and LRS measurements of reaction products were conducted at pre-determined time intervals (3, 8, 16, 32, 56, 120, 192 ... hours) to monitor the dehydration processes.

2.4. Gravimetric measurements

A Citizon[®] balance with resolution 0.1 mg was used to make gravimetric measurements. The net mass loss or gain of a sample in a reaction vial is calculated by subtracting the initial mass of powder sample from the mass of dehydration product, to derive the net loss or gain of the number of H_2O per $Al_2(SO_4)_3$.17 H_2O

(or FeSO₄·7H₂O) molecule. From the gravimetric measurements of 10 reaction vials from vacuumed desiccator, the standard deviation of mass change at each time interval was calculated.

2.5. XRD measurement

XRD diffraction patterns obtained from initial alunogen and melanterite samples were used to confirm their identity, status of crystallinity, and hydration degree. XRD diffraction patterns were also obtained from some dehydration products to confirm the phase transitions observed by laser Raman spectroscopy.

A Rigaku Geigerflex X-ray diffractometer with a Cu Ka radiation source was used. A scan sequence from 5° to 55°, 0.04° per step with 1 s dwell time was used. Data reduction was made using the JadeTM software. A protocol for XRD measurement of highly hydrated sulfates was used, during which the alunogen and melanterite crystalline samples were first checked by multi-spots LRS measurement on their homogeneity, then about 0.2–0.3 g of each sample was quickly ground together with CaF₂ powder (as an internal XRD standard) and used for the collection of a powder XRD pattern. After each XRD measurement, multi-spots LRS spectra were collected again from the XRD powder sample, which showed no detectable change in hydration degree occurred during the course of the XRD measurements.

2.6. Laser Raman spectroscopic (LRS) measurement

Laser Raman spectra were taken on two initial alunogen and melanterite powder samples to confirm their homogeneity in hydration degree, and then on dehydration products through the glass wall of sealed reaction vials to identify, non-invasively, the phase changes occurred during the dehydration process.

A HoloLab5000-532 laser Raman spectrometer (Kaiser Optical Systems Inc.) was used to obtain Raman spectra of the samples from 150 to 4000 cm⁻¹ with 4–5 cm⁻¹ spectral resolution. A $20\times$ microscopic objective (NA = 0.4) was used to focus the laser beam (\sim 6 µm in diameter) of 532 nm wavelength through the glass wall of sealed sample vials onto multiple spots at the sample surface and to collect the Raman photons produced by the sample. Each measurement typically uses 2 s exposure time and 16 accumulations to get a Raman spectrum with good signal/noise ratio. About \sim 9 mW laser power was used for measuring the reaction products from alunogen, and about \sim 4 mW laser power was used for measuring the reaction products from melanterite. Full range wavelength calibration and correction are made by using the emission lines of a Ne lamp. The laser line correction is made by using the Raman line (520.7 cm^{-1}) of a Si sample. The wavelength accuracy and precision were found to be better than 0.1 cm⁻¹ in the spectral region of interest as determined by the spectral peak fitting using the GRAMS/Al software.

2.7. MIR-ATR and Near-IR DRF measurements

A Nicolet Nexus 670 Fourier transform infrared interferometer (FTIR) spectrometer was used to make Mid-IR attenuated total reflectance (ATR) measurements $(2.5-25 \,\mu\text{m})$ of the initial alunogen and melanterite samples, using a Golden-Gate ATR accessory (Harrick Scientific). The Nicolet Nexus 670 FTIR spectrometer is purged constantly using dry-N₂ in order to reduce H₂O vapor in the system and to prevent H₂O adsorption onto the samples.

Using the same Nexus 670 FTIR spectrometer, Near-IR diffuse reflectance (DRF) spectra (1–5 μ m) were measured, for which a Cricket DRF accessory (Harrick Scientific) was used with a gold-coated rough surface as the reflectance standard.

3. Crystal structures, Raman, MIR-ATR, NIR-DRF spectra of alunogen and melanterite

3.1. Structure and characteristic spectral feature of alunogen

Alunogen (Al₂(SO₄)₃·17H₂O) has a triclinic crystal structure (Fig. 1a) with unit cell parameters a = 7.42, b = 26.97, c = 6.062, Z = 2. This structure consists of isolated $[SO_4]^{2-}$ tetrahedra and isolated Al(H₂O)₆ octahedra, and has two types of crystallographic sites for aluminum atoms marked as Al₁ and Al₂. The symmetric stretching vibration mode of $[SO_4]^{2-}$ tetrahedra contributes a Raman peak at 992 cm^{-1} , the asymmetric mode contributes a MIR peak at 1064 cm⁻¹. Twelve of structural H₂O (among 17 per alunogen molecule) are coordinated with Al₁ and Al₂. The bond lengths from six H₂O to Al₁ and to Al₂ in two types of octahedra, however, are all different, which produce an extremely broad spectral band centered around 3246 cm⁻¹ in Raman spectrum (Fig. 2a) and around 2935 cm⁻¹ in MIR-ATR spectra (Fig. 3). The rest five structural H₂O (colored in yellow in Fig. 1a) occur in the interstitial spaces among tetrahedra and octahedra, bonded to alunogen structure through weak hydrogen bonding. The site symmetry differences among these H₂O bring further broadening of H₂O band in vibrational spectra.

3.2. Structure and characteristic spectral features of melanterite

Melanterite ($Fe^{2*}SO_4 \cdot 7H_2O$) has a very similar crystal structure (Fig. 1b) to epsomite (MgSO₄ · 7H₂O, Fig. 1c), whose dehydration

process and rate have already been investigated experimentally (Wang et al., 2006c, 2009, 2011, 2013) and will be compared with the results of this study. Melanterite has a monoclinic crystal structure with unit cell parameters, a = 14.040, b = 6.502, c = 10.952, Z = 4. Its structure consists of isolated $[SO_4]^{2-}$ tetrahedra and isolated Fe²⁺(H₂O)₆ octahedra. The symmetric stretching vibration mode of $[SO_4]^{2-}$ contributes a Raman peak at 976 cm⁻¹ (Fig. 2b), and the asymmetric mode contributes a MIR peak at 1073 cm⁻¹ (Fig. 3). Six of structural H₂O (among 7 per melanterite molecule) are coordinated with Fe²⁺ cation, that contribute a broad H₂O vibrational band centered around 3432 cm⁻¹ in Raman spectrum (Fig. 2a) and around 3330 cm⁻¹ in MIR-ATR spectrum (Fig. 3). The remained one structural H₂O (colored in yellow in Fig. 2a) occur in the interstitial spaces among tetrahedra and octahedra, bonded to melanterite structure through weak hydrogen bonding.

3.3. Comparing the spectral features of Al-, Fe^{2+} -, Fe^{3+} -, Mg-, and Ca-sulfates

Laser Raman spectra of alunogen and melanterite are compared with those of epsomite MgSO₄·7(H₂O), gypsum CaSO₄·2(H₂O), and ferricopiapite Fe_{4.67}(SO₄)₆(OH)₂·20H₂O in Fig. 2. We notice that the v₁ symmetric starching vibration mode of SO₄ in these five Al-, Fe²⁺-, Mg-, Ca-, and Fe³⁺-sulfates occur at 992, 976, 984, 1008, and 990/1019 cm⁻¹ respectively (Fig. 2b). With other minor peaks shown in Fig. 2, these five sulfates can be distinguished on the basis of their finger-print Raman spectra.

Based on the previous studies by us and other groups on the Mg-, Fe^{2+} -, Fe^{3+} -, and Ca-sulfates with different hydration degrees,



Fig. 1. Crystal structures of alunogen (a), melanterite (b), epsomite (c), and starkeyite (d). The first three structures are made of isolated $[SO_4]^{2-}$ tetrahedra and isolated $A^{3+}(H_2O)_6$ (or $Fe^{2+}(H_2O)_6$, or $Mg(H_2O)_6$) octahedra. The rest five (or one in melanterite and epsomite) structural H_2O (colored in yellow) occur in the interstitial spaces among tetrahedra and octahedra, bonded to the host structure through weak hydrogen bonding. The starkeyite (rozenite as well) structure in (d) contains a sub-unit, four-member rings made of two SO₄ tetrahedra and two $MgO_2(H_2O)_4$ octrahedra by sharing corner oxygen. The size and stability of ring are determined by the sizes of tetrahedra and octahedra.

fundamental modes of SO₄

Fig. 2. Raman spectra of alunogen, melanterite, ferricopiapite, epsomite, and gypsum: (a) spectral range for H₂O vibrational modes and (b) spectral range for



Fig. 3. Mid-IR attenuated total reflectance (ATR) spectra of alunogen, melanterite, ferricopiapite, epsomite, and gypsum.

the v₁ peak position changes in their spectra are affected mainly by their hydration degrees, rather than the mass-effect of Al, Fe, Mg, Ca cations. For example, the hydration degree changes in Mgsulfates from anhydrous (0w) to epsomite (7w) would cause v₁ shift from 1048 to 984 cm⁻¹ (Wang et al., 2006c, 2011); in Casulfates from anhydrite (0w) to gypsum (2w) would cause v₁ shift from 1017 to 1008 cm⁻¹ (Wang et al., 2009); in Fe²⁺-sulfate from szomolnokite (1w) to melanterite (7w) would cause v₁ shift from 1018 to 976 cm⁻¹ (Chio et al., 2007); in Fe³⁺-sulfates from rhomboclase (4w) to ferricopiapite (20w) would cause v₁ shift from 1030 to 1019 cm⁻¹ (Ling and Wang, 2010). No experimental investigation on Al-sulfates with different hydration degrees has been done, which is obviously very much needed to understand the details of their Raman spectral features. It is worth to notice that a general trend exists in all four types of sulfates, i.e., v_1 downshift to low wavenumber with increasing hydration degree. Another significant difference among the Raman spectra of five sulfates is the position and width of H₂O spectral bands, where alunogen has the broadest H₂O band and greatest band-center downshift to low wavenumber.

A similar H₂O band broadening and downshift are observed in MIR-ATR spectrum of alunogen, when compared with Fe²⁺-, Fe³⁺-, Mg-, Ca-sulfates (Fig. 3). The bending vibrational modes of H₂O of all five sulfates appear more obviously in MIR-ATR than in Raman spectra. In contrast, the peak position shift (marked by a dotted line in Fig. 3) of v₃ mode of $(SO_4)^{2-}$ group in MIR-ATR spectra are not as remarkable as the v₁ mode in Raman spectra. A sharp peak appears at low-wavenumber-side of v₃ mode in MIR-ATR spectra of both alunogen and epsomite. The peak positions suggest that they are Raman-active v₁ mode of $(SO_4)^{2-}$ group. These peaks demonstrate the narrow peak width than those of MIR-ATR spectral peaks. Apparently, the MIR-ATR peaks from H₂O vibrations would serve the best criteria to distinguish these sulfates.

The absorption bands in Near-IR diffuse reflectance (DRF) spectra (1–2.5 μ m) are contributed by the overtone and combinational modes of H₂O vibrations, and by metal–OH vibrations of the sulfates. Because the large number of H₂O molecules in alunogen structure and their high variability in site symmetry, the NIR-DRF spectrum of alunogen has much less spectral contrast than those obtained from Fe²⁺-, Fe³⁺-, Mg-, Ca-sulfates (Fig. 4). The absorption bands near 1.4 μ m, 1.9 μ m, 2.4 μ m do exist in alunogen spectrum (marked by three dotted lines in Fig. 4), but are barely visible. The spectrum of alunogen is totally absorption saturated in the spectral range longer than 2.7 μ m.

4. Results of dehydration experiments at Mar relevant conditions

The dehydration and rehydration processes, especially the reaction rates, of a hydrous salt depend on many factors. The temperature (*T*), atmospheric pressure (*P*), and partial H₂O pressure in atmosphere (P_{H2O}) are the major environmental affecting parameters. The crystal structure, stability field, phase transition pathway, and activation energy of the salt itself are the internal determining parameters. The laboratory experiments that we and other research teams have conducted in the past on Mg-, Fe³⁺-, Ca-sulfates, as well as Al-, Fe²⁺-sulfates in current studies, are purposed to drive the dehydration and rehydration processes of a salt by controlling the environmental parameters, in order to gain a better understanding on the internal parameters of the studied salt.

When the goal is to understand the dehydration and rehydration processes of a salt that happened on Mars, two types of experimental conditions, i.e., under Mars relevant atmospheric pressure (P_{Mars}) and under Earth atmospheric pressure (P_{Earth}), must be used for one essential reason: that is the collisions among gas molecules (including H₂O) and the collisions between gas molecules and solid surface at different atmospheric conditions will affect the progress of a dehydration or a rehydration process of the studied salts. Thus any observed dehydration (or rehydration) process would be the net result of dehydration minus rehydration that is caused by the recapture of H₂O by salt surface due to the collisions.

Based on this understanding, only the parameters extracted from the experiments conducted under P_{Mars} can be reasonably used to estimate the dehydration and rehydration processes on Mars (Wang et al., 2013). However, there is an experimental difficulty. Although a dehydration process on Mars can be approximately simulated in laboratory, such as to conduct experiments in a low-vacuum environment with controlled *T* and approximate P_{H2O} (we used a vacuumed desiccator in three *T* environments to



do so, Section 2.2); the rehydration process under Mars relevant Pand P_{H2O} would be so slow that cannot be reasonably simulated during a feasible laboratory experimental duration (e.g., a few months or years). For that reason, the experiments under P_{Earth} with controlled T and RH (i.e., P_{H2O}) were conducted to provide an overview on the fundamental properties of targeting salts, especially the difference among the different dehydration and rehydration processes, which could in turn help the understanding of dehydration-rehydration cycles on Mars. For example, the rate ratios of the dehydration and rehydration of Mg-sulfates as function of T were found through the experimental study under P_{Earth} (Wang et al., 2006c, 2009, 2011), which are used in combination with the activation energy value derived by dehydration experiments under P_{Mars} to model the preservation potential of hydrous Mg-sulfates in subsurface salty layer on Mars within certain T range (Wang et al., 2013).

The experiments reported here are conducted under P_{Mars} , intended to gain the first order information on the relative dehydration rates of hydrous sulfates with different cations and the highest hydration degrees under Mars relevant P and P_{H2O} . The purpose of running the experiments at different Ts is to find the *T* dependence differences of the dehydration process of Al-, Fe²⁺-, and Mgsulfates. The selection of *T* range (21 °C, 0 °C, -12 °C) in this experiment was based on a compromise between Mars' surface temperature range at equatorial region (e.g., -88 °C to 22 °C) measured by the Spirit and Opportunity rovers, and the need to have a reasonable experimental duration in laboratory.

A full set of dehydration and rehydration experiments of common Al- and Al-bearing sulfates under P_{Earth} with controlled Ts and RHs will need to be conducted, in order to gain a comprehensive knowledge basis on their thermodynamic and kinetic properties.

4.1. Results of gravimetric measurements – the loss of structural H₂O

The results from gravimetric measurements of two sets of experiments at three Ts are plotted in Fig. 5a–c, as n(t)/n(0) (%) vs. time duration (in minutes), where n(t) is the number of structural H₂O per molecule (alunogen or melanterite) at a time (t) and n(0) is the same value at the beginning of experiment. n(0) = 17 and 7 were used in calculations for alunogen and melanterite respectively. Each point in these plots is calculated from the average mass value at each time interval based on the mass measurements of 10 sample vials after removing the maximum and minimum value, and the standard deviation of the ten values is calculated and shown as error bar in Fig. 5a–c. The data from dehydration experiments of epsomite under P_{Mars} relative pressure (experiments reported in Wang et al., 2009) were also plotted in Fig. 5a–c for comparison.

The resolution of the Citizon[®] balance used for gravimetric measurements is 0.1 mg. If we use 0.5 mg as the uncertainty in mass measurements, it would correspond an uncertainty of 0.3 in calculated number of structural H₂O per alunogen molecule $(60 \pm 5 \text{ mg} \text{ net mass per alunogen sample used, Table 1})$, and 1.8% in a n(t)/n(0)/(%) plot (Fig. 5). Similarly, it corresponds an uncertainty of 0.1 in calculated the number of structural H₂O per melanterite molecule $(120 \pm 5 \text{ mg} \text{ net mass per melanterite sample used, Table 1})$, and 1% in a n(t)/n(0)/(%) plot. Apparently, the mass measurement uncertainties brought by balance are smaller than the calculated standard deviations from the measurements on ten reaction vials for each set of experiments, which involve the differences in sample preparation among the reaction vials; porosity can be one of them.

Fig. 5a first reveals the very different dehydration pathways among alunogen, melanterite, and epsomite at 294 K. Alunogen dehydrated very fast in first 10 min, reached a hydration degree



of ~13.4 H₂O per Al₂(SO₄)₃ molecule, and then being maintained at that value during the rest period of dehydration experiment. Melanterite loss its H₂O slowly at the beginning, gradually reached a hydration degree of ~4.3 H₂O per FeSO₄ molecule in 2 h. This level of hydration was maintained for next 13 h, then started to decrease again and reached ~2.8 H₂O per FeSO₄ molecule by the end of 102 h experiment. In comparison, epsomite dehydrated with a similar slope as melanterite in first 20 min. After that, it behaved quite different from melanterite: the dehydration continued without going through a middle-stable stage, and reached a much deeper dehydration of ~1.8 H₂O per MgSO₄ molecule.

At lower temperature (Fig. 5b and c), the dehydration of alunogen went much slower, gradually reached ~14w after 90 min at 273 K and 95 h at 261 K in reactions. At these Ts, the first stage of melanterite dehydration (~3.8–4.3w) was reached with longer durations (28 h at 273 K and 174 h at 261 K), but no further dehydration was observed within the durations of experiments. At 273 K, the dehydration of epsomite reached the same low hydration degree (1.8w) as at 294 K (but took much longer duration, 178 h compare with 19 h). At 265 K, the epsomite sample reached much less dehydration level, ~4.1w.

When placing two vertical dotted lines in Fig. 5a, and compare the pattern on left side of first line with Fig. 5b and the pattern on left side of second line with Fig. 5c, we can see the similarities among the two pairs of plots. These comparisons show a slow down dehydration by low temperature, without observable differences in the dehydration processes at different temperatures.

These experimental results reveal that first, very similar to epsomite, the dehydration of both alunogen and melanterite are strongly dependent on temperature. At low temperatures, not only the percentage of lost structural water is less (61% at 294 K, 45% at 273 K, and 33% at 261 K for about 100 h dehydration of melanterite), but also the dehydration process took a much longer time to reach the same degree of hydration (for alunogen to reach ~14w, it took 10 min at 294 K, 90 min at 273 K, and 95 h at 261 K). Secondly, the dehydration pathways and the ending hydration degrees of three sulfates are very different, which





Fig. 5. Number of H₂O per sulfate molecule (Al₂(SO₄)₃·17H₂O, FeSO₄·7H₂O, and MgSO₄·7H₂O), as n(t)/n(0)m (%) vs. experimental duration in minutes, during the process of dehydration under Mars relevant *P* and *P*_{H2O}, calculated based on gravimetric measurements. Each point is the average mass value at specific time interval during dehydration, calculated from the averaged mass measurements of 10 sample vials after removing the maximum and minimum value. The standard deviation of the ten values is calculated and shown as error bars. Temperates of the experiments are (a) at 294 K; (b) at 273 K, (c) at 261–265 K. Larger symbols with black edge represent the time intervals when a sample were taken out for laser Raman spectroscopy measurement and the Raman spectra were presented in Figs. 6–8.



Fig. 6. Raman spectra of dehydration products of epsomite under Mars relevant pressure and partial H_2O pressure at 294 K: (a) spectral range for H_2O vibrational modes and (b) spectral range for fundamental modes of SO₄.

obviously relate to their structural and chemical features, which would affect the activation energy values for phase transitions.

4.2. Results of LRS measurements - the dehydration pathways

Laser Raman spectroscopic (LRS) measurements were taken on five reaction vials from each of six sets of dehydration experiments of alunogen and melanterite. Those reaction vials were taken out from the vacuumed desiccator at pre-determined different time intervals that are larger than those for gravimetric measurements. These reaction vials were never put back, thus the dehydration products in the vials maintained the same structural form and hydration degree as they were taken out. In addition to LRS measurements, XRD measurements were made on the samples to confirm LRS phase identifications. The mass measurements of the dehydrated samples corresponded with the five LRS measurements are marked as large diamonds with black edge in Fig. 5. The averaged numbers of H_2O per salt molecule were marked in Figs. 6–8, next to their Raman spectra.

For comparison purpose, Raman spectra of dehydration products of epsomite from a similar set of experiment run under Mars relevant conditions were first shown in Fig. 6 (experiments reported in Wang et al., 2009). At 294 K, epsomite first dehydrated partially to hexahydrite (MgSO₄·6H₂O) in 20 min, shown as v_1 peak at 984.1 cm⁻¹ shifting to 983.6 cm⁻¹ (Fig. 6b) accompanied by a change of H₂O peak shape and additional peak shoulder near 3200 cm⁻¹ (top three spectra in Fig. 6a). This phase transition reflects the lost of one structural H₂O per epsomite that is not coordinated with Mg cation but weakly bonded in crystal lattice by hydrogen bonding (the H₂O molecule colored in yellow in epsomite structure, Fig. 1c). The continuous dehydration caused the collapse of hexahydrite lattice that produced the amorphous MgSO₄·xH₂O, shown as the appearance (starting at 40 min) and growth of a very broad v_1 Raman peak (Fig. 6b). Following the development of dehydration (from 5.5w to 1.8w), the central position of this broad peak continued a shift from 1025 to 1034 cm⁻¹ (indicated by a dotted line in Fig. 6b). The last four spectra in Fig. 6b suggests that the entire Mg-sulfate sample became



Fig. 7. Raman spectra of dehydration products of melanterite under Mars relevant pressure and partial H₂O pressure at 294 K: (a) spectral range for H₂O vibrational modes and (b) spectral range for fundamental modes of SO₄.



Fig. 8. Raman spectra of dehydration products of alunogen under Mars relevant pressure and partial H₂O pressure at 294 K: (a) spectral range for H₂O vibrational modes and (b and c) spectral range for fundamental modes of SO₄.

amorphous $MgSO_4 \cdot xH_2O$, with *x* value change from 2.9 to 1.8. Similar structural change happened in the experiment at 273 K and 265 K for epsomite (not shown here, see Wang et al., 2009).

The Raman spectra of dehydration products from the dehydration experiment of melanterite under Mars relevant conditions show a different phase transition pathway (Fig. 7a and b, based on Choi et al., 2007). 40 min after the dehydration started, the original melanterite [FeSO₄·7H₂O] partial converted to rozenite [FeSO₄·4H₂-O], demonstrated by the appearance of a new Raman peak at 990 cm⁻¹, next to the v₁ mode of SO₄ of melanterite at 976 cm⁻¹ (Fig. 7b), accompanied by a change of H₂O multi-component peak pattern from that of melanterite to rozenite (Fig. 7a). After 30 h into the dehydration, a weak and broad spectral shoulder centered near 1012 cm⁻¹ started to appear, accompanied by the total disappearance of melanterite 976 cm⁻¹ peak. This shoulder continued to grow and became a strong and very broad peak in the measurement taken on the products after 102 h into the dehydration, in which the Raman v₁ peak (990 cm⁻¹) of rozenite still remained (bottom spectrum in Fig. 7b). This change is accompanied by the reduction of the spectral contrast of H₂O multi-component peak pattern (bottom spectrum Fig. 7a). If szomolnokite [FeSO₄·H₂O] formed from the dehydration of rozenite, a v₁ peak at 1018 cm⁻¹ would appear with similar peak width as melanterite and rozenite (Chio et al., 2007). The growth of broad 1012 cm⁻¹ peak (Fig. 7b) and the reduction in spectral contrast in H₂O range (Fig. 7a) all suggest the formation of amorphous (Am) FeSO₄·xH₂O, instead of szomolnokite. Based on a general trend of Raman v₁ peak position shift with hydration degrees (discussed in Section 3.3), the central peak position at 1012 cm⁻¹ suggest a FeSO₄·xH₂O with x > 1. The final hydration degree reached after 102 h dehydration was 2.8w per FeSO₄. molecule (Fig. 5a at 294 K), which is consistent with a mixture of Am-FeSO₄· xH₂O (with x > 1) and FeSO₄· 4H₂O, as indicated by its Raman spectrum (Fig. 7b).

Based on both gravimetric and LRS data, and the early Raman spectroscopic study of melanterite, rozenite, and szomolnokite made by Chio et al. (2007), we see during the first step dehydration of melanterite in our experiment not only the hydrogen bonded single H₂O (colored in yellow in Fig. 1b) got lost, but also a deeper dehydration was achieved, i.e., rozenite FeSO₄:4H₂O was formed without going through a ferrohexahydrite FeSO₄·6H₂O stage, in comparing the occurrence of hexahydrite MgSO₄·6H₂O in epsomite dehydration (Fig. 6). On Earth, ferrohexahydrite is extremely rare in nature (Hemingway et al., 2002; Fleischer, 1963). The second difference was that FeSO4·4H2O continued to dehydrate after a metastable 13 h period at 294 K (Fig. 5a), whereas the dehydration of starkevite MgSO₄·4H₂O under the same conditions has not occurred (Wang et al., 2006c) suggesting a structurally much stable MgSO₄·4H₂O. Furthermore, it is very interesting to observe the formation of amorphous FeSO₄·xH₂O during the dehydration of rozenite, whereas the formation of amorphous MgSO₄·xH₂O was always from epsomite or hexahydrite, but never from starkeyite MgSO₄·4H₂O.

The Raman spectra of dehydration products from the dehydration experiments of alunogen under Mars relevant conditions show another different phase transition pathway (Fig. 8). After 26 h into experiment at 294 K, the Raman peak contributed by v1 mode of original alunogen at 992 cm⁻¹ (top spectrum in Fig. 8b) converted into a double peak at 999 cm⁻¹ and 993 cm⁻¹ plus a spectral shoulder at 983 cm⁻¹ (bottom spectrum in Fig. 8b), accompanied by the peak narrowing from ${\sim}14\ cm^{-1}$ (full-width at half-height, FWHH) of alunogen v_1 mode to 6–9 cm⁻¹ of the new phase (using a spectral peak curve fitting procedure in Grams/AI package). In addition, among the peaks contributed by v_3 mode, a new peak at 1778 cm⁻¹ and the strengthening of 1086 cm^{-1} peak appeared. In H₂O/OH spectral range (Fig. 8a), a new peak at 3404 cm⁻¹ and the intensity changes in spectral shoulders at 3078 cm⁻¹ and 2927 cm⁻¹ occurred. Among the peaks contributed by v_2 , v_4 , and lattice modes (Fig. 8c, the top and bottom spectra), the change was basically the increases of spectral contrast.

The increase of Raman spectral contrast normally suggests the formation of a crystal structure with higher degree of structural ordering, i.e., with better defined crystallographic sites for polyhedral SO₄, Al(H_2O)₆, and structural H_2O . Please note the Raman peak of v_1 mode from alunogen is the widest (~14 cm⁻¹) compared with similar peaks of melanterite (9 cm^{-1}), epsomite (11 cm^{-1}) and gypsum (10 cm^{-1}) (Fig. 2b). In addition, alunogen structure has five hydrogen-bonded H₂O that are not coordinated with Al cation (colored in yellow, Fig. 1a). After 26 h' dehydration at 294 K, the remain hydrogen-bonded H₂O (yellow H₂O in Fig. 1a) dropped to almost one per $Al_2(SO_4)_3$ molecule (13.4w, Fig. 5a). The Raman spectral feature variations following the dehydration suggest the generation of three sets of crystallographic equivalent sites for SO_4 tetrahedra (corresponding three v₁ peaks in bottom spectrum of Fig. 8b) in newly formed crystal lattice, as well as more distinct sites for remained H_2O (new peak at 3404 cm⁻¹, Fig. 8a), while the main crystal framework remained unchanged (no obvious change in spectra patterns in Fig. 8c) except the increase of structural ordering. The X-ray diffraction pattern from this sample matched with a phase called meta-alunogen, $(Al_2(SO_4)_3, 12H_2O)$, whereas no structural information was given and we did not found a report in literature.

The middle two spectra in Fig. 8 were taken from the dehydration products of alunogen at 261 K, at two intermediate stages (shown as larger symbols with black edge in Fig. 5c). These spectra revealed the development of second peak at 999 cm⁻¹ for v_1 mode and of the peak at 3404 cm⁻¹ for H₂O. The dehydrations at lower Ts (273 K and 261 K) were not developed as fast at that at 294 K, while these spectra demonstrated that they followed the same phase transition pathway.

5. Comparison among Al-, Fe^{2+} -, Fe^{3+} -, Mg-, and Ca-sulfates and implication to sulfate dehydrations on Mars

The results of six sets of dehydration experiments on alunogen and melanterite under Mars relevant atmospheric pressure and partial H_2O pressure, in comparison with the results of similar dehydration experiments of epsomite, revealed very different phase transition pathways and very different rates of dehydration process. They reflect the differences in fundamental compositional and structural properties of these three sulfates.

5.1. Comparison in dehydration pathways

Obviously, from the structures of all three hydrous sulfates, the hydrogen-bonded structural H₂O molecules (five in alunogen, one in epsomite and in melanterite) are the first one to lose during their dehydration processes. Among them, alunogen lost its hydrogen-bonded structural H₂O much faster than epsomite and melanterite, reached 20% H₂O loss in 15 min at 294 K while the other two reached the same level of H₂O loss in 40 min (Fig. 5a), suggesting an highly unstable structure of $Al_2(SO_4)_3$.17H₂O.

Oppositely, the meta-alunogen $Al_2(SO_4)_3 \cdot 12H_2O$ (4 H₂O per SO₄) has a much stable structure than hexahydrite (MgSO₄·6H₂O) and rozenite(FeSO₄·4H₂O), that showed almost no change in hydration degree when the later two dehydrated to 1.8 or to 2.8 H₂O per SO₄ under the same *P*, *P*_{H2O}, *T*, and time duration.

The comparison of dehydration processes of melanterite and epsomite are complicate because both can have two different pathways, involving crystalline-to-crystalline or crystalline-toamorphous phase transitions. During fast dehydration, i.e., vacuumed desiccators experiment under Mars relevant P, P_{H2O} at T above -12 °C, the dehydration of epsomite went through hexahydrite, then amorphous $MgSO_4 xH_2O$ (x changes from 3w to 1.8w. Wang et al., 2009). The dehydration of melanterite went through rozenite, then amorphous $FeSO_4 \cdot xH_2O(x > 1w in this study)$. From those experiments, we have observed that (1) compared with hexahydrite, ferrohexahydrite is much less stable that does not appear as an intermediate stage of dehydration even when the dehydrations progressed very slow, i.e., at 273 K and 261 K (Fig. 7); (2) compared with rozenite, amorphous MgSO₄·xH₂O is less stable that dehydrated to 1.8w at 294 K while the dehydration of rozenite reached 2.8w under the same conditions (Fig. 5a); (3) compared with starkeyite, rozenite is less stable that dehydrated and amorphosized to 2.8w (Fig. 5a) while starkeyite stayed unchanged under the same conditions (Wang et al., 2006c).

We believe, after losing the hydrogen-bonded H₂O, the dehydration pathways, the stability of crystalline intermediate phases, and the possibility of forming amorphous phases of those hydrous salts are reflections of $M(H_2O)_6$ (M = Al, Mg, Fe²⁺) octahedra structures. The stability of M(H₂O)₆ sub-unit during a dehydration process are apparently determined by their sizes, which are the function of M-H₂O bonding length of the octahedra. It is because in a smaller $M(H_2O)_6$ octahedron, the electrostatic force employed by metal cation would hold its coordinating H₂O tighter, thus more resistant to dehydration. Based on this concept, the ultra-stability of Al(H₂O)₆ in meta-alunogen against dehydration is the result of its smallest size compared with Mg(H₂O)₆ and Fe(H₂O)₆. The average distance of Al-H₂O bonding in Al(H₂O)₆ octahedra of alunogen is 1.888 Å, with maximum of 1.916 Å and minimum of 1.866 Å. In comparison, the extreme instability of ferrohexahydrite is due to the large size of $Fe(H_2O)_6$ with the average distance of $Fe^{2+}-H_2O$ bonding in melanterite to be 2.12 Å, with maximum of 2.184 Å and minimum of 2.062 Å. The similar values for Mg $-H_2O$ bonds in epsomite are 2.066, 2.098, and 2.045 Å, thus the stability of Mg $(H_2O)_6$ (and of hexahydrite) is in between of meta-alunogen and ferrohexahydrite.

The structural similarity of rozenite and starkeyite is that both have a sub-structural unit, a four-member ring made of two SO₄ tetrahedra and two (Fe or Mg)O₂(H₂O)₄ octahedra by sharing corner oxygen (starkeyite shown in Fig. 1d). This four-member ring would help maintaining the structural stability against dehydration, because additional activation energy would be needed to break-off the ring, in order to form kieserite MgSO₄·H₂O and szomolnokite FeSO₄·H₂O. The observed higher stability of starkeyite than that of rozenite against dehydration is caused by the smaller size of its four-member ring, with smaller SO₄ tetrahedra (average S–O bond length of 1.472 Å) and MgO₂(H₂O)₄ octahedra (average lengths of similar bonds in rozenite are 1.489 Å and 2.120 Å respectively.

5.2. A comparison of dehydration rates

When comparing the dehydration rates, the dehydration pathways have to be considered. Fig. 5a revealed that under the same P and P_{H2O} (Mars relevant conditions), Ts, the dehydration of epsomite (when going through amorphous phases) has the fastest rate. During a similar length of dehydration duration, epsomite would loss more structural H₂O, e.g., 80% at 294 K in \sim 20 h, while alunogen has the lowest dehydration rate, \sim 20% at 294 K in \sim 20 h, and melanterite has a median rate, lost \sim 50% of structural H₂O at 294 K in \sim 20 h. The highest dehydration rate of epsomite under this set of conditions is due to the easiness of removing structural H₂O from an amorphous phase with irregular structural sub-units and low translational symmetry than from a highly order crystalline lattice. The amorphous MgSO₄·xH₂O formed at the earlier stage of dehydration (40 min into dehydration at 294 K) than amorphous FeSO₄·xH₂O (30 h into dehydration at 294 K) could be the reason to generate an overall fast dehydration rate of epsomite (Fig. 5).

When a similar dehydration experiment of epsomite being conducted at lower temperature (265 K, Wang et al., 2009), a competition between forming amorphous or crystalline species occurred. Although the amorphization dominated eventually in that specific experiment, it suggests, however, the formation of crystalline phase, starkeyite, may dominate at even lower temperature. As discussed, crystalline starkeyite has a higher stability than razonite. It is thus very possible that epsomite would have a lower dehydration rate than melanterite at much lower temperature (lower than the Ts reached by our experiments), when amorphous phase will not occur during the dehydration processes of Mg- and Fe²⁺-sulfates.

To demonstrate this hypothesis, we conducted a set of 30 dehydration/rehydration experiments on melanterite using RH buffer technology under 1 atm (P_{Earth}). In Fig. 9, we compare the dehydration of melanterite at 323 K and 31%RH with the dehydration of epsomite under the same conditions. In both experiments, only crystalline-to-crystalline phase transformations happened. It is very interesting to see that when amorphization was not involved in dehydration processes of these two sulfates, melanterite has a faster dehydration rate than epsomite, which is consistent with the discussion of Section 5.1, i.e., Fe(H₂O)₆ has a larger size than Mg(H₂O)₆.

Fig. 9 also shows the dehydration of a ferric sulfate, ferricopiapite $Fe_{4.67}(SO_4)_6(OH)_2 \cdot 20H_2O$, under the same conditions, it has a much slower dehydration rate than that of epsomite. Note although the experiments shown in Fig. 9 were conducted at P_{Earth} , the relative rates among three sulfates are meaningful for the implication on Mar, because they reflect the fundamental differences in their properties. In order to compare our results with the dehydration process of Ca-sulfate, i.e., gypsum CaSO₄·2H₂O, we used data reported by Robertson and Bish (2013), who conducted the laboratory investigation on the phase transition among three CaSO₄·*x*H₂O (*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 323 K in vacuum of 15 Pa (0.15 mbar). If compare their observation (20,160 min) with the starting time of dehydrations of alunogen, epsomite, and melanterite (20–40 min) at similar atmospheric pressure but a lower temperature at 294 K (Fig. 5a), it can be readily concluded that gypsum has the lowest dehydration rate among all tested Al-, Fe²⁺-, Fe³⁺-, Mg- and Ca-sulfates with the highest hydration degree.

Therefore the order of dehydration rates among these sulfates with the highest hydration degree should be, from fast to slow, epsomite (through amorphization), melanterite, epsomite (not through amorphization), alunogen, ferricopiapite, and gypsum.

5.3. Implication to sulfate dehydration on Mars

From the dehydration experiments of epsomite under Mars relevant P and P_{H2O} at three temperatures (through amorphization), Wang et al. (2013) extracted the value of activity energy Ea for epsomite dehydration for that specific pathway, i.e., epsomite \rightarrow hexahydrite \rightarrow amorphous MgSO₄·*x*H₂O (*x* changes continuously). Based on this *Ea* value, the half-life $(t_{1/2})$ of epsomite dehydration (through amorphization) within a model predicted T range for subsurface sulfate-rich layer at Mars equator was estimated. The half-life at different temperatures were then used to calculate the dehydration-rehydration cycles of Mg-sulfates in that environment as the function of Mars obliquity cycles (Laskar et al., 2004). Wang et al. (2013) found that subsurface hydrous Mg-sulfates formed at equatorial regions on Mars during past high obliquity periods (>45°, the most recent one was \sim 5.4 Million years ago) have a high probability to maintain mid-to-high degrees of hydration even until the present epoch.

The experimental results reported in this manuscript demonstrated that epsomite dehydration (through amorphoization) has the fastest dehydration rates in our experimental temperature



Fig. 9. Number of H₂O per sulfate molecule (Fe_{4.67}(SO₄)₆(OH)₂·20H₂O, FeSO₄·7H₂O, and MgSO₄·7H₂O), as n(t)/n(0)m (%) vs. experimental duration in minutes, during the process of dehydration at 1 atm (P_{Earth}), 31%RH, and 323 K, calculated based on gravimetric measurements. Phase identifications made by LRS for end-products of dehydrations were marked. Only crystalline-to-crystalline phase transformation happened during these reactions.

range of 294–261 K. Based on that, and extrapolating from the conclusion of Wang et al. (2013), the implication of current study suggests that if Al-, Fe³⁺-, and Ca-sulfates formed during high obliquity periods in subsurface salt-rich layers, even higher% of structural H_2O in them (than that in Mg-sulfate through amorphization) would remain until today.

This prediction based on experiments is consistent with an observation made by the Spirit rover at Gusev on Mars. A color change of Fe^{3+} -sulfate-rich salty soil layer excavated by the Spirit rover was observed (Wang et al., 2008). The change in Vis–NIR spectra extracted from this soil is consistent with what would be caused by the dehydration of ferricopiapite $Fe_{4.67}(SO_4)_6(OH)_2 \cdot 20H_2O$ (Wang and Ling, 2011).

Our current study further support 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 (Feldman et al., 2004b; Jakosky et al., 2005; Fialips et al., 2005).

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References

- Adele, M. et al., 2010. Mineral species control of aluminum solubility in sulfate-rich acidic waters. Geochim. Cosmochim. Acta 75, 965–977.
- Altheide, T.S. et al., 2010. Mineralogical characterization of acid weathered phyllosilicates with implications for secondary martian deposits. Geochim. Cosmochim. Acta 74, 6232–6248.
- Arvidson, R.E. et al., 2006. Overview of the Spirit Mars Exploration Rover mission to Gusev crater: Landing site to Backstay rock in the Columbia Hills. J. Geophys. Res. 111, E02S01. http://dx.doi.org/10.1029/2005JE002499.
- Bibring, J.P. et al., 2006. Global mineralogical and aqueous mars history derived from OMEGA/Mars express data. Science 312, 400–404.
- Bigham, J.M., Nordstrom, D.K., 2000. Iron and aluminum hydroxysulfates from acid sulfate waters. Rev. Miner. Geochem. 40, 351–403.
- Bish, D.L. et al., 2003. Stability of hydrous minerals on the martian surface. Icarus 164, 96–103.
- Bish, D.L. et al., 2013. First X-ray diffraction results from mars science laboratory: Mineralogy of Rocknest aeolian bedform at Gale crater. Lunar Planet. Sci. 44. Abstract #1111.
- Blake, D. et al., 2013. Mineralogy and elemental composition of wind drift soil at Rocknest, Gale crater. Lunar Planet. Sci. 44. Abstract #1289.
- Carter, J., Poulet, F., 2012. Orbital identification of clays and carbonates in Gusev crater. Icarus 219, 250–253.
- Chio, C.H. et al., 2007. The hydrates and deuterates of ferrous sulfate (FeSO₄): A Raman spectroscopic study. J. Raman Spectrosc. 38, 87–99.
- Chipera, S.J., Vaniman, D.T., 2007. Experimental stability of magnesium sulfate hydrates that may be present on Mars. Geochim. Cosmochim. Acta 71, 241–250.
- Chou, I.M., Seal, R.R., 2003. Determination of epsomite–hexahydrite equilibria by the humidity-buffer technique at 0.1 MPa with implications for phase equilibria in the system MgSO₄–H₂O. Astrobiology 3, 619–630.
- Chou, I.M., Seal, R.R., 2007. Magnesium and calcium sulfate stabilities and the water budget of Mars. J. Geophys. Res. 112, E11004. http://dx.doi.org/10.1029/ 2007JE002898.
- Chou, I.M. et al., 2002. Determination of melanterite-rozenite and chalcanthitebonattite equilibria by humidity measurements at 0.1 MPa. Am. Miner. 87, 108– 114.
- Chou, I.M. et al., 2013. The stability of sulfate and hydrated sulfate minerals near ambient conditions and their significance in environmental and planetary sciences. J. Asian Earth Sci. 62, 734–758.
- Clark, B.C. et al., 2005. Chemistry and mineralogy of outcrops at Meridiani Planum. Earth Planet. Sci. Lett. 240, 73–94.
- Clark, B.C. et al., 2007. Evidence for montmorillonite or its compositional equivalent in Columbia Hills, Mars. J. Geophys. Res. 112, E06S01. http://dx.doi.org/10.1029/ 2006JE002756.
- Feldman, W.C. et al., 2004a. Recharge mechanism of near-equatorial hydrogen on Mars: Atmospheric redistribution or sub-surface aquifer. J. Geophys. Res. 109, E09006. http://dx.doi.org/10.1029/2003JE002160.
- Feldman, W.C. et al., 2004b. Hydrated states of MgSO₄ at equatorial latitudes on Mars. Geophys. Res. Lett. 31, L16702. http://dx.doi.org/10.1029/2004GL020181.

- Fialips, C.I. et al., 2005. Hydration state of zeolites, clays, and hydrated salts under present-day martian surface conditions: Can hydrous minerals account for Mars Odyssey observations of near-equatorial water-equivalent hydrogen? Icarus 178, 74–83.
- Fleischer, M., 1963. New mineral names. Am. Miner. 48, 433p.
- Gaines, R.V. et al., 1997. Dana's New Mineralogy. John Wiley & Sons, Inc.
- Grevel, K.D., Majzlan, J., 2009. Internally consistent thermodynamic data for magnesium sulfate hydrates. Geochim. Cosmochim. Acta 73, 6805–6815.
- Haskin, L.A. et al., 2005. Water alteration of rocks and soils from the spirit rover site, Gusev crater, Mars. Nature 436, 66–69.
- Hemingway, B.S. et al., 2002. Thermodynamic Data for Modeling Acid-Mine Drainage Problems. Part I. Selected Soluble Ironsulfate Minerals. U.S. Geol. Surv. Open File Rep., 02-161.
- Jakosky, B.M. et al., 2005. Mars low-latitude neutron distribution: Possible remnant near-surface water ice and a mechanism for its recent emplacement. Icarus 175. http://dx.doi.org/10.1016/j.icarus.2004.11.014.
- Klingehofer, G. et al., 2004. Jarosite and hematite at Meridiani Planum from Opportunity's Mossbauer spectrometer. Science 306, 1740–1745.
- Kong, W.G. et al., 2011a. Experimental determination of the phase boundary between kornelite and pentahydrated ferric sulfate at 0.1 MPa. Chem. Geol. 284, 333–338.
- Kong, W.G. et al., 2011b. A comprehensive spectroscopic study of synthetic Fe²⁺, Fe³⁺, Mg²⁺ and Al³⁺ copiapite by Raman, XRD, LIBS, MIR and vis–NIR. J. Raman Spectrosc. 42, 1120–1129.
- Kounaves, S.P. et al., 2010. Soluble sulfate in the martian soil at the Phoenix landing site. Geophys. Res. Lett. 37. http://dx.doi.org/10.1029/2010GL042613.
- Langevin, Y. et al., 2005. Sulfates in the north polar region of Mars detected by OMEGA/Mars express. Science 307, 1584–1586.
- Laskar, J. et al., 2004. Long term evolution and chaotic diffusion of the insolation quantities of Mars. Icarus 170, 343–364.
- Lichtenberg, K.A. et al., 2010. Stratigraphy of hydrated sulfates in the sedimentary deposits of Aram Chaos, Mars. J. Geophys. Res. 15, E00D17. http://dx.doi.org/ 10.1029/2009JE003353.
- Lide, D.R., 2001. CRC Handbook of Chemistry and Physics, 82nd ed. CRC Press, London.
- Ling, Z.C., Wang, A., 2010. A systematic spectroscopic study of eight hydrous ferric sulfates relevant to Mars. Icarus 209, 422–433.
- Majzlan, J., Michallik, R., 2007. The crystal structures, solid solutions and infrared spectra of copiapite-group minerals. Miner. Mag. 71, 553–569.
- Majzlan, J. et al., 2004. Thermodynamic properties, low-temperature heat-capacity anomalies, and single-crystal X-ray refinement of hydronium jarosite, (H₃O)Fe₃(SO₄)₂(OH)₆. Phys. Chem. Miner. 31, 518–531.
- Majzlan, J. et al., 2005. The crystal structures of synthetics Fe₂(SO₄)₃(H₂O)₅ and the type specimen of lausenite. Am. Miner. 90, 411–416.
- Majzlan, J. et al., 2006. Thermodynamic properties and crystal structure refinement of ferricopiapite, coquimbite, rhomboclase, and Fe₂(SO₄)₃(H₂O)₅. Eur. J. Miner. 18, 175–186.
- Maurice, S. et al., 2011. Mars Odyssey neutron data: 1. Data processing and models of water-equivalent-hydrogen distribution. J. Geophys. Res. 116, E11008. http:// dx.doi.org/10.1029/2011JE003810.
- Ming, D.W. et al., 2006. Geochemical and mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater, Mars. J. Geophys. Res. 111, E02S12. http://dx.doi.org/10.1029/2005JE002560.
- Morris, R.V. et al., 2006. Mossbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: Spirit's journey through weakly altered olivine basalt on the plains and pervasively altered basalt in the Columbia Hills. J. Geophys. Res. 111, E02513. http://dx.doi.org/10.1029/2005/E002584.
- Morris, R.V. et al., 2008. Iron mineralogy and aqueous alteration from Husband Hill through Home Plate at Gusev crater, Mars: Results from the Mossbauer instrument on the Spirit Mars Exploration Rover. J. Geophys. Res. 113, E12S42. http://dx.doi.org/10.1029/2008/E003201.
- Murchie, S. et al., 2009. Evidence for the origin of layered deposits in Candor Chasma, Mars, from mineral composition and hydrologic modeling. J. Geophys. Res. 114, E00D05. http://dx.doi.org/10.1029/2009JE003343.
- Peterson, R.C., Wang, R., 2006. Crystal molds on Mars: Melting of a possible new mineral species to create martian chaotic terrain. Geology 34, 957–960.
- Peterson, R.C. et al., 2007. Meridianiite: A new mineral species observed on Earth and predicted to exist on Mars. Am. Miner. 92, 1756–1759.
- Rennó et al., 2010. Possible physical and thermodynamical evidence for liquid water at the Phoenix landing site. J. Geophys. Res. 114, E00E03. http://dx.doi.org/ 10.1029/2009/E003362.
- Robertson, K., Bish, D.L., 2013. Constraints on the distribution of $CaSO_4$ center dot nH(2)O phases on Mars and implications for their contribution to the hydrological cycle. Icarus 223, 407–417.
- Smith, M.D., 2002. The annual cycle of water vapor on Mars as observed by the thermal emission spectrometer. J. Geophys. Res. 107, 5115. http://dx.doi.org/ 10.1029/2001[E001522.
- Squyres, S.W. et al., 2006. Overview of the Opportunity Mars Exploration Rover mission to Meridiani Planum: Eagle crater to Purgatory ripple. J. Geophys. Res. 111, E12S12. http://dx.doi.org/10.1029/2006JE002771.
- Squyres, S.W. et al., 2007. Pyroclastic activity at home plate in Gusev crater, Mars. Science 316, 738–742.
- Squyres, S.W. et al., 2008. Detection of silica-rich deposits on Mars. Science 320, 1063–1067.
- Squyres, S.W. et al., 2009. Exploration of Victoria Crater by the Mars Rover Opportunity. Science 324, 1058–1061.

- Squyres, S.W. et al., 2012. Ancient impact and aqueous processes at Endeavour crater, Mars. Science 336, 570. http://dx.doi.org/10.1126/science.1220476.
- Swayze, G.A. et al., 2008. Discovery of the acid-sulfate mineral alunite in Terra Sirenum, Mars, using MRO CRISM: Possible evidence for acid-saline lacustrine deposits? Eos (Suppl.), Trans. American Geophysical Union (Fall), 89(53). Abstract P44A-04.
- Tosca, N.J. et al., 2007. Application of the Pitzer ion interaction model to the Fe₂(SO₄)₃-H₂SO₄-H₂O system. Geochim. Cosmochim. Acta 71, 2680–2698.
- Vaniman, D.T., Chipera, S.J., 2006. Transformations of Mg- and Ca-sulfate hydrates in Mars regolith. Am. Miner. 91, 1628–1642.
- Vaniman, D.T. et al., 2004. Magnesium sulphate salts and the history of water on Mars. Nature 431, 663–665.
- Wang, A., Ling, Z.C., 2011. Ferric sulfates on Mars A combined mission data analysis of salty soils at Gusev crater and laboratory experimental investigations. J. Geophys. Res. 116, E00F17. http://dx.doi.org/10.1029/ 2010JE003665.
- Wang, A. et al., 2006a. Evidence of phyllosilicates in Wooly Patch, an altered rock encountered at West Spur, Columbia Hills, by the Spirit rover in Gusev crater, Mars. J. Geophys. Res. 111, E02S16. http://dx.doi.org/10.1029/2005JE002516.
- Wang, A. et al., 2006b. Sulfate deposition in subsurface regolith in Gusev crater, Mars. J. Geophys. Res. 111, E02S17. http://dx.doi.org/10.1029/2005JE002513.

- Wang, A. et al., 2006c. Sulfates on Mars: A systematic Raman spectroscopic study of hydration states of magnesium sulfates. Geochim. Cosmochim. Acta 70, 6118–6135.
- Wang, A. et al., 2008. Light-toned salty soils and co-existing Si-rich species discovered by the Mars Exploration Rover Spirit in Columbia Hills. J. Geophys. Res. 113, E12S40. http://dx.doi.org/10.1029/2008JE003126.
- Wang, A. et al., 2009. Phase transition pathways of the hydrates of magnesium sulfate in the temperature range 50–5 °C: Implication for sulfates on Mars. J. Geophys. Res. 114. http://dx.doi.org/10.1029/2008JE003266.
- Wang, A. et al., 2011. Stability of Mg-sulfates at-10 °C and the rates of dehydration/ rehydration processes under conditions relevant to Mars. J. Geophys. Res. 116, E12006. http://dx.doi.org/10.1029/2011JE003818.
- Wang, A. et al., 2012. Stability field and phase transition pathways of hydrous ferric sulfates in the temperature range 50–5 °C: Implication for martian ferric sulfates. Icarus 218, 622–643.
- Wang, A. et al., 2013. The preservation of subsurface sulfates with mid-to-high degree of hydration in equatorial regions on Mars. Icarus 226, 980–991.
- Wilson, S.A., Bish, D.L., 2012. Stability of Mg-sulfate minerals in the presence of smectites: Possible mineralogical controls on H₂O cycling and biomarker preservation on Mars. Geochim. Cosmochim. Acta 96, 120–133.
- Xu, W.Q. et al., 2009. Humidity-induced phase transitions of ferric sulfate minerals studied by in situ and ex situ X-ray diffraction. Am. Miner. 94, 1629–1637.