

DEHYDRATION OF NA-JAROSITE, FERRICOPIAPITE, AND RHOMBOCLASE AT HIGH T AND IMPLICATIONS ON MARTIAN FERRIC SULFATES. Yang Liu and Alian Wang, Department of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, Campus Box 1169, Saint Louis, MO 63130, USA (liuyang@levee.wustl.edu)

Introduction: Sulfate is one of the major types of secondary minerals found on Mars by both orbital observations (OMEGA and CRISM) and surface explorations (Mars Exploration Rovers) [e.g., 1, 2, 3, 4, 5]. Among the Martian sulfates, Ca- and Mg-sulfates were identified by orbital remote sensing with wide distributions and large quantities. In contrast, Fe-sulfates have been observed only in localized areas [e.g., 6, 7, 8, 9] and the overall quantity is not comparable with those of Mg-sulfates. The surface exploration of MERs have found a variety of ferric sulfates, and more importantly, the dehydration of ferric sulfates in the subsurface regolith after excavated by Spirit rover was implied on the basis of a set of consecutive Pancam observations [10]. The changes in spectral characters of ferric sulfates after dehydration are important to uncover the mystery of relatively rarely detected ferric sulfates on Mars surface by orbital remote sensing. The stability field,

the intermediate (5 weeks) and final stage (10 weeks) of experiments. Gravimetric measurements were made on the same samples to monitor the loss of structural H₂O/OH. VIS-NIR spectra (0.4–2.5 μm) were taken using Analytical Spectral Device (ASD) on the final dehydration product to investigate the change of spectral properties.

Results and Discussion: Peaks in laser Raman spectra provide the information on the fundamental vibration modes of the dehydration products of three ferric sulfates, thus can be directly linked to the potential crystal structural changes. Calculated H₂O/OH per molecule based on gravimetric data would provide an independent evidence to support (or to question) the Raman ID. The spectral peaks of VIS-NIR are the overtones and combinational modes that have the highest application potentials for interpreting the data from planetary orbital remote sensing.

T (°C)	week	50		95	
RH		11.1%	5.5%	10.1%	5.3%
Na-jarosite	5	LOPD ^a , v ₃ shift	LOPD	LOPD, v ₃ shift	LOPD
	10	LOPD, v ₃ shift	LOPD, v ₃ shift	LOPD, v ₃ shift	LOPD, v ₃ shift
ferricopiapite	5	Quasi-Am ^b	Quasi-Am	Quasi-Am + Fe(OH)SO ₄	Quasi-Am + Fe(OH)SO ₄
	10	Quasi-Am	Quasi-Am	Quasi-Am + Fe(OH)SO ₄	Fe(OH)SO ₄
rhomboclase	5	I _{H2O} ↓, LOPD	4w + UK 19 ^c	UK 19	UK 19
	10	I _{H2O} ↓, LOPD	4w + UK 19	UK 19	UK 19

Table 1 The phase identifications made by non-invasive laser Raman measurements. (^aLOPD = lost of peak detail; ^bQuasi-Am = Quasi-amorphous ferric sulfate with a distorted structure from ferricopiapite and lost some of six hydrogen-bonded H₂O, reported in [11]; ^cUK 19 = an anhydrous crystalline ferric sulfate with different XRD pattern from mikasaite, but no match was found in XRD database PDF2006, reported in [11])

including the dehydration, of ferric sulfates in T ≤ 50 °C range was investigated previously [11]. We report here an experimental study on the dehydration of ferric sulfates in a higher T range, to learn the mineral form of dehydration products and their spectral characters that might be produced by hydrothermal processes post-volcanic and post-impact event on Mars.

Samples and Experiments: Na-Jarosite (NaFe³⁺₃(SO₄)₂(OH)₆), ferricopiapite (Fe³⁺_{0.66}Fe³⁺₄(SO₄)₆(OH)₂•20(H₂O)), and rhomboclase (HFe³⁺(SO₄)₂•4(H₂O)) were used as the starting phases in the experiments. The dehydrations were conducted at 50 and 95 °C at two relative humidity levels (5% and 10–11%) controlled by humidity buffers [12, 13]. Non-invasive Raman spectroscopy (HoloLab5000-532, KOSI) were used to make phase identifications based on the standard Raman spectra published by [14, 15] at

Phase ID from Raman spectroscopy:

The phase identifications made by non-invasive laser Raman measurements are shown in Table 1. All of the dehydration products of Na-jarosite have lost peak details in OH vibrational region, and some of them have down shifted v₃ (SO₄) (Fig 1). The changes in these spectral features imply a slight structural distortion without a large reduction of the hydration degree. At 50 °C and 5–11%RH, ferricopiapite dehydrated into a disordered structure, quasi-Am as reported by [11] that can maintain 14–19 structural H₂O per molecule. At 95 °C, the dehydration of ferricopiapite developed further: it converted totally to a dehydrated form Fe(OH)SO₄ in fibroferrite-

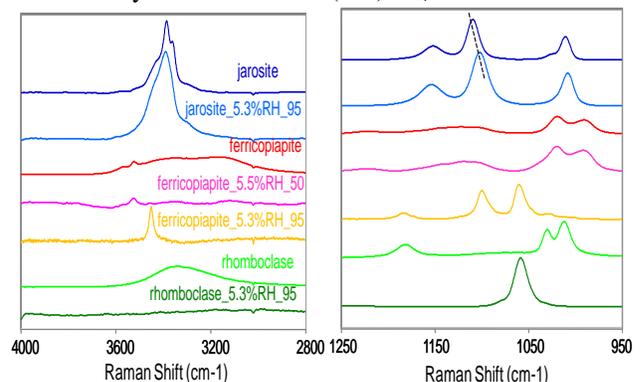


Figure 1 Raman spectra of three ferric sulfates and examples of their dehydration products.

butlerite group at 5%RH after 10 weeks(Fig 1). The dehydration of rhomboclase under 50 °C and 11% RH appeared as the intensity reduction of H₂O Raman peak (4000-2800 cm⁻¹), and the lost of peak details of its fundamental modes (1250-950 cm⁻¹), which signify the starting of structural distortion. Under higher T (95 °C) or lower RH (5%), rhomboclase converted to an anhydrous crystalline phase that has a different structure from mikasaite (Fe₂(SO₄)₃). This phase has a distinct XRD pattern that has found not match in XRD database PDF2009, and was named temporally as UK19 [11]. The flat Raman spectrum in 4000-2800 cm⁻¹ (Fig. 1) shows that it is anhydrous.

T (°C)	RH	week	50		95	
			11.1%	5.5%	10.1%	5.3%
Na-jarosite (WPM ^a)	5		5.9	5.8	5.8	5.8
	10		5.9	5.8	5.8	5.8
ferricopiapite (WPM)	5		19	16	5	0
	10		19	16	5	0
rhomboclase (WPM)	5		2.8	2.7	1.5	0.7
	10		2.8	2.7	1.5	0.7

Table 2 Changes in the number of structural OH/H₂O per molecule calculated from gravimetric measurements of intermediate and final dehydration products. (^aWPM = OH/H₂O per molecule)

Loss of H₂O/OH during the dehydration: Losing one structural H₂O/OH would cause about 3.4 wt%, 1.5 wt%, and 5.6 wt% mass variations in jarosite, ferricopiapite, and rhomboclase molecules, respectively. The balance (Mettler PM480 DeltaRange) used for gravimetric measurements has an accuracy of ± 1 mg. The mass ranges we used in this study is ~400 mg for jarosite, ~50 mg for ferricopiapite, and ~250 mg for rhomboclase, thus the uncertainty in calculating the number of structural H₂O/OH held by these molecules based on the gravimetric measurement uncertainty was about ± 0.1 OH for jarosite, ± 1 H₂O for ferricopiapite, and ± 0.1 H₂O for rhomboclase. The changes in the number of structural H₂O/OH per molecule for the intermediate (5 weeks) and final stage (10 weeks) are shown in Table 2. In general, the data in Table 2 fully support the mineral ID made by Raman spectroscopy, i.e., (1) very slight dehydration in Na-jarosite; (2) lost of 1-4 structural H₂O from ferricopiapite by forming Quasi-Am and lost almost all H₂O by forming Fe(OH)SO₄; (3) lost of almost all H₂O from rhomboclase by forming UK19.

VIS-NIR spectral characters: The examples of VIS-NIR spectra of Na-jarosite, ferricopiapite, and rhomboclase and their dehydration products are shown in Fig 2. Consistent with Raman ID and gravimetric data, the OH spectral features of Na-jarosite do not significantly

change, suggesting very low degree of dehydration, while there are subtle shortward wavelength shift of iron absorption feature at ~0.9 μm and decreasing of the slope from 0.4 to 0.7 μm.

Comparing to ferricopiapite, quasi-Am has a very similar spectral pattern except a slight increasing of the slope from 0.43 to 0.5 μm and shortward

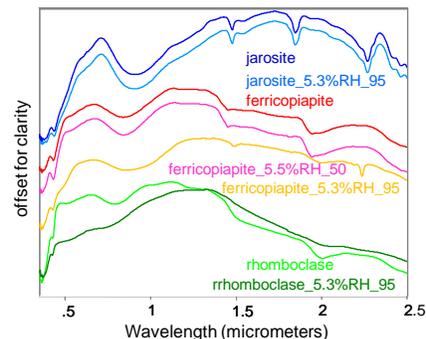


Figure 2 VIS-NIR spectra of three ferric sulfates and examples of their dehydration products.

wavelength shift of iron absorption feature at ~0.85 μm. The dehydration product Fe(OH)SO₄ has a distinct spectral pattern, with almost no absorption near 1.9 μm but a sharp absorption band at ~2.235 μm due to metal-OH vibration. The formation of Fe(OH)SO₄ in our experiments through heating of ferricopiapite at mid-high temperature and low RH level is quite different from a previously reported path, i.e. heating melanterite at a much higher temperature (240 °C) [16]. The VIS-NIR spectrum of the dehydration product UK19 of rhomboclase [11] consists with Raman ID, as an anhydrous phase of ferric sulfates, no structural H₂O and OH related absorption features observed in VIS-NIR spectral range.

Conclusions: Our dehydration experiments show that OH-bearing Na-jarosite is relatively stable at 95 °C and RH ≤ 11%, while H₂O/OH-bearing ferricopiapite and rhomboclase have converted entirely to anhydrous phases. It means if on Mars these two Fe-sulfates were found (Tyronite site at Gusev), the location should not have experienced a T > 95 °C.

Acknowledgement: This work was supported partially by a NASA Mars Fundamental Research Project NNX10AM89G and by EPSc in WUSTL.

References: [1] Bibring et al. (2005) *Science*, 307, 1576-1681. [2] Gendrin et al. (2005) *Science*, 307, 1587-1591. [3] Arvidson et al. (2005) *Science*, 307, 1591-1594. [4] Murchie et al. (2009a) *JGR*, 114, E00D06. [5] Bishop et al. (2009) *JGR*, 114, E00D09. [6] Lichtenberg et al. (2010) *JGR*, 115, E00D17. [7] Milliken R.E. (2008) *Geology*, 36, 847-850. [8] Roach et al. (2010b) *Icarus*, 207, 659-674. [9] Liu et al. (2012), *this volume*. [10] Wang et al. (2011) *JGR*, 116, E00F17. [11] Wang et al., (2012) *Icarus*, submitted. [12] Chou et al. (2002) *Am. Mineral.* 87, 108-114. [13] Greenspan et al. (1997) *Phys. Chem.* 81A, 89-96. [14] Ling & Wang (2010), *Icarus*, 209, 422-433. [15] Wang & Ling (2011) *JGR*, 116, E00F17. [16] Lichtenberg et al (2010) *JGR*, 115, E00D17.