Characterization of Fe-sulfate minerals: Preparation for Mars sample return B. C. Hyde[1], P. L. King[1,2], M. N. Spilde[2] and A.-M. S. Ali[3] [1]Dept. Earth Sciences, Univ. Western Ontario, London, ON N6A 5B7 Canada. [2]Inst. Meteoritics, Univ. New Mexico, Albuquerque, NM 87131 USA. [3]Dept. Earth & Planetary Sciences, Univ. New Mexico, Albuquerque, NM 87131 USA.

Introduction: Fe-sulfates have been observed on Mars [e.g. 1] and in martian meteorites [e.g. 2] and will possibly be returned from Mars. The characterization of these minerals will provide information that may be used to calculate depositional environment, fluid and atmospheric interactions (water activity and oxygen fugacity), and formation temperature of salts on Mars [e.g. 3; 4]. However, it is not straightforward to characterize Fe-sulfates for four main reasons: 1) they readily change hydration [5; 6] and oxidation [7] states and such changes may occur during analysis; 2) these minerals may be small (<1-5 μm), making them difficult to analyze even with micro-analytical techniques; 3) we lack standards; and 4) Fe-sulfates contain multi-valent and light elements that are difficult to analyze with traditional techniques (e.g. electron microprobe, EMP). Overcoming analysis issues prior to return of small volumes of martian samples is essential for obtaining knowledge about the surface of Mars. Hence, we are developing methods to analyze ~pure synthetic, fine-grained samples for Fe, S, and light elements (O, C, and N) using bulk and micro-analysis. Knowledge of the light element content is critical for determining the Fe-sulfate type and thus environments on Mars.

Synthesis methods: To synthesize Fe-sulfates, we used ferric sulfate ($Fe^{3+}_2(SO_4)_3 \cdot 5H_2O$, Acros Organics; 97%), ferrous sulfate ($Fe^{2+}SO_4 \cdot 7H_2O$, EMD Chemicals; Extra Pure ~100%), sulfuric acid (BDH, 98%) and deionized water. Szomolnokite [$Fe^{2+}SO_4 \cdot 1H_2O$] was produced by heating ferrous sulfate to 60 °C for 24 hours. The product was stored in a relative humidity (RH) environment with a saturated $MgCl_2$ solution (RH=~33%, T=20-25 °C) following [8]. Melanterite [$Fe^{2+}SO_4 \cdot 7H_2O$] was synthesized by placing ferrous sulfate at RH=~75%, T=20-25 °C using a saturated NaCl solution following [8]. Rhomboclase [$HFe^{3+}(SO_4)_2 \cdot 4H_2O$] was synthesized using a method similar to [9]. A mixture of 9.64 g ferric sulfate, 20.91 mL of deionized water and 5.05 mL of sulfuric acid was left in air for one week. The precipitate was filtered with acetone to remove remaining liquid. Schwertmannite [$Fe^{3+}_8O_8(OH)_6(SO_4)_x \cdot nH_2O$] (where $1 \leq x \leq 1.75$) synthesis followed a method similar to that of [10]. Ferric sulfate (1.54 g) was added to 500 mL of deionized water. The solution was mixed at 85 °C for one hour, then filtered and the remaining precipitate was filtered twice more with 100 mL of deionized wa-

ter. The product was left to dry at 60 °C for 24 hours. A mixture of ferricopiapite [fcop, $Fe^{3+}_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2 \cdot 20H_2O$] and paracoquimbite [p-coq, $Fe^{3+}_2(SO_4)_3 \cdot 9H_2O$] was made by deliquescing ferric sulfate at RH=~75%, T=20-25 °C, then solidifying the gel-like substance at RH=~33%, T=20-25 °C. The two minerals may be separated because fcop is bright yellow and p-coq is white/pale yellow.

The melanterite and szomolnokite samples were kept in their RH chambers until analysis. To transport these two samples we sealed them in vials within the RH chamber and placed them in smaller chambers with sponges soaked in saturated salt solutions. The remainder of the samples were kept sealed in glass vials with Teflon/Kapton®/electrical tapes.

Analysis methods: *X-ray Diffraction (XRD) analysis.* The samples were analyzed using a Rigaku Rotaflex RTP 300 RC with a cobalt source at the University of Western Ontario (UWO). Powders were dry-mounted on glass slides and scanned in steps of 0.02° 2θ from 2° to 82° at a speed of 10°/minute. In total the sample was exposed to lab air for 8 minutes of scan time plus preparation time.

Reflectance infrared (IR) analysis. A Nicolet Nexus 670 FT-IR with a Pike Technologies Automated Diffuse Reflectance attachment was used at UWO to collect biconical reflectance IR data. The samples were sieved to <45 μm., 2 mg of sample was mixed with 43 mg of KBr and 300 scans were run. Backgrounds were taken before and after each run to ensure that no atmospheric signals were introduced into the spectrum, a dry-air purge chamber was not used because it caused samples to dehydrate.

Electron microprobe (EMP) analysis. EMP analysis used a JEOL 8200 microprobe equipped with wavelength and energy dispersive spectrometers (WDS and EDS) at the University of New Mexico (UNM). Fe-sulfate powders were pressed into discs and C-coated.

Scanning electron microscope (SEM) analysis. SEM analysis used a JEOL 5800LV SEM equipped with an Oxford Analytical ultrathin-window EDS at UNM. Analysis was done in low vacuum (31-45 Pa) using uncoated pressed discs, a 0.15 nA beam current and a 15 kV accelerating voltage. A thin section and a pressed pellet of jarosite from Peña Blanca, New Mexico [11] were used for calibration.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ion chromatography (IC) analysis. A PerkinElmer Optima 5300DV ICP-AES and

Dionex DX500 IC were used for analysis. Samples were run in axial mode for the ICP-AES and the AS9-HC (High Capacity) separation column with Ultra ASRA suppression were used in IC. Fe-sulfates were dissolved in dilute nitric acid and in some cases nitric plus hydrofluoric acid. The dissolved samples were then diluted with deionized water to a volume of 50 mL for initial analysis. The samples were rediluted by 100x to measure Fe and for IC analysis of anion contents.

Bulk C and N analysis. A Costech ECS 4010 elemental analyzer at UNM was used to quantify C and N in the samples. The sample ($\sim$5 mg) was combusted and CO_2 and N_2 analyzed with a mass spectrometer.

Results: XRD analysis of the synthetic samples shows the szomolnokite, melanterite and rhomboclase to be single phases. The schwertmannite also contains goethite. The fcop and p-coq samples are dominated by these two phases, but contain other ferric sulfates.

The IR analysis helped confirm the XRD identification of the phases and future work will aim to quantify water contents [e.g. 12].

The EMP WDS analysis showed that there was no measurable accumulation of trace elements in samples synthesized from the 97% pure $Fe^{3+}_2(SO_4)_3 \cdot 5H_2O$. It was not possible to analyze for O, C or N using WDS or EDS on the EMP due to the C coat, scattering on the rough pellet surface, and the relatively high vacuum.

The SEM allowed for analysis in low vacuum without a C coat and it was possible to analyze for O (C and N were not possible to quantify). Early results show promise, but the work is still in progress. In some cases it seems that dehydration has likely occurred (e.g. melanterite). Table 1 shows the ideal formula for seven fine-grained, powdered samples with the SEM, ICP-AES and IC results converted to moles and normalized to the ideal formulaic number of Fe atoms. When we have quantified O and H using mass spectrometry it will be possible to calculate exact wt. % values for ICP-AES and IC data rather than ratios.

Bulk N and C analysis showed that N is below detection limits, however, C is present (Table 1).

Conclusions & Implications for Mars Sample Return: Multiple analysis techniques are required to calibrate and confirm analyses of Fe-sulfate samples, particularly for light element analysis. Future calibration of SEM analysis will provide methods to use these techniques for microanalytical work on samples returned from Mars.

References: [1] Klingelhöfer, G. et al. (2004) *Science*, 306, 1740-1745. [2] Herd, C. D. K. (2006) *LPI Contrib.*, 1331, p.53. [3] King, P. L., and McSween, H. Y. (2005) *JGR*, 110, doi: 10.1029/2005JE002482. [4] Papike, J. J. et al. (2006) *GCA*, 70, 1309-1321. [5] Chou, I-M, et al. (2002), *Am. Min.*, 87, 108-114. [6] Peterson, R. C. and Grant, A. H. (2005), *Can. Min.*, 43, 1171-1181. [7] Jerz, J. K. and Rimstidt, J. D. (2003), *Am. Min.*, 88, 1919-1932. [8] Greenspan, L. (1977), *J. Res. NBS-Phys. & Chem.*, 81A, 89-96. [9] Majzlan, J. et al. (2006) *Eur. J. Mineral.*, 18, 175-186. [10] Loan, M. et al. (2004) *Am. Min.*, 89, 1735-1742. [11] Papike, J. J. (2007) *Am. Min.*, 92, 444-447. [12] Milliken, R. E. and Mustard, J. F. (2005) *JGR*, 110, doi: 10.1029/2005JE002534.

	Ideal Moles From Formula				SEM (molar ratio normalized to ideal Fe values) for fine-grained powders pressed into discs. Errors calculated from standard deviation of 7 analyses				ICP-AES/IC (molar ratio normalized to ideal Fe values)			Wt %
	Fe	K	S	O	Fe	K	S	O	Fe	K	S	C
Samples identified as pure phases with XRD												
Szomolnokite	1	0	1	5	1±0.05	0	0.86±0.04	3.98±0.41	1	0	0.93	0.09
Melanterite	1	0	1	11	1±0.05	0	0.87±0.03	4.92±0.25 #	1	0	0.76	0.02
Rhomboclase	1	0	2	12	1±0.03	0	2.33±0.03	10.09±0.70	1	0	2.37	0.04
Samples identified as mixed phases with XRD												
Schwertmannite*	8	0	1-1.75	≥18	8±0.07	0	1.25±0.05	21.03±1.27	8	0	1.56	0.08
fcop+	4.67	0	6	46	-	-	-	-	4.67	0	3.53	0.03
p-coq+	2	0	3	21	-	-	-	-	2	0	3.51	0.03
Natural sample (Ideal values taken from past analysis [11])												
Peña Blanca jar.	2.89	1.07	1.96	13.58	2.89±0.08	0.98±0.02	1.74±0.03	11.76±0.95	2.89	0.91	1.53	0.04

Table 1. Ideal atomic values, SEM and ICP-AES/IC normalized values for major elements. Bulk C analysis in final column. *Contains goethite. +Mixtures dominated by fcop and p-coq respectively. #Dehydration of melanterite to szomolnokite in the SEM.