Visible and Infrared Spectral Characteristics and Morphology of Amorphous Iron Sulfates. E. C. Sklute,[1] H. B. Jensen[1], A. D. Rogers[1], and R. J. Reeder[1], [1]Stony Brook University, Department of Geosciences, Stony Brook, NY. 11794, elizabeth.sklute@gmail.com

Introduction: The discovery of sulfates on Mars has led to the hypothesis that ancient Mars experienced acidic fluid conditions near the surface [1-2]. Oxidative weathering of sulfides and volcanic activity would have led to sulfate-rich fluids. These solutions would have precipitated sulfates as they become saturated with respect to a given phase [3]. For iron sulfates, iron- and sulfur-rich fluids tend to precipitate fine grained, crystalline phases at Earth's surface temperatures and pressures [4]. Cloutis et al. (2008) showed that, once formed, many sulfates are stable under simulated Martian conditions [5], however, Xu et al. (2009) showed that amorphous phases form when iron sulfate fluids are subjected to low relative humidities [6], as one would expect on Mars under certain conditions [7].

The recent discovery by MSL that 27% of the soil at Rocknest in Gale Crater is x-ray amorphous material containing both iron and sulfur [8], raises new questions regarding the presence of amorphous sulfates on Mars. Yet the spectral properties, physical characteristics, morphologies, and formation pathways for amorphous iron sulfates are not well understood. This is critical for recognizing these phases in existing landed and remote data sets. This abstract describes the spectral and morphological characteristics of amorphous iron sulfate phases and describes implications for MSL observations. A companion abstract [Jensen et al.] describes multiple formation pathways for amorphous sulfate phases and discusses possible path-dependent differences that can help constrain formation pathways.

Methods: For this work, ferric iron sulfates were synthesized from two starting materials: first using unaltered Acros Organics 97% $Fe(SO_4)_3 \bullet 5H_2O$, identified by XRD to be the monoclinic phase lausenite ($Fe(III)(SO_4)_3 \bullet 6H_2O$); second by heating the starting material for 2 h at 350 ºC to form the anhydrous trigonal phase mikasaite ($Fe(III)(SO_4)_3$) [6]. Both powders were placed in 92% RH at RT, using DI water as a humidity buffer. Once hydrated, the materials were dehydrated via vacuum ($3x10^{-2}$ mbar) for 2 weeks to simulate the rapid loss of water that crystalline phases would likely experience once precipitated on the Martian surface. These samples will be referred to as L-amorphous and M-amorphous to reflect their starting materials of lausenite and mikasaite, respectively. Amorphous ferrous sulfate was prepared by vacuum dehydrating melanterite ($FeSO_4 \bullet 7H_2O$) for 3 days.

The materials were confirmed amorphous by XRD. Synchrotron X-ray total scattering data were also collected at the Advanced Photon Source (Argonne National Lab) for pair distribution function (PDF) analysis [9]. Once created, the ferric sulfates were kept at low RH (less than 11%) except during spectral analyses (< 20min). Lack of crystallinity was checked by XRD after each analysis. VNIR spectra were collected on an ASD Fieldspec3 Max UV-VIS-NIR bidirectional spectrometer (referenced to Spectralon, average of 300 scans). When laboratory humidity exceeded 20%, VNIR spectra were collected in an N_2 filled glove bag. Spectral emissivity measurements were taken in a dry air purged chamber and only collected when laboratory humidity was less than 15%. To avoid phase changes that could occur upon heating, the samples were cooled to 30° below the detector temperature (rather than heated above detector temperature) to achieve adequate signal to noise for spectral measurement [10]. Thermogravimetric analysis (TGA) was used to determine sample water contents, and SEM was used to image sample morphologies.

Results and Discussion: When processed in a low humidity environment after synthesis, amorphous ferric sulfates grind from an amber into a fine powder that is X-ray amorphous (Figure 1). Ferrous sulfates transform into a silky gray powder and maintain the shape of the crystals from which they formed(Figure 1 inset).

Figure 1. Image of partially ground, vacuum dehydrated, amorphous *ferric* sulfate. Inset: image of vacuum dehydrated amorphous *ferrous* sulfate.

SEM shows that the amorphous ferric sulfates display conchoidal fracture and are morphologically similar to glass (Figure 2). SEM of the ground ferric sulfates showed that, although shards can be as small as 20 nm, the majority of the powders are large enough that, were they crystalline, they would produce reflections in the XRD patterns, i.e., they are not XRD amorphous because they are nanophase.

The M-amorphous and L-amorphous samples contained 4.5 and 5.3 structural waters, respectively, based on TGA. These results were used for normalization of total scattering data. Figure 3 shows the PDF for the M-amorphous sample overlaid on that of ferricopiapite

and mikasaite for reference. The peaks give the distribution of interatomic distances weighted by the scattering power of the atom. The PDF for the M-amorphous sample reveals that peaks are damped beyond ~ 10 Å, indicating short- and medium-range structure and the absence of long-range structure, as expected for an amorphous phase. In contrast, peaks for ferricopiapite and mikasaite extend beyond the r-range shown, as expected for a crystalline phase. Because SEM confirmed that particle size is larger than 10 Å, we can conclude that these are truly amorphous materials with similar short- and medium range structure as in ferricopiapite.

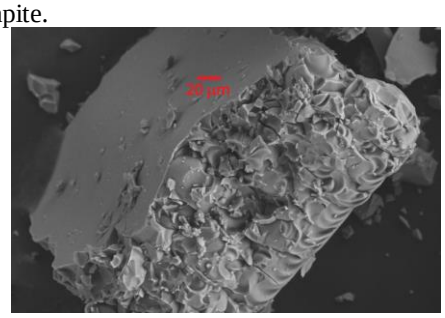

Figure 2. SEM image of the L-amorphous sample. The M-amorphous sample is morphologically identical.

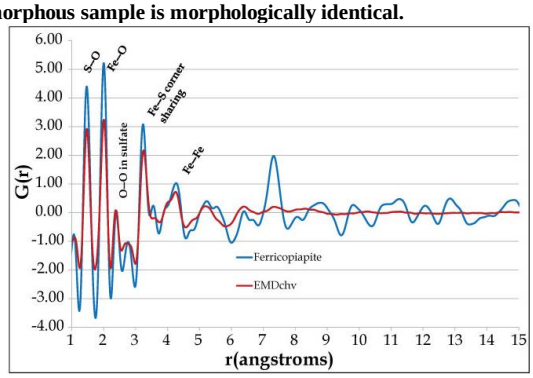

Figure 3. Pair distribution function of M-amorphous ferric sulfate overlaid on the PDF of crystalline ferricopiapite.

VNIR spectra of the M-amorphous, L-amorphous, and ferrous sulfate samples are plotted against several common sulfates in Figure 4. The reference samples are the same as those used by Cloutis et al. [5]. Also included are samples for which there were emissivity data [11]. In the VNIR, the amorphous samples lack sharp features at 1.4 and 1.9 μm and also show altered iron coordination, as evidenced by shifts in the energies of spin forbidden crystal field transitions (<1.2 μm absorptions). And, although they share common features with many other sulfates, they do appear spectrally unique.

Emissivity spectra of both amorphous ferric and ferrous sulfates display absorptions consistent with all four sulfate anion vibrational modes [11]. The absorptions are, however, less distinct in the amorphous spectra than they are in the crystalline spectra and are shifted in position.

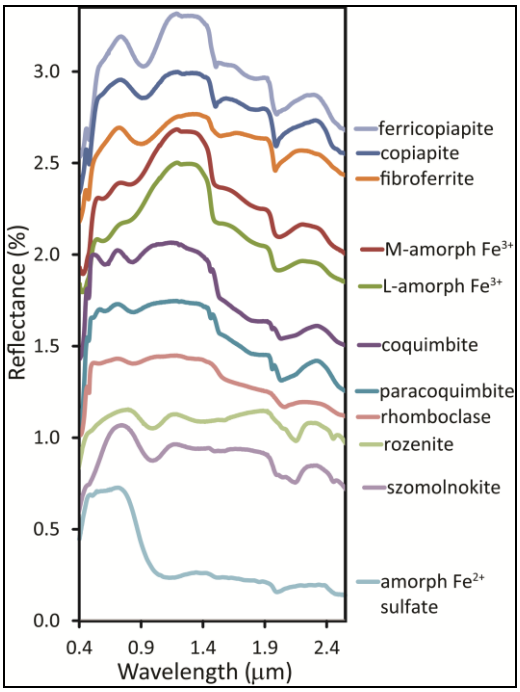

Figure 4. VNIR spectra of (from the top) S35, spt117, spt121, M-amorphous Fe^{3+} sulfate, L-amorphous Fe^{3+} sulfate, S40, spt137, spt139, S78, S60, and Fe^{2+} amorphous. Reference samples are from the RELAB spectral library.

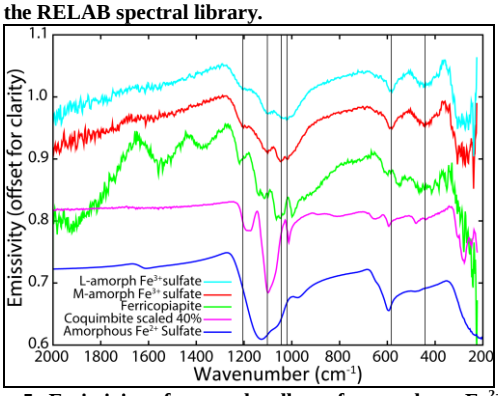

Figure 5. Emissivity of pressed pellets of amorphous Fe^{2+} and Fe^{3+} sulfates along with S46 and S35, which can be found in Brown's spectral library.

Conclusion: Amorphous ferric and ferrous sulfates are spectrally distinct from crystalline sulfates and exhibit coherent structure on the length scale up to 10 Å. These materials are powders at low RH and are not inconsistent with the textures of the Martian soil.

References: [1]Bibring J. P. et al. (2006) *Science*, *312*, 400. [2] Hurowitz J. A. and Mclennan S. M. (2007) *Earth Planet Sci. Lett.*, *260*, 432-443. [3] Hurowitz J. A. et al. (2009) *Am. Mineral.*, *94*, 409-414. [4] Jerz J. K. and Rimstidt J. D. (2003) *Am. Mineral.*, *88*, 1919-1932. [5]Cloutis E. A. et al. (2008) *Icarus*, *195*, 140-168. [6]Xu W. et al. (2009), *Am. Mineral.*, *94*, 1629-1637. [7] Savijarvi H. (1995) *Icarus*, *117*, 120-127. [8]Bish D. L. et al. (2013) *Science*, *341*. [9]Reeder R. J. and Michel F. M. (2013) *Method. Enzymol*, *532*, 477-500. [10] Baldridge A, M. and Christensen P. R. (2009)*Appl. Spectrosc.*, *63*,678-688. [11]Lane M. D. (2007)*Am. Mineral.*, *92*, 1-18.