LOW-TEMPERATURE TOTAL X-RAY SCATTERING OF AMORPHOUS AND AQUEOUS IRON(III) SULFATE

J. C. Gregerson[1], A. D. Rogers[1], L. Ehm[1,2], J. B. Parise[1,2], and S. Tu[1], [1]Stony Brook University, Geosciences Dept. 255 ESS Building, Stony Brook, NY. 11794-2100. [2]Brookhaven National Lab, Photon Sciences, Building 745 P.O. Box 5000, Upton, NY 11973-5000.

Introduction: Both soils and rocks analyzed in Gale crater by MSL Curiosity using the CheMin instrument have an abundance of X-ray amorphous material. This amorphous material accounts for 30-45wt% of soils and 15-45wt% of rocks [1-4] and is enriched in both iron and sulfur [1,2,5,6].

Amorphous Sulfates, which are hydrated and can be produced via dehydration of aqueous sulfate brines [7-9], could be important components of Martian soils. Amorphous iron(III) sulfate could account for up to 9% of Martian soils by weight [7].

Understanding the formation and stability of amorphous iron(III) sulfate and an associated aqueous brine at Mars-relevant temperatures could provide insight into their likelihood and persistence as possible amorphous soil components on Mars. The study of these phases and their transformation behavior is also important for understanding their potential role in hydrologic surface processes on Mars. This work utilizes total X-ray scattering data with temperature control to measure phase changes at low temperatures, of two initial phases of iron(III) sulfate. Amorphous iron(III) sulfate was examined using this method, to determine phase stability at low temperatures as well as for minor changes in atomic structure. The aqueous iron(III) sulfate brine parent phase of the amorphous material was also studied to measure the freezing and thawing temperatures of the brine and to constrain the temperature range of melting.

Although low-temperature experiments have been done before on iron(III) sulfate brines [10,11], part of this work seeks to carry out similar experiments. The purpose of this repetition is to examine the temperatures at which melting begins and ends with total X-ray scattering methods.

Methods: An aqueous solution of iron(III) sulfate was made by deliquescing 99.998% $Fe_2(SO_4)_3$ (anhydrous) in a 99% RH chamber buffered by deionized water. This solution has a concentration of 32.3wt% $Fe_2(SO_4)_3$ (1.15M).

Amorphous $Fe_2(SO_4)_3$ was made via desiccation of this solution in a low RH chamber (LiCl buffering salt at 298K; 11% RH) to emulate rapid evaporation as per a previous study [7].

X-ray total scattering data was obtained from beamline 28-ID-1 at the National Synchrotron Light Source – II at Brookhaven National Lab. A cryostream was used to control the temperature of samples while X-ray data was being obtained.

A capsule of aqueous $Fe_2(SO_4)_3$ was subjected to a cooling and heating cycle starting at 273K, cooling to 213K, and heating to 293K over the course of about 9 hours (Figure 1). The heating/cooling rate was approximately 1K/minute with 5 minute scans every 2K.

A sample of amorphous $Fe_2(SO_4)_3*8.33H_2O$ was cooled in a capsule using the same method as the aqueous sample, but cooled to much lower temperatures in an attempt to induce crystallization. The amorphous sample was cooled at a rate of 0.5K/minute down to 223K with 5minute scans every 5K and 1K/minute down to 123K with 5 minute scans every 10K. The total cooling time from 273K to 123K was 5 hours.

Results: Crystallization of the aqueous iron(III) sulfate solution from cooling began at 233K and crystalline peaks became more pronounced throughout cooling (Figure 2a). During heating, crystalline peaks began to dimish at 239K (not shown) and were completely gone by 257K, indicating sample melting and becoming entirely liquid at this temperature (Figure 2b). Both the freezing and melting temperatures of this aqueous sample were lower than those measured for a sample with a similar concentration by Hennings et al., 2013.
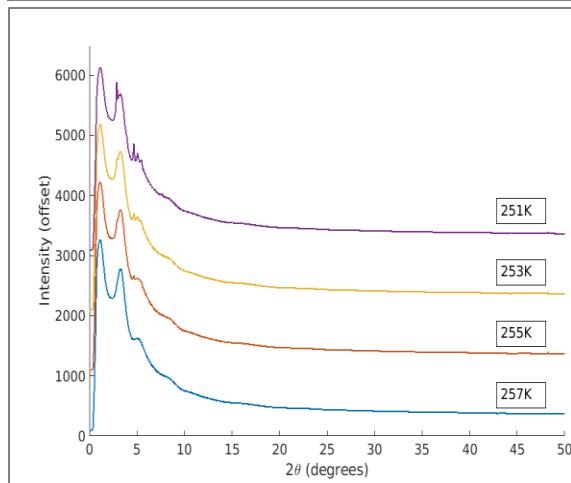
The amorphous sample exhibited no change in phase throughout the entire cooling process. This is shown by the X-ray diffraction pattern through the stages of the experiment which shows no major changes throughout cooling (Figure 3).
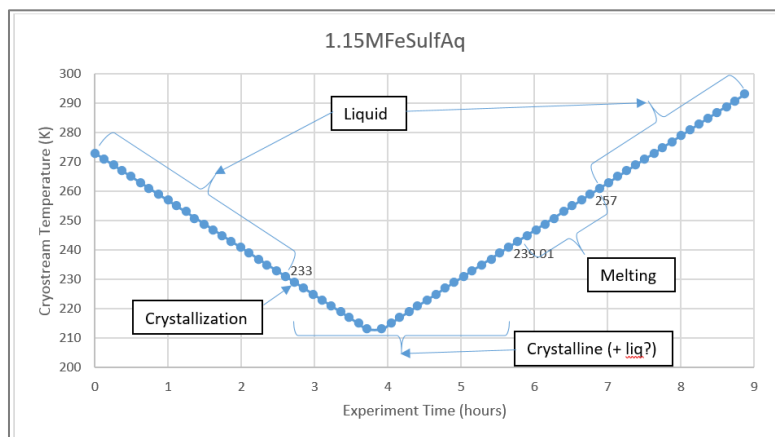
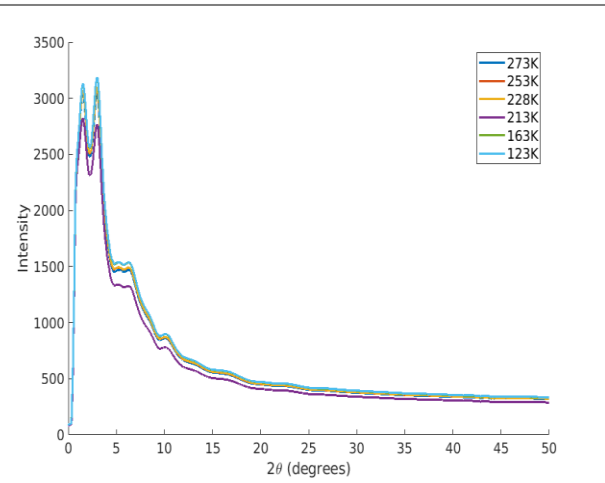**Figure 1**. Time-series of a heating/cooling cycle of aqueous $Fe_2(SO_4)_3$ with brackets indicating phase.
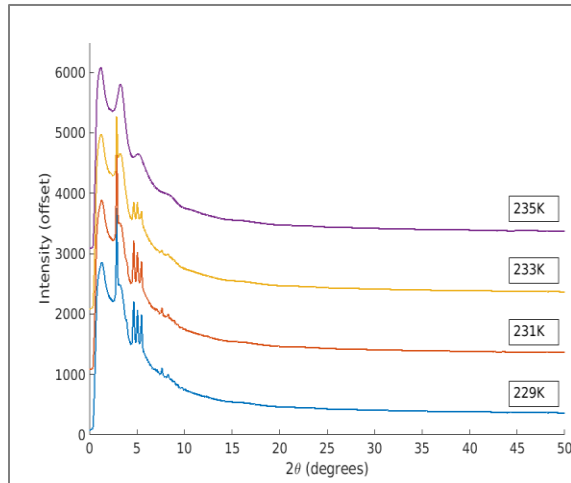
Figures 2a, 2b. X-ray diffraction patterns of aqueous $Fe_2(SO_4)_3$ through crystallization during cooling (2a, above) and melting during heating (2b, below)

Figure 3. X-ray diffraction patterns of amorphous $Fe_2(SO_4)_3*8.33H_2O$ from various stages throughout cooling ranging from 273K to 123K (0°C to -150°C).

Discussion: When cooling and heating at a rate of 1K/minute, aqueous 1.15M $Fe_2(SO_4)_3$ appears to begin to freeze from cooling at 233K, begin to melt from heating at 239K and finish melting at 257K. This shows a lag in freezing and melting temperatures indicative of kinetic processes inhibiting thermodynamic equilibrium. For this reason, it is difficult to pinpoint the actual thermodynamic freezing or melting temperature from this data. It also appears that a significant fraction of the sample does not crystallize, indicating that there could be a multi-phase system of crystalline sample plus aqueous or possibly amorphous sample with an unknown composition.

Hennings et al., 2013 reports an equilibrium solid-liquid phase boundary for a similar concentration of aqueous iron(III) sulfate (31.89wt%) at -14.2°C (258.8K). This temperature is not only higher than the freezing temperature recorded in this study but the melting temperature as well. Whereas this difference in freezing temperature could be explained by kinetics inhibiting thermodynamic equilibrium from a lack of physical mixing, it is unknown why the melting temperatures are lower as such an inhibiting effect would cause the measured melting to occur at a higher temperature (Hennings et al., 2013 stirred their samples during their cooling and heating experiments, whereas this work's samples were not stirred). One such possibility could include the concentration of the remaining solution as ice is formed, lowering the melting point as the system approaches eutectic composition. If so, it is possible that such partial freezing of sulfate brines could produce a concentrating (dehydrating) effect that may provide an additional formation mechanism of amorphous sulfates.

Amorphous $Fe_2(SO_4)_3*8.33H_2O$ was unable to produce any crystalline phase from cooling for the parameters of this cooling experiment. This suggests that amorphous $Fe_2(SO_4)_3$ is unlikely to crystallize on relatively short timescales, even at temperatures much lower than those observed on the Martian surface at non-polar latitudes. The implications of this could speak to the perseverance of such an amorphous phase that might be present on the surface or near-subsurface of Mars.

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