

EXPERIMENTATION TO STUDY THE FORMATION OF AMORPHOUS CALCIUM SULFATE IN AN ENVIRONMENT ANALOGOUS TO MARS. R. J. Hopkins¹, A. D. Rogers¹, and L. Ehm¹, ¹Department of Geosciences, Stony Brook University, 255 Earth and Space Science Building, Stony Brook, NY 11794. reed.hopkins@stonybrook.edu

Introduction: Throughout the traverse of Mars Science Laboratory Curiosity in Gale crater, Mars, there have been extensive detections of X-ray amorphous materials, comprising a high weight-percentage of the rocks and soils [1-7]. The chemical composition of the amorphous component of many Gale crater samples has been determined through mass balance calculations [4, 8, 9, 6]. With this method, the calculated composition of the crystalline component from CheMin X-ray Diffraction (XRD) is subtracted from the bulk sample composition from the Alpha Particle X-ray Spectrometer (APXS) instrument [10]. The difference is assigned to the amorphous component.

The amorphous component in the rocks and soils is enriched in sulfur and implies the presence of amorphous sulfate phases. With the Sample Analysis on Mars (SAM) instrument [11], evolved gas analysis at many drill sites in Gale crater show evidence for the presence of sulfates, and the lack of CheMin XRD detections of these phases also implies that these phases are in the amorphous component [12, 13]. A significant percentage (~20-90 wt%, Figure 1) of the bulk SO₃ content of Gale crater dill hole samples is included in the amorphous component. On average, these samples contain ~2.6 wt% crystalline SO₃ and ~4.1 wt% amorphous SO₃ [13]. The sulfur phases within this component likely include variable mixtures of Fe, Mg, and Ca-sulfates [13]. Of these sulfates, Ca-sulfate is of particular interest, as it is not known to be stable, except for as a very short-lived intermediate precursor in the precipitation of gypsum [14-16]. Gypsum can dehydrate on Mars to form bassanite or anhydrite [17], but this is not known to cause the destabilization of the crystal structure, as with hydrated magnesium sulfates. Yet, there is compelling evidence for what appears to be long-lived ACS in the sedimentary rocks of Gale crater [13]. This prompts the question of how this phase was formed and whether this Martian amorphous Ca-sulfate is truly amorphous. To address these questions, experiments studying the formation of amorphous Ca-sulfate in a Mars-analog environment are critical.

Experiments: Desiccated samples from two different solutions were synthesized that appear to contain some amount of amorphous Ca-sulfate in addition to crystalline gypsum.

First, a powder 50/50 wt% mixture of 25-63 μm gypsum and anhydrous Fe₂(SO₄)₃ was deliquesced at high relative humidity (92%) until it reached saturation.

During this deliquescence, the gypsum visibly appeared to partially dissolve or mix into the ferric sulfate brine. This mixture was rapidly desiccated at low relative humidity (11%) and formed a single brittle solid. Rietveld refinement and crystallinity analysis of this solid suggested that the bulk sample was ~80±10 wt% amorphous, with the crystalline percentage comprised entirely of gypsum. A purely ferric sulfate brine desiccates 100% into amorphous ferric sulfate. Thus, it was expected that a mixture that started as 50/50 wt% ferric sulfate and gypsum would be at or close to 50 wt% amorphous, not ~80 wt%. While it is likely that the amorphous ferric sulfate in this mixture is no longer anhydrous and has the added mass of structural H₂O [18], it is unlikely that amorphous ferric sulfate alone could account for the high amorphous wt%. This suggests that some amorphous Ca-sulfate is possibly present, or alternatively nanocrystalline gypsum that appears as amorphous Ca-sulfate.

Second, a similar powder 50/50 wt% mixture of anhydrous Fe₂(SO₄)₃ and CaCl₂·2H₂O was deliquesced at 92% relative humidity until the mixture reached saturation. This solution was rapidly desiccated at 11% relative humidity and formed a rough and brittle solid. XRD analysis of the sample indicated the precipitation of crystalline gypsum, as well as a broad elevated background due to multiple amorphous phases (Figure 1). Subtracting the amorphous curve of amorphous ferric sulfate from the pattern of the desiccated Fe₂(SO₄)₃ and CaCl₂ sample leaves a remaining elevated background. This is indicative of an additional amorphous phase other than amorphous ferric sulfate, which may possibly be amorphous Ca-sulfate.

Future Work: Future work will analyze these samples with a variety of techniques, including pair distribution function and micro-Raman analysis, as well as observing the stability of amorphous sulfates over time. These experiments will be completed while the samples are at Martian temperature, pressure, and/or relative humidity. Both of the above experimental mixtures include ferric sulfate, as this material forms an amorphous solid relatively easily. Future experiments will also attempt to form amorphous Ca-sulfate from the rapid desiccation of a brine that only includes the components of Ca-sulfate, to see whether or not the amorphous matrix from a material such as ferric sulfate is required for the apparent amorphous Ca-sulfate signature.

Implications: This work will help address the uncertainties about the formation mechanism and stability of apparent Martian amorphous Ca-sulfate. Amorphous Ca-sulfate would not be stable over geologic time, but a nano or poorly crystalline Ca-sulfate may be more stable. It is important to understand the local structure of these Ca-sulfates formed under Martian conditions to help interpret whether similar sulfates on Mars could be geologically older or more recent. Additionally, detailed Raman spectra of these amorphous sulfates will help to interpret data from Gale and Jezero crater.

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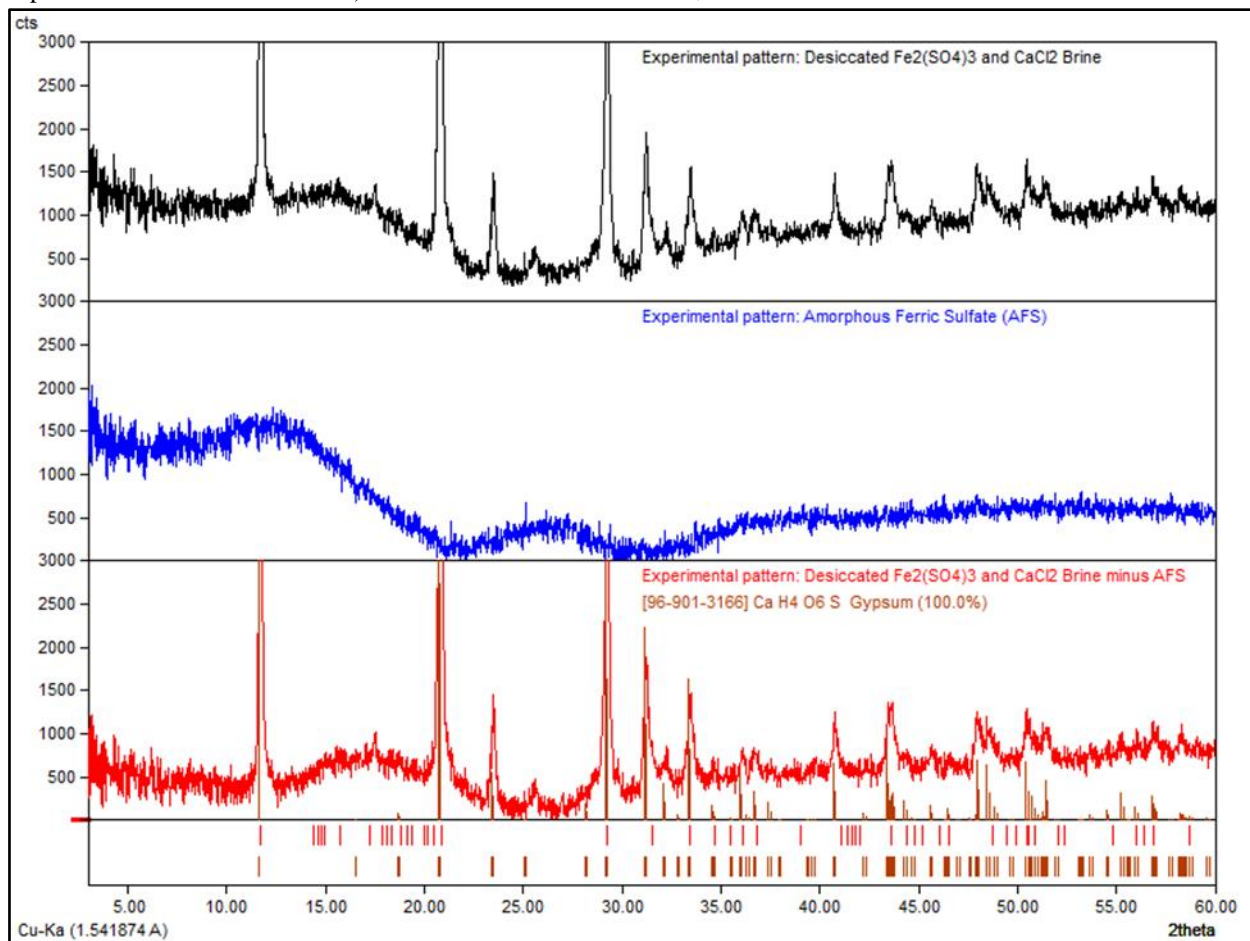


Figure 1. (Top) XRD pattern of the desiccated product of a saturated brine of Fe₂(SO₄)₃ and CaCl₂. (Middle) XRD pattern of amorphous ferric sulfate, AFS. (Bottom) The resulting XRD pattern from subtracting the amorphous pattern of AFS from the pattern of the desiccated product of the Fe₂(SO₄)₃ and CaCl₂ brine, with crystalline peaks indicating gypsum. All patterns shown have the same background pattern of the sample holder subtracted.