

RAMAN SPECTRA OF AMORPHOUS FERRIC SULFATE REACTED WITH MARS REGOLITH ANALOGUES: A COMPATIBLE TECHNIQUE TO ASSIST IN XRD IDENTIFICATION. E. C. Sklute¹, R. J. Hopkins², R. McKeegan³, M. D. Dyar^{1,4}, A. D. Rogers², and R. N. Clark¹, ¹Planetary Science Institute, 1700 E. Fort Lowell Rd Suite 106, Tucson, AZ 85719; ecsklute@psi.edu, ²Stony Brook University, Dept. of Geoscience, 255 ESS Building, Stony Brook, NY. 11794, ³Amherst College, Dept. of Geology, 220 S. Pleasant St. Amherst, MA 01002, ⁴Mount Holyoke College, Dept. of Astronomy, 50 College St. South Hadley, MA 01075.

Introduction: The significant amount (up to 70 wt%) of x-ray amorphous material in Martian samples analyzed by Mars Science Laboratory's CheMin X-ray diffractometer [1-5] continues to present a unique identification challenge. X-ray diffraction (XRD) is the mainstay for identifying materials with repeating crystal structures. However, when a material has no long-range order, i.e., it is nanophase or amorphous, XRD is limited in what it can tell us about the sample. This is primarily because the pattern produced by an amorphous material consists of broad, low intensity peaks that are both non-unique and heavily overlapped between individual components [6]. Tools and algorithms have been developed and applied to the CheMin XRD data in order to extend the amount of information that can be extracted from each measurement [7-10]. While these methods have sound theoretical and experimental backing, it is worth noting that all such tools are based on a series of assumptions and steps that lead to a degree of uncertainty in the result. These have been well described and reviewed [6,8-10].

Several steps must be taken to quantify the amount of and/or identify components in the amorphous fraction. **A) Identification of major phases using a library** assumes that all phases present are represented in that library. **B) Refinement of crystal structures** assumes that differences between sample and library crystal structure are due entirely to the parameter being refined, i.e., composition in a solid solution. **C) Identification of minor phases** assumes that unique and definitive markers for these phases can be extracted from a mixed pattern, also assumption from A). **D) Use of bulk chemical information to determine the components that remain in the amorphous fraction** assumes that modal mineralogies determined from above steps are accurate. **E) A library of potential amorphous phases is used to compute amorphous abundance and composition** assumes that the library of amorphous materials encompasses potential phases, or at least phases with similar scattering power as the amorphous phase(s) in the sample.

Fundamentally, the largest limitation to almost all matching based analysis techniques is the need for a library that covers all potential phases. However, work with the rapid dehydration of mixed brines [11] and mixed brines with regoliths [12] shows that the

composition of amorphous components with similar XRD baseline swell can be incredibly varied. It is, therefore, of interest to determine combinations of techniques that can be used to constrain the composition of such phases, reduce some of these uncertainties, and provide more robust identifications.

To that end, here we present Raman data for a series of amorphous ferric sulfates precipitated with representative Martian regolith materials. These same samples have been analyzed by XRD, Fourier transform infrared (FTIR), visible and near infrared (VNIR), ultraviolet (UV) spectroscopies [12-14].

Methods: Five regolith-analog starting materials were used in this study: magnesite (Mag), gypsum (Gyp), hematite kidney ore (Hem), fresh Hawaii basalt (Bas), and nontronite Nau-1 (Non). Anhydrous ferric sulfate (AFS) was made by heating ferric sulfate hydrate at 350°C for 2 h. Mixtures consisted of 0.5 g of AFS and 0.5 g of one of the regolith analogues alone or with 0.5 g of NaCl. These were hydrated in individual containers buffered to 92% relative humidity (RH) using DI water for 4 days, then dehydrated for 4 days at 11% RH in individual LiCl-buffered containers. Samples were transferred to an anaerobic chamber where they were ground and divided into aliquots so that each form of spectroscopy could be applied to an identical sample. All analysis was completed within 48 hours. Samples were transported in parafilm glass vials to the XRD laboratory of Kevin Kittilstved, University of Massachusetts, Amherst. XRD scans were acquired oxically using a Rigaku Smartlab II SE XRD (lab RH 35%, zero background sample holder, Bragg-Brentano geometry, Cu K α radiation, 10-60 2 θ , 0.01° step, 3°/min). Samples were photographed before and after XRD to qualitatively monitor hydration; no change was noted. XRD results were analyzed using both the Rigaku SmartLab software as well as using Match! Version 3; both methods provided similar results.

Raman spectra were acquired using a Bruker Bravo (758 and 852 nm lasers). Each sample was analyzed within its glass vial to maintain its low-humidity environment. To reduce the risk of transforming samples under the heat of the Raman laser, 100 1000ms scans were averaged. Each sample was then agitated and analyzed a second time to ensure homogeneity.

Results: Hydration/dehydration-cycled mixtures of AFS with Bas are XRD amorphous except for small

basalt-related features (Figure 1). When NaCl is added, the XRD pattern shows crystalline NaCl as well as a small amount of metasideronatrite (<10% of crystalline). Raman spectra for these samples along with references are shown in Figure 2. Raman spectra clearly show the presence of AFS, whose broad, slightly asymmetric features at 474 and 1046 cm^{-1} distinguish it from many of the crystalline sulfates. For the sample reacted with NaCl, there are sharper features overlaid on these, which correlate well with metasideronatrite, as well as a unique peak at $\sim 332 \text{ cm}^{-1}$. The fine structure at 1148 and 1126 cm^{-1} indicates our crystalline sulfate may be structurally distinct from the reference spectrum.

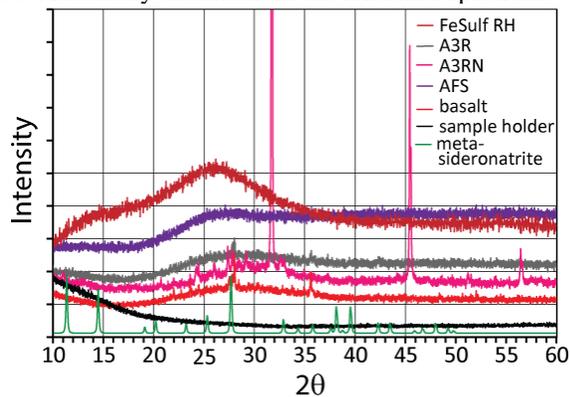


Figure 1: XRD data for AFS + BAS and AFS + NaCl + Bas that has undergone one hydration/dehydration cycle. FeSulf RH is an amorphous ferric sulfate spectrum taken on a Rigaku Miniflex to show the potential variation between XRDs.

The benefit of Raman for this sample is that basaltic glass and amorphous ferric sulfate appear quite similar via XRD. However, Raman spectra of the sulfates are quite distinct from the largely invisible basaltic glass.

Conclusions: Raman spectroscopy provides much needed information when analyzing potential phases in the amorphous fraction of the Martian soil

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2051. [15] Lafuente B. et al. (2015) W. De Gruyter, Berlin Germany, pp 1-30. [16] Gregerson J. et al. (2020) *51st LPSC*, Abstract # 2280.

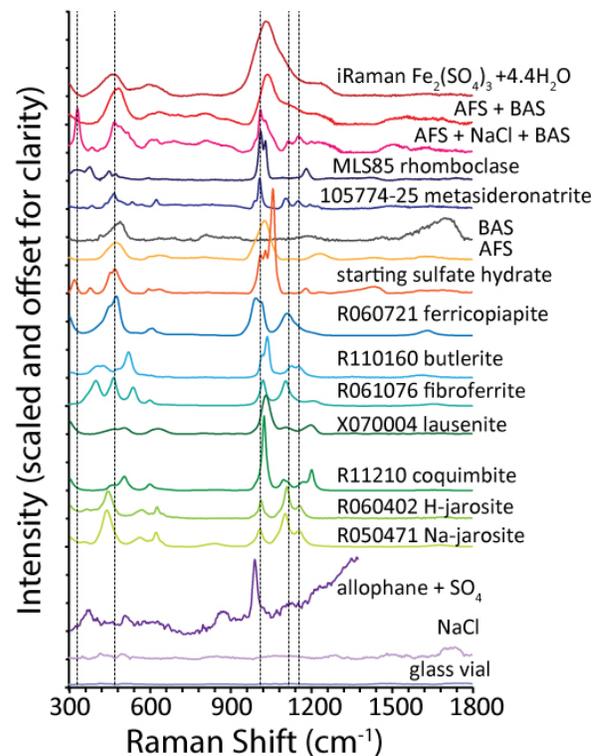


Figure 2. Raman spectra of AFS + Bas and AFS + NaCl + Bas as in Figure 1. Reference spectra are from DEVAS (<http://nemo.mtholyoke.edu>). Sample names beginning with R***** indicate spectra from the RRUFF database [15]. Allophane + SO_4 spectrum is of sulfate chemisorbed onto allophane [16].