# Raman and Near-Infrared Spectroscopy of Candidate X-Ray Amorphous Phases in Martian Rocks and Soils: Implications for Mars 2020 and ExoMars 2020 Data

Jason Gregerson<sup>1</sup>, Deanne Rogers<sup>1</sup>, Lars Ehm<sup>1</sup>, Elizabeth Sklute<sup>2</sup>, and John B. Parise<sup>3</sup>

<sup>1</sup>Stony Brook University <sup>2</sup>Planetary Science Institute <sup>3</sup>State University of New York

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#### Abstract

Martian soils and rocks contain a significant fraction of amorphous materials, based on previous lander-based x-ray diffraction and orbital infrared measurements. However, the exact nature and chemistry of the phases that make up this component are not well constrained. The upcoming Mars2020 and ExoMars rovers will carry Raman and visible/near-infrared (VNIR) reflectance spectrometers, offering new methods for characterizing Martian surface materials in-situ. Raman spectroscopy in particular has the potential to discriminate between amorphous phases; however, many of the candidate amorphous phases are absent from Raman spectral databases. We synthesized and spectrally characterized candidate x-ray amorphous phases for Martian soils (amorphous ferric sulfate, allophane, ferrihydrite, allophane with adsorbed sulfate and phosphate, and ferrihydrite with adsorbed sulfate and phosphate) with Raman and VNIR spectroscopy and document the Raman peak locations for these materials. We found that sulfate and phosphate anions were Raman-detectable when adsorbed to allophane, but were not observed when adsorbed to ferrihydrite; a possible cause for this includes decomposition of the adsorbed species during the Raman acquisition. We show that candidate sulfur-bearing species – amorphous ferric sulfate and allophane with adsorbed sulfate - are distinguishable in Raman data. Allophane, ferrihydrite and amorphous ferric sulfate exhibit distinctive VNIR spectra, but are not likely to be distinguishable in the VNIR if mixed with other materials. The potential for detecting adsorbed species is a unique strength of Raman spectroscopy compared to other spectral methods, however further studies are needed to understand the acquisition conditions, abundances and matrix compositions under which adsorbed species can be detected.

## 1 Raman and Near-Infrared Spectroscopy of Candidate X-Ray Amorphous

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3 **2020 Data** 

4 Gregerson, J. C.<sup>1</sup>, A. D. Rogers<sup>1\*</sup>, L. Ehm<sup>1</sup>, E. C. Sklute<sup>2</sup>, and J. B. Parise<sup>1</sup>

<sup>1</sup>Stony Brook University, 255 Earth and Space Sciences Bldg., Stony Brook, NY 11794-2100
 <sup>2</sup>Planetary Science Institute, 1700 E. Fort Lowell Rd Suite 106, Tucson, AZ 85719

- 8 \*Corresponding author: deanne.rogers@stonybrook.edu
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Martian soils and rocks contain a significant fraction of amorphous materials, based on previous 12 13 lander-based x-ray diffraction and orbital infrared measurements. However, the exact nature and chemistry of the phases that make up this component are not well constrained. The upcoming 14 Mars2020 and ExoMars rovers will carry Raman and visible/near-infrared (VNIR) reflectance 15 spectrometers, offering new methods for characterizing Martian surface materials in-situ. Raman 16 17 spectroscopy in particular has the potential to discriminate between amorphous phases; however, many of the candidate amorphous phases are absent from Raman spectral databases. We 18 synthesized and spectrally characterized candidate x-ray amorphous phases for Martian soils 19 (amorphous ferric sulfate, allophane, ferrihydrite, allophane with adsorbed sulfate and phosphate, 20 21 and ferrihydrite with adsorbed sulfate and phosphate) with Raman and VNIR spectroscopy and 22 document the Raman peak locations for these materials. We found that sulfate and phosphate anions were Raman-detectable when adsorbed to allophane, but were not observed when 23 adsorbed to ferrihydrite; a possible cause for this includes decomposition of the adsorbed species 24 during the Raman acquisition. We show that candidate sulfur-bearing species -- amorphous ferric 25 26 sulfate and allophane with adsorbed sulfate -- are distinguishable in Raman data. Allophane, ferrihydrite and amorphous ferric sulfate exhibit distinctive VNIR spectra, but are not likely to 27 be distinguishable in the VNIR if mixed with other materials. The potential for detecting 28 adsorbed species is a unique strength of Raman spectroscopy compared to other spectral 29 30 methods, however further studies are needed to understand the acquisition conditions, abundances and matrix compositions under which adsorbed species can be detected. 31

#### 32 Plain Language Summary

Martian sediments consist of a mixture of rock fragments, minerals, and other materials that lack 33 a well-defined crystalline structure ("x-ray amorphous" materials). The nature and species of the 34 35 x-ray amorphous materials has not been determined using instrumentation from currently active or past missions. Upcoming rover missions will carry a different kind of instrumentation (Raman 36 37 spectrometers) that are very commonly used in terrestrial laboratories but that have never before been brought to Mars. We measured some of the candidate amorphous materials using this 38 39 instrumentation and show that they can be distinguished from one another. We documented the diagnostic Raman features of these materials, for comparison to data that will be returned from 40 41 future missions. Knowing which species are present is important for understanding the origin of Martian rocks and soils, as well as for understanding the potential changes over time that rocks 42 43 and soils may experience due to burial or interaction with later fluids.

#### 44 **1. Introduction**

45 Amorphous and nanocrystalline materials have been shown to constitute a significant portion of Martian surface materials from both rover-based in-situ X-ray diffraction measurements as well 46 47 as from landed and orbital spectroscopic measurements. Using data from the CheMin X-ray diffractometer instrument, the Mars Science Laboratory (MSL) science team has inferred that up 48 49 to 70 wt% of rocks and 50 wt% of soils in Gale crater contain "X-ray amorphous" material (Bish et al. 2013; Blake et al. 2013; Dehouck et al. 2014; Vaniman et al. 2014; Rampe et al., 2017; 50 51 Achilles et al. 2020; Rampe et al. 2020). "X-ray amorphous" implies material that lacks the longrange atomic ordering necessary to exhibit Bragg peaks in X-ray diffraction patterns, and can 52 53 include a range of amorphous materials, like glasses, or poorly-/nano-crystalline phases. Using supplemental chemical data from the Alpha Particle X-ray Spectrometer (APXS) instrument and 54 55 evolved gas analysis (EGA) data from the Sample Analysis at Mars (SAM) instrument suite on MSL, the X-ray amorphous fraction likely consists of multiple phases. Potential materials 56 57 include silicate glass, allophane, nanophase iron oxides, amorphous salts, and other poorly crystalline weathering products; however, despite the constraints on chemistry, it is unknown 58 what combination of phases make up the X-ray amorphous fraction of Martian rocks and soils. 59 Amorphous materials have also been inferred spectroscopically from orbit and ground and are 60 likely dominated by various forms of amorphous silicate (e.g., glass/altered glass, amorphous 61

62 silica, allophane, imogolite) and ferric oxides (e.g. Bell et al., 1993 Bandfield, 2002; Michalski et

al., 2005; Glotch et al., 2006; Milliken et al., 2008; Ruff et al., 2011; Horgan and Bell, 2012;

64 Rampe et al., 2012; Farrand et al., 2016; Cannon et al., 2017).

65 Of particular interest to this study is the nature of the sulfur-bearing amorphous component(s).

66 Relative to the crystalline fraction of Gale soils, the amorphous fraction is enriched in iron,

sulfur and  $H_2O$ , with ~3-6 wt% water (Bish et al. 2013; Dehouck et al. 2014; Leshin et al. 2013;

68 McAdam et al. 2014). Proposed sulfur-bearing amorphous phases include amorphous sulfates

69 (Dehouck et al., 2014; McAdam et al., 2014; Sklute et al., 2015) and/or chemisorbed sulfate

anions onto nanocrystalline weathering products such as ferrihydrite or allophane (Dehouck et

al., 2014; McAdam et al., 2014; Rampe et al., 2016). Amorphous iron sulfates have been shown

to form by path dependent dehydration from concentrated brines or crystalline sulfate hydrates,

and thus could potentially form under certain Martian conditions (e.g. Xu et al., 2009; Wang et

al., 2012; Sklute et al., 2015). Nanophase minerals and mineraloids including ferrihydrite and

allophane are common immature weathering products in terrestrial basalts and volcanic soils.

76 These nanophase materials can collect ions such as sulfate and phosphate with their hydroxylated

surfaces and large amount of surface area (e.g. Wada, 1987; Rampe et al., 2016).

78 Just like crystalline minerals, amorphous species are tracers of environmental conditions, during formation, diagenesis, and later episodes of alteration. Thus it is critically important to identify 79 80 and distinguish between these species. For example, allophane, imogolite and hisingerite are 81 common immature products of silicate weathering (particularly in ashy/glassy protoliths) (e.g. 82 Wada, 1987; Dahlgren et al. 2004; Bishop et al. 2013). Thus identification of these phases could signify water-limited alteration and/or a higher proportion of glass in the protolith material. For 83 another example, take the sulfur-bearing components described above. The presence of 84 85 amorphous Mg, Fe(II) or Fe(III) sulfate phases, which form from rapid brine evaporation or

dehydration of crystalline sulfates, depending on the cation (e.g. Vaniman et al., 2004; Xu et al.,

87 2009; Sklute et al., 2015), could indicate acid sulfate weathering conditions and/or an

88 evaporative process. But, if the sulfur instead arises from chemisorbed sulfate anions on

89 nanophase silicate weathering products (e.g. allophane/ferrihydrite), this could indicate circum-

90 neutral water-limited alteration with later exposure to sulfur-bearing fluids (e.g. Wada, 1987;

91 Rampe et al., 2016). Last, amorphous phases can be indicators of aqueous activity after

92 formation. For example, ferrihydrite is relatively unstable on Earth and rapidly transforms to

93 hematite or goethite upon exposure to aqueous solutions. However, its fate does depend on

94 fluid:rock ratio, temperature, and solution chemistry (Dehouck et al. 2017). For example, low

95 fluid:rock ratio (Dehouck et al., 2017), as well as the presence of chemisorbed  $PO_4^{3-}$  on

96 ferrihydrite (Galvez et al., 1999) have both been shown to inhibit the transformation of

97 ferrihydrite to other iron oxides. However, exposure to high temperatures, such as through burial,

98 would likely preclude the preservation of ferrihydrite (e.g. Dehouck et al., 2017).

A potential method to distinguish between candidate X-ray amorphous phases is to use Raman 99 100 spectroscopy. Raman spectrometers will be sent to surface of Mars via both the Mars 2020 rover 101 mission and the ExoMars 2022 rover mission. Mars 2020 will carry the SuperCam instrument, which includes a remote, time-resolved Raman spectrometer that uses a 532 nm excitation laser 102 (Weins et al., 2017) and the SHERLOC instrument, which includes a microimaging Raman 103 spectrometer with a 248 nm excitation laser (Beegle et al., 2015). The ExoMars rover will 104 105 include a Raman spectrometer with a 532 nm excitation laser, to analyze drilled and powdered 106 samples at close range within the rover body (Rull et al., 2017). Additionally, both rovers will 107 carry near-infrared (NIR) reflectance spectrometers (Wiens et al., 2017; Bibring et al., 2017) that

108 may also provide supporting characterization of amorphous components. For example,

109 differences in NIR band shape and position are observed between amorphous sulfates and

silicate weathering products (e.g. Sklute et al., 2015; Rice et al., 2013; Bishop et al., 2013);

111 however, some amorphous samples are not well distinguished from crystalline hydrated samples

112 (e.g. amorphous Mg sulfate vs Mg hexahydrite, Wang et al., 2009). Nevertheless, the

accompanying NIR data could help to distinguish between some species.

114 An extensive literature review has shown that, with the exception of nanophase iron

115 (oxyhydr)oxides (e.g. Das and Hendry, 2011; Sklute et al., 2018) and amorphous ferric sulfate

116 (Ling and Wang, 2010; Wang et al., 2012), Raman characterizations are absent for many of the

117 proposed x-ray amorphous phases. Additionally, though Raman characterization of amorphous

118 ferric sulfate has been presented previously (e.g. Ling and Wang, 2010), those phases are not

119 publicly available. In this work, we characterize and compare Raman and visible/near-infrared

120 (VNIR) spectra of a selection of candidate x-ray amorphous phases: synthetic amorphous ferric

121 sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·~6-8H<sub>2</sub>O), allophane (1.0-2.0SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>·2.5-3.0H<sub>2</sub>O), ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub>

 $\cdot \sim 9H_2O$ ), and allophane and ferrihydrite with chemisorbed sulfate and phosphate (**Table 1**). The

samples with chemisorbed phosphate were included in our study because the amorphous

- 124 component of Gale soils also includes minor phosphate, and additionally, phosphate is
- 125 commonly chemisorbed on terrestrial volcanic soils (e.g. Rampe et al., 2016). Our spectra could
- help these phases to be identified or ruled out based on returned data from the upcoming rover
- 127 missions, and might be used to test hypotheses regarding the sulfur-bearing amorphous
- 128 component in Martian soils and rocks.

#### 129 **2. Materials and Methods**

#### 130 **2.1 Sample synthesis**

#### 131 **2.1.1** Amorphous ferric sulfate. allophane, and ferrihydrite synthesis

Anhydrous  $Fe_2(SO_4)_3$  (99.998% purity) was deliquesced in a 99% RH environment buffered by

deionized water to form a solution with a concentration of 32.3 wt% Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. This solution was

dehydrated via vacuum for seven days to form an amorphous solid as per Sklute et al. (2015).

135 Synthesis of allophane was adapted from Ohashi et al. (2002). 0.1 M solutions of AlCl<sub>3</sub> and

136 Na<sub>4</sub>SiO<sub>4</sub> were prepared by dissolving reagents (99% and 99.5% purity, respectively) in deionized

137 water. Solutions were combined at a ratio of Si/Al = 0.75 and stirred for 1h. The resulting

mixture was centrifuged for 30 minutes at 6000 rpm to separate the allophane precursor gel from

the saline supernatant. The precursor was then placed in an autoclave at 100 °C for 48 hours. The

solids were washed with deionized water and then separated by centrifuge three times and then

141 dried at 40 °C overnight. Solids were ground with an agate mortar and pestle.

142 Synthesis of two-line ferrihydrite was adapted from Schwertmann and Cornell (2000). 40 g of

143 Fe(NO<sub>3</sub>)\*9H<sub>2</sub>O (reagent) was dissolved in 500 mL of deionized water and then brought to a pH

of 7.15 using 1 M KOH. The mixture was stirred for 24 hours and centrifuged for 30 minutes at

145 6000 rpm to separate the solids from the supernatant. Solids were washed with deionized water

and centrifuged three times and then dried at 40  $^{\circ}$ C overnight. Solids were ground with an agate

147 mortar and pestle.

#### 148 2.1.2 Adsorption of Sulfate and Phosphate

Methods for sulfate and phosphate adsorption onto the surface of allophane and ferrihydrite wereadapted from Rampe et al. (2016). For all sulfate and phosphate solutions, a background solution

151 of 0.1 M KCl was made by dissolving KCl (reagent) in deionized water.

152 For allophane, 0.015 M solutions of K<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub> were prepared by adding solid K<sub>2</sub>SO<sub>4</sub>

and K<sub>2</sub>HPO<sub>4</sub> (reagents) to the 0.1 M KCl background solutions. The pH of each solution was

adjusted to 5.84 (sulfate solution) and 5.53 (phosphate solution) using HCl and KOH (reagents).

155 0.6164 g of allophane was added to 45 mL of this sulfate solution and 0.6235 g of allophane was

added to 45 mL of this phosphate solution. Each was then stirred for 24 h before being

157 centrifuged for 30 minutes at 6000 rpm to separate the solids from the supernatant. Solids were

158 washed with deionized water and centrifuged three times and then dried at 40 °C overnight.

159 Samples were ground with an agate mortar and pestle for sample analysis.

160 For ferrihydrite, 0.015 M solutions of K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> were prepared by adding solid K<sub>2</sub>SO<sub>4</sub>

and Na<sub>2</sub>HPO<sub>4</sub> (reagents) to the 0.1 M KCl background solutions. The pH of each solution was

adjusted to 4.18 (sulfate solution) and 4.11 (phosphate solution) using HCl and NaOH (reagents).

163 1.2009 g of ferrihydrite was added to 90 mL of this sulfate solution and 1.2008 g of ferrihydrite

164 was added to 90 mL of this phosphate solution. Each was then stirred for 24 h before being

165 centrifuged for 30 minutes at 6000 rpm to separate the solids from the supernatant. Solids were

166 washed with deionized water and centrifuged three times and then dried at 40 °C overnight.

167 Samples were ground with an agate mortar and pestle for sample analysis.

#### 168 **2.2 Sample Analysis**

#### 169 **2.2.1 Chemical analysis**

We used thermogravimetric analysis (TGA) to determine the water content of allophane and
ferrihydrite. The instrument used is a Netzsch STA 449 C. For amorphous ferric sulfate, weight

percent of water was determined by mass loss from dehydration. We determined the amount of

173 water by weight percent by mass loss from heating for allophane and ferrihydrite.

174 We determined the chemistry of each allophane and ferrihydrite sample using inductively

175 coupled plasma optical emission spectrometry (ICP-OES). A small amount of each sample was

dissolved in 10% HNO<sub>3</sub> for chemical analysis. Reference solutions were also prepared in 10%

177 HNO<sub>3</sub> for each element analyzed. The reference and sample solutions were analyzed using a

178 Thermo iCAP 6300 radial view inductively coupled plasma-atomic emission spectrometer. The

179 Thermo Scientific iTEVA software was used to produce final concentrations from the data.

#### 180 2.2.2 X-ray Diffraction

X-ray diffraction (XRD) was used to confirm the amorphous nature and/or the phase identity of 181 182 the synthetic amorphous ferric sulfate, allophane, and ferrihydrite samples. XRD measurements were carried out on two instruments: (1) a Rigaku Miniflex (15 mA; 40 kV; 0.02 °/step; 0.40 183 s/step) with a Cu K $\alpha$  radiation source, and using a quartz zero-background sample holder, and (2) 184 an Olympus BTX-II (30 kV, 0.05 20, 64 exposures) with a Co Ka radiation source using a 185 186 Kapton sample holder. The BTX-II was used for a more direct comparison to diffraction patterns 187 taken by CheMin whereas the Miniflex offered a wider range of scattering vector (Q) values for better phase identification. 188

#### 189 2.2.3 Raman Spectroscopy

190 All samples were examined and characterized using continuous wave Raman spectroscopy.

191 Raman spectra were acquired using three different excitation wavelengths (UV: 325 nm, green:

192 532nm, and red: 785 nm) to compare the Raman response for each material as a function of

193 excitation energy. Peak locations were determined by finding the intensity maxima after

smoothing with a 5-channel boxcar filter.

The green laser Raman setup is a WiTEC alpha300R confocal Raman microscope system equipped with a 532 nm Nd:YAG excitation laser. Spectra were acquired at 7 mW power (P) with 120 accumulations of 10 second exposures under 20x magnification (~1.6  $\mu$ m laser spot size, *d*). Under these conditions, we estimate a power density of ~3.5 mW /  $\mu$ m<sup>2</sup>, using the following equation (Xi et al., 2019):

$$\mathbf{D} = 4\mathbf{P} / (\pi d^2) \tag{1}$$

The 532 nm laser excitation wavelength matches that of the upcoming Mars 2020 rover
SuperCam Raman subsystem (Wiens et al., 2017) as well as the Raman spectrometer on the
ExoMars 2020 rover (Rull et al., 2017).

For amorphous ferric sulfates, additional Raman spectra were acquired with a B&W Tek
iRamanPlus portable spectrometer using a 532 nm laser, under 50mW power for 30-120 s, under

a nitrogen-purged atmosphere to prevent hydration or deliquescence. The additional 532 nm
Raman measurements were done to evaluate any spectral changes with instrument setup as well
as any potential changes with exposure to humidity.

209 All samples were characterized using two additional laser excitation wavelengths, 785 nm and 325 nm. These measurements were taken using a Renishaw InVia confocal Raman microscope, 210 211 using 5x magnification, 100 mW (UV) and 320 mW (red) power and ten, 10-second exposures. Estimated spot sizes and power densities for the UV and red acquisitions are  $\sim 3 \mu m / \sim 12.0$ 212  $mW/\mu m^2$  and ~8  $\mu m$  / ~6.4  $mW/\mu m^2$ , respectively, using equation (1). These additional spectra 213 214 were acquired in order to characterize any spectral changes with excitation laser wavelength. The 325 nm laser is closer to the laser wavelength of the micro-Raman spectrometer on the 215 SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics & 216 Chemicals) instrument on Mars 2020 (248 nm, Beegle et al., 2015), but likely more susceptible 217 to fluorescence than the deep UV range of SHERLOC (e.g. Tarcea et al., 2007). 218

All Raman spectra were baseline-corrected with a "rubberband" correction (Warterwig, 2003; Dyar et al., 2016) using the Mt. Holyoke College DEVAS web interface, using parameters of 12 iterations and over a range of 64 channels (Carey et al., 2017). Rare noise spikes due to galactic cosmic rays were manually removed from the baseline-corrected spectra. Finally, spectra were then smoothed using a 5-channel boxcar filter. Uncorrected Raman data, as well as filtered and baseline-corrected data are included in the data repository.

## 225 2.2.4 Visible/Near-Infrared Reflectance (VNIR)

Visible/near-infrared reflectance (VNIR) spectra (350-2500 nm) were collected for allophane
and ferrihydrite samples with an ASD Fieldspec3 spectrometer using incidence and emergence
angles of 30° and 0°, respectively, and measured relative to Spectralon. VNIR spectra of
amorphous ferric sulfate were previously presented by Sklute et al. (2015) and were not reacquired in this study.

231 **3. Results** 

#### 232 **3.1 Chemistry and hydration**

- **Table 1** shows the chemical information of allophane and ferrihydrite samples obtained using
- 234 ICP-OES. This includes wt% of adsorbants and Si/Al atomic ratio for allophane as well as water
- contents for amorphous ferric sulfate, allophane, and ferrihydrite.

Table 1. Sample Compositions							
Sample	Water Content (wt %)	Adsorbant	Si/Al				
Amorphous Ferric Sulfate	22.3						
Allophane	26.7		0.59				
Allophane $+$ SO <sub>4</sub>		4.2 wt% SO <sub>4</sub>	0.58				
Allophane $+ PO_4$		8.7 wt% PO <sub>4</sub>	0.57				
Ferrihydrite	22.0						
Ferrihydrite + SO <sub>4</sub>		2.9 wt% SO <sub>4</sub>					
Ferrihydrite + PO <sub>4</sub>		8.3 wt% PO <sub>4</sub>					

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### 237 **3.2 X-ray Diffraction**

X-ray diffraction (XRD) data from the Miniflex for all samples are shown in Figure 1. Our 238 sample of amorphous ferric sulfate does not exhibit any sharp Bragg peaks, and shows only a 239 broad diffraction pattern peaking at 25  $2\theta$ , consistent with Sklute et al. (2015). Allophane shows 240 broad, diffuse peaks centered at  $2\theta$  values of 29, 42 and 68. These peaks correspond to the 241 allophane d-spacing features at 1.4, 2.2, and 3.4 Å, consistent with those reported by Ohashi et 242 243 al. (2002) and Rampe et al. (2016). The allophane features did not change position or shape with the addition of adsorbed ions, confirming that the allophane crystal structure is constant 244 throughout the adsorption experiments. Ferrihydrite shows broad diffuse peaks at 20 values of 36 245 and 65. These peaks correspond to ferrihydrite d-spacing features at 1.5 and 2.6 Å, consistent 246 with those reported by Schwertmann and Cornell (2000) and Rampe et al. (2016). As with 247 allophane, the structure of ferrihydrite was preserved throughout the adsorption experiments. 248

Diffraction patterns acquired with the BTX-II are shown in **Figure S1**; no significant differences in broad peak locations were observed between instruments, once adjusted for differences in radiation source (Co vs Cu). However, the amorphous ferric sulfate XRD pattern acquired with the BTX-II is more similar to a previously published pattern (Sklute et al., 2015) than that acquired with the Miniflex. Nevertheless, both instruments confirm the x-ray amorphous nature of the sample.



Figure 1. Miniflex XRD Data for all samples. Diffraction patterns are offset with all allophane
 and ferrihydrite superposed to emphasize the lack of change in diffraction pattern from
 adsorption.

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## 259 3.3 Raman Spectroscopy

- Raman spectra for all phases, grouped by excitation energy, are shown in Figure 2. Table 2
- shows the observed Raman modes of all materials examined in this study as well as those of
- related materials from previous studies.
- For each sample, Raman spectra collected from each excitation energy (UV, green, red) show
- differences in peak location, magnitude, and shape (Figure 2, Table 2). In some cases, Raman

- peaks are present in one excitation energy but absent in another; for example, the 1356 cm<sup>-1</sup> peak
- in allophane is only present in the 785 nm laser data. The biggest differences observed across
- 267 excitation energies was for the ferrihydrite samples. As will be described in more detail below,
- these large differences are due to a phase transformation that occurred during the 532 nm Raman
- 269 data acquisition, and probably also during the 325 nm acquisition.



**Figure 2.** Raman spectra acquired of amorphous ferric sulfate (A), allophane with and without adsorbants (B), and ferrihydrite with and without adsorbants (C). The ferrihydrite samples acquired at higher energies likely transformed during acquisition; see text. Vertical lines highlight peaks of interest shown in the 532 nm data.

Table 2 material	2 <b>.</b> Ram ls.	an mo	odes f	for the	X-ra	iy an	norp	hous	s ma	ateria	als e	xam	ined	in tl	his st	udy and	l for re	la
Phase of	Exci- tation	H₂	0		SO4	1			Р	04			s	iO <sub>2</sub>			Other peaks	R
Interest	(λ, nm)	Stretch	Bend	ν <sub>1</sub>	v <sub>2</sub>	ν <sub>3</sub>	ν4	ν1	ν <sub>2</sub>	ν <sub>3</sub>	ν4							
SO <sub>4</sub>	532	-	-	983	450	1105	611									]		
PO.	532							938	420	1017	567							

d 

Fe <sub>3</sub> (SO <sub>4</sub> )         532         3057 323         1653         1074 165         416 468 1199         599 614 662         1 <th1< th="">         1         1         &lt;</th1<>										-	-									
Al-(SO-4)- 17H2O         S32         324         992         470         1086 12.6         612         I <thi< th="">         I         <thi< th="">         &lt;</thi<></thi<>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	532	3057 3195 3323 3425	1605 1653	1017 1036 1051	416 441 457 468	1087 1119 1189	599 614 631 652											253 281	4
1         1	Al₂(SO₄)₃ · 17H₂O	532	3246		992	494	1086 1126	612											309	8
Am. Ferric Sulfavi Sulfavi Sulfavi Normalization         3180 3321         1634         993 1035         424 472         1089 1231         598 628 628 628         I <thi< th="">         I         I</thi<>		325			1047	(450)	1214	623												1
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Hanesch (2009); 7--Das and Hendry (2011); 8--Wang and Zhou (2014)

#### **3.3.1 Samples without adsorbants**

In the amorphous ferric sulfate sample, the most distinctive peak is observed at 1045-1074 cm<sup>-1</sup> 297 (Figure 2), due to the  $SO_4^{2-}$  v<sub>1</sub> fundamental mode (Table 2). Other major peaks can be identified 298 299 below 600 cm<sup>-1</sup>; these vary slightly depending on excitation energy. Though the sample is 300 hydrated, Raman features due to hydration are not apparent. The  $v_1$  mode location is similar in position to hydrated crystalline ferric sulfate (Table 2); however, the peak is significantly 301 broadened in the amorphous phase (Ling and Wang, 2010). In the data acquired with the 785 nm 302 303 excitation, three sharp narrow peaks are superimposed on the broad  $v_1$  feature, suggesting that the sample may have undergone partial crystallization before measurement. 304

Allophane shows peaks at  $\sim$ 360,  $\sim$ 510, and 870 cm<sup>-1</sup>, taking the average of the peak centers from 305 each excitation energy (Figure 2, Table 2). These peaks are similar to those reported by Coccato 306 307 et al. (2016) for a purported sample of allophane (no sample characterization was reported) at 364, 502, and 858 cm<sup>-1</sup>. In the 532 nm Raman data, there is also a large broad feature centered at 308 about 1666 cm<sup>-1</sup> that spans from  $\sim$ 1200 to  $\sim$ 2600 cm<sup>-1</sup>; this is likely a fluorescence affect. With 309 the 785 nm laser, a broad feature at 1527 cm<sup>-1</sup> is present, and is superposed by a narrower peak at 310 311 ~1356 cm<sup>-1</sup>. We were unable to attribute that feature to a particular molecular group, however we 312 note that it is present in both our allophane and ferrihydrite samples (Figure 2), and is also common in other iron oxides (Hanesch, 2009) (Figure 3) and carbon-bearing species. We do not 313 consider the  $\sim 1356 \text{ cm}^{-1}$  peak to be diagnostic of either of these phases. 314

The spectra of ferrihydrite are variable with excitation energy. Those taken with the 532 nm laser 315 show peaks at Raman Shift values of 282, 398, and 595 cm<sup>-1</sup>. These peaks are inconsistent with 316 previously reported values for ferrihydrite (Hanesch, 2009; Sklute et al., 2018), but rather closely 317 resemble those of hematite (Hanesch, 2009; Sklute et al., 2018) (Figure 3, Table 2). This 318 suggests that all three of our ferrihydrite samples were transformed into hematite from exposure 319 320 to the 532 nm laser. We were unable to obtain a ferrihydrite signal using lower laser power and 321 longer integration times. This is discussed further in **Section 4**. The spectra acquired with the 325 nm excitation energy generally lack features except for a sharp peak at 320 cm<sup>-1</sup> and broad 322 hump at 445 cm<sup>-1</sup>. These features generally match those of the amorphous ferric sulfate sample, 323 with the exception of the 1047 cm<sup>-1</sup> peak in the amorphous ferric sulfate. It is unclear whether 324

the ferrihydrite sample also experienced transformation; however, because of the higher power
density associated with our UV measurements, we would expect the sample to have converted,
as with the green laser.

328 Our ferrihydrite samples measured with the 785 nm laser match closely with those previously

reported by Das and Hendry (2011) and Sklute et al. (2018), indicating little-to-no

transformation during measurement (Figure 3). These spectra exhibit broad peaks at Raman

shifts of 355, 504 and 714 and 1352  $\text{cm}^{-1}$ . The first three of these peaks are likely ferrihydrite

peaks, which have been reported at 361, 508, and 707  $\text{cm}^{-1}$  for this laser wavelength (Das and

Hendry, 2011). Das and Hendry did not present spectra above 1200 cm<sup>-1</sup>. We note that

maghemite and ferrihydrite are spectrally similar (Sklute et al., 2018), and that our ferrihydrite

- sample may have minor amounts of maghemite based on the minor dip at  $430 \text{ cm}^{-1}$  (see also
- **Section 4.1**).



337

Figure 3. Comparison of our ferrihydrite samples with ferrihydrite and hematite spectra from
Sklute et al., (2018), who used much lower laser power and longer integration times. Our sample
measured using a 532nm excitation exhibits peaks consistent with hematite. Our sample

measured using 785 nm excitation is consistent with ferrihydrite, with possibly minor amounts of

maghemite. The sample measured using 325 nm excitation is not consistent with either

343 ferrihydrite, magnetite, or hematite.

344

## 345 **3.3.2 Samples with adsorbants**

In all three excitation energies, allophane with adsorbed sulfate shows a sharp peak at 980-990

347 cm<sup>-1</sup>, consistent with sulfate (Ross, 1974a). The absorbed sulfate peak is clearly shifted to lower

348 frequencies than that of the broad sulfate peak associated with amorphous ferric sulfate (**Figure** 

**2**). We note that the adsorbed sulfate peak position (990 cm<sup>-1</sup>,  $\lambda$ =532nm) is nearly identical to the

 $v_1$  sulfate peak in crystalline aluminum sulfate (992 cm<sup>-1</sup>,  $\lambda$ =532nm) (Wang and Zhou, 2014)

(**Table 2**); however, aluminum sulfate also contains clear  $v_4$  and  $v_2$  peaks at ~612 and ~470 cm<sup>-1</sup>

that would permit its distinction from allophane with adsorbed sulfate complexes. Allophane

with adsorbed phosphate shows a somewhat broad peak at  $\sim 1025$  cm<sup>-1</sup> in all three excitation

energies consistent with phosphate (Ross, 1974b); however, the 1025 cm<sup>-1</sup> feature is very weak

in the 785 nm data (**Figures 2,3; Table 2**).

In contrast with allophane, no evidence of adsorbed sulfate anions are observed in the

ferrihydrite Raman data, and only a very weak hump near  $\sim 1025$  cm<sup>-1</sup> is present in the

358 phosphate-bearing ferrihydrite sample in the red laser acquisitions. Potential causes for the lack

359 of detection are discussed in **Section 4.1**.

## 360 3.4 Visible / Near Infrared (VNIR) Spectroscopy

Allophane reflectance spectra (Figure 4) exhibit a blue slope, with greater reflectance at shorter 361 wavelengths. Spectral features are observed at 970, 1160, 1438, 1940, and 2209 nm, with little to 362 no observable differences between allophane and allophane with adsorbed sulfate and phosphate, 363 except for an increase in overall reflectance. The ferrihydrite reflectance spectra show 364 absorptions at 1437 and 1934 nm, due to H<sub>2</sub>O vibrational overtones and combinations. Similar to 365 366 allophane, ferrihydrite with adsorbed sulfate and phosphate does not exhibit any additional features, but shows a greater reflectance with adsorbed sulfate and phosphate. These findings are 367 consistent with those presented by Rampe et al. (2016). 368



370

**Figure 4**. VNIR reflectance spectra of allophane and allophane with adsorbed sulfate and

phosphate. Amorphous ferric sulfate from Sklute et al., (2015) is shown for comparison.

Allophane spectra are offset from ferrihydrite spectra by 0.35; amorphous ferric sulfate is offset

from ferrihydrite spectra by 1.0. Vertical lines designate features observed in allophane and

permit easier comparison of feature positions between all samples.

#### 376 **4. Discussion**

#### **4.1 Lack of detection of adsorbed species on ferrihydrite**

Unlike our allophane samples, SO<sub>4</sub><sup>2-</sup> was not detected in Raman spectra when adsorbed to 378 ferrihydrite, and  $PO_4^{3-}$  was barely discernible in only one excitation energy (Figure 2, Section 379 **3.3**). The lack of detection suggests that either the adsorbed phases are somehow obscured in the 380 sample, or that they were lost either before or during the measurement. We note that our ICP 381 data confirms the presence of the sulfate and phosphate anions, and also that these samples 382 383 showed a noticeable brightening in the VNIR data. Both of these observations indicate that the 384 adsorbed phases were indeed present in the samples and that the samples were visibly changed by the adsorption process. Thus, we suggest that the sulfate anions, and much of the phosphate 385 anions, may have been volatilized during the Raman acquisitions of ferrihydrite. Evolved gas 386 387 analyses (EGA) of ferrihydrite and allophane samples (with and without adsorbed species) by 388 Rampe et al. (2016) showed evolved SO<sub>2</sub> peaks at ~400, 490, and 700 °C in their ferrihydrite + adsorbed sulfate sample, indicating that adsorbed  $SO_4^{2-}$  begins to decompose at temperatures as 389 low as ~400  $^{\circ}$ C. The temperature at which ferrihydrite dehydrates and transforms to hematite, 390 when containing adsorbed sulfate, was suggested to occur at 440 °C, again based on EGA 391 392 measurements of evolved H<sub>2</sub>O (Rampe et al., 2016). Given that we observed a hematite transformation in our 532 nm Raman data, this suggests that our sample was likely heated to a 393 temperature that decomposed the adsorbed  $SO_4^{2-}$ . 394

As for the 785 nm Raman acquisitions, we suggest that the ferrihydrite sample may also have 395 experienced enough heating to remove all of the  $SO_4^{2-}$  and much of the  $PO_4^{3-}$  (phosphate 396 discussed below). Our spectra were acquired with a power density of ~6.4 mW /  $\mu$ m<sup>2</sup>. Previous 397 work by Novak et al. (2016), who modeled the laser-induced heating of amorphous silicon films, 398 399 showed that temperatures would exceed ~400 °C for power densities of ~5 mW/  $\mu$ m<sup>2</sup> or greater. 400 These temperatures would likely be even higher for our dark, iron-bearing samples. Thus, we conclude that it is plausible that adsorbed sulfate was lost from ferrihydrite during our Raman 401 402 acquisitions. Finally, we note that ferrihydrite is spectrally similar to maghemite in Raman data (Sklute et al., 2018), and that our ferrihydrite sample ( $\lambda$ =785nm) contains weak features that may 403 be consistent with a maghemite component (Figure 3). Maghemite has been reported as an 404

405 intermediate product during the transformation of ferrihydrite to hematite (Mazzetti and 406 Thistlethwaite, 2002), thus it is possible that our sample also underwent partial transformation in 407 addition to losing adsorbed anions. We note that Mazzetti and Thistlethwaite (2002) reported 408 loss of  $SO_4^{2-}$  Raman peaks during prolonged measurement of scwhertmannite (a ferric 409 oxyhydroxysulfate), providing another example of sulfate decomposition during Raman 410 acquisitions, and transformation to maghemite then hematite.

411 The loss of the  $PO_4^{3-}$  peak in the 532 nm data, and its weakening in the 785nm data, is more

412 puzzling as Rampe et al. (2016) reported no phosphate gas released within temperature range of

their EGA measurements (<1150 °C). It is unclear whether our ferrihydrite samples would have

reached high enough laser-induced temperatures to decompose or transform the adsorbed

- 415 phosphate. However, we note that the  $PO_4^{3-}$  features were much weaker than the  $SO_4^{2-}$  features
- 416 in the allophane Raman acquisitions, thus presumably the  $PO_4^{3-}$  features would be easier to
- 417 obscure if any type of thermal modification occurred.

#### 418 **4.2 Applicability to Mars2020 and ExoMars data**

419 The X-ray amorphous phases allophane, ferrihydrite and amorphous ferric sulfate (Figure 1), 420 each have unique spectral features that can be used to identify them using Raman spectroscopy 421 (Figure 2). Though amorphous materials have generally lower Raman cross-sections than 422 crystalline materials (making them potentially difficult to detect in mineral mixtures), they may be distinguishable in cases where amorphous materials make up the bulk of the measurement 423 footprint. Given that such a substantial fraction of the materials could be amorphous (based on 424 425 XRD measurements at Gale crater, Section 1), there are likely to be many SuperCam and ExoMars observations in which amorphous phases dominate the Raman signal rather than being 426 obscured by peaks from crystalline phases. 427

In the VNIR, hydration features at ~1.4 and ~1.9  $\mu$ m are present in all samples, but appear more asymmetric and shifted to slightly longer wavelengths in the amorphous ferric sulfate sample (**Figure 4**). If measured in isolation, for example, with ExoMars MicrOmega (Bibring et al., 2017), it would likely be possible to distinguish allophane, ferrihydrite and amorphous ferric sulfate from one another. However if measured within a mixture, the diagnostic differences at wavelengths below ~1.5  $\mu$ m would likely be obscured by other iron-bearing phases. Thus, Raman spectroscopy is likely to be the best way to detect and distinguish between amorphous
phases at Jezero crater and Oxia Planum, the landing sites for the Mars2020 and ExoMars rovers.

436 The power of Raman to detect adsorbed species is unique compared to remote IR spectroscopic 437 methods, and may prove to be a major benefit in understanding the measured chemistry of Martian soils. On Earth, adsorption on mineral surfaces may have played a major role in 438 439 prebiotic reactions and chemistry (e.g. Schoonen et al., 2004; Hazen, 2006) and thus the potential to characterize mineral surfaces in Martian soils and rocks might provide a new understanding of 440 441 potential pathways for any microbial beginnings on Mars. Among potential sulfur-bearing amorphous species, we showed that Raman spectroscopy can be used to distinguish between 442 443 amorphous ferric sulfate and adsorbed sulfate on allophane, with a strong spectral signal from the adsorbed sulfate anions (Figures 2). Adsorbed phosphate on allophane is also detectable with 444 445 Raman. However, the same adsorbed species could not be detected on ferrihydrite, suggesting possible loss of these anions during the Raman acquisition (Section 4.1). More studies are 446 447 needed to better understand the Raman detectability of different inorganic and organic adsorbed species on different soil components and the potential to alter or remove the adsorbed species 448 449 during measurement.

One important issue related to Raman analysis of amorphous/nanophase materials is the potential 450 for phase transformation during the data acquisition. Specifically, some nanophase iron oxides 451 452 are notorious for transformation during Raman (532nm) acquisitions, even under low laser power (e.g. Hanesch, 2009). For example, goethite and ferrihydrite have been observed to 453 454 convert to hematite, and magnetite to maghemite (Li et al., 2012; Sklute et al., 2018); we 455 observed this in our own Raman spectra of ferrihydrite. With a continuous wave Raman system, 456 this problem can be overcome using hundreds of short-duration (<1 s) accumulations at low power (<1 mW) (e.g. Sklute et al., 2018). We speculate that the pulsed-laser, time-resolved 457 458 Raman system of SuperCam might permit avoidance of this issue. Though Fau et al. (2019) did 459 investigate the potential for mineral transformation or structural damage with SuperCam and observed little evidence for transformations, they did not include nanophase ferric oxides other 460 than hematite, or other amorphous phases, in their study. More work is needed to assess the 461 462 behavior of other nanophase/amorphous materials under a time-resolved Raman system to 463 understand whether these phases are likely to be detectable on Mars.

#### 464 5. Conclusions

1. The following phases were synthesized and characterized with Raman spectroscopy using three different excitation energies (325, 532, 785 nm): amorphous ferric sulfate, allophane with and without adsorbed sulfate and phosphate anions, ferrihydrite with and without adsorbed phosphate anions. With the exception of amorphous ferric sulfate, all of these phases were also characterized with VNIR reflectance spectroscopy.

470 2. Adsorbed sulfate and phosphate anions were Raman-detectable on allophane but not on

471 ferrihydrite. The lack of detection of adsorbed species on ferrihydrite is not fully understood, but

one plausible explanation is that the species were decomposed under laser illumination during

473 the Raman acquisition (**Section 4.1**).

As previously shown by Rampe et al. (2016) for these phases, adsorbed species were notdetectable in the VNIR.

476 3. Raman spectroscopy can be used to distinguish between two candidate sulfur-bearing

amorphous phases: amorphous ferric sulfate and allophane with adsorbed sulfate anions.

478 4. Using the 532 nm excitation, ferrihydrite was converted to hematite during Raman acquisition.

479 We were unable to acquire a ferrihydrite signal using lower laser power and longer integrations.

480 Phase transformations are a potential concern for remote Raman measurements, however, the

481 pulsed-laser style of Raman acquisition that will be used by Mars2020 SuperCam may reduce

this effect. More work is needed to understand the resistance to phase transformations of

amorphous and nano-crystalline materials under a pulsed-laser Raman system.

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## 489 Data Availability Statement

- 490 All Raman, VNIR and XRD data produced in this work will be made publicly available in
- 491 Gregerson et al., (2020) [a Zenodo repository at 10.5281/zenodo.4289411].

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