RECOGNIZING SULFATE AND PHOSPHATE COMPLEXES ADSORBED ONTO NANOPHASE WEATHERING PRODUCTS ON MARS.

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Introduction: Nanophase weathering products (i.e., secondary phases that lack long-range atomic order) have been recognized on the martian surface via orbital observations and *in-situ* measurements from landed missions. Allophane, a poorly crystalline, hydrated aluminosilicate, has been identified at the regional scale in models of thermal-infrared (TIR) data from the Thermal Emission Spectrometer (TES) [1] and at the local scale from visible/near-IR (VNIR) data from the Compact Reconnaissance Impact Spectrometer for Mars (CRISM) instrument [2] and phase calculations of Alpha Particle X-ray Spectrometer (APXS) data of rocks encountered by the Mars Exploration Rovers (MER) *Spirit* and *Opportunity* [3,4]. Nanophase iron oxides (npOx) have been recognized in rocks and soils measured by the Mössbauer Spectrometer on *Spirit* and *Opportunity* [5,6]. Furthermore, analyses of X-ray diffraction data measured by the CheMin instrument onboard the Mars Science Laboratory rover *Curiosity* indicate rock and soil samples are comprised of ~20-50 wt.% X-ray amorphous materials [7-9].

Chemical measurements by landed missions indicate the presence of sulfur and phosphorus in martian rocks in soils, and APXS data from Gusev crater demonstrate abundances of up to ~5 wt.% P_2O_5 and ~30 wt.% SO_3 [4]. However, the speciation of phosphorus and sulfur is not always evident. On Earth, phosphate and sulfate anions can be chemisorbed onto the surfaces of nanophase weathering products. This process may also occur on Mars, and calculations of the composition of the amorphous component at Gale crater using CheMin mineral models and APXS data show that amorphous material is enriched in volatiles, including S [7-10]. Here, we examine the ability to detect chemisorbed sulfate and phosphate complexes by analyzing sulfate- and phosphate-adsorbed nanophase weathering products using instruments similar to those on landed and orbital missions.

Methods: We synthesized two nanophase weathering products that are common in terrestrial volcanic soils and have been identified on the martian surface: allophane and ferrihydrite (a npOx). We adsorbed sulfate and phosphate anions separately onto the mineraloid surfaces using techniques outlined by [11-13]. We analyzed the untreated and ion-adsorbed materials using instruments similar to those on landed and orbital Mars missions, including X-ray diffraction, evolved gas analysis (EGA), Mössbauer spectroscopy, and TIR emission and VNIR reflectance spectroscopy to determine whether adsorbed sulfate and phosphate complexes are detectable in martian datasets. VNIR spectra were measured under lab air and at room temperature and also in a glove box purged with dry N_2 gas at room temperature, 110 °C, and 220 °C to measure spectral signatures under desiccating conditions as might be encountered on Mars.

Results: X-ray diffraction patterns of untreated synthetic allophane and ferrihydrite demonstrate that these materials lack long-range crystallographic order because their patterns display a few broad peaks with low intensities (data not shown). The patterns of the synthetic materials are similar to those of natural allophane and ferrihydrite [14,15]. The adsorption of sulfate and phosphate anions onto allophane or ferrihydrite does not affect the position of the XRD peaks and generally does not affect peak intensities.

Evolved gas analyses of untreated and ion-adsorbed nanophase weathering products show the most intense releases from mass/charge (m/z) 18 (i.e., H_2O) and show minor releases from adsorbed complexes (Fig. 1). The releases of H_2O from allophane at ~120 and ~275 °C are from the removal of adsorbed and structural H_2O, respectively. The release of H_2O from ferrihydrite at ~50-350 °C is from the loss of adsorbed and structural H_2O as the ferrihydrite transforms to hematite [14]. EGA of m/z 48 (i.e., SO) from sulfate-adsorbed ferrihydrite and allophane display relatively high-temperature releases (>400 °C and >900 °C, respectively); however, analyses of phosphate-adsorbed ferrihydrite and allophane do not show definitive evidence of the presence of phosphate because phosphate decomposition temperatures exceed our maximum measurement temperatures.

Results from Mössbauer spectroscopy show that the untreated ferrihydrite spectrum is similar to the phosphate- and sulfate-adsorbed spectra (data not shown). Mössbauer spectroscopy was not performed on the allophane samples because allophane does not contain Mössbauer active elements (e.g., Fe).

Near-IR spectra of untreated and ion-adsorbed nanophase weathering products show broad spectral bands from overtones and combinations of the fundamental vibrations of OH and H_2O, from (Si,Al)OH bending vibrations in the case of allophane, and from Fe_2OH bending vibrations in the case of ferrihydrite.

Ion-adsorbed allophane and ferrihydrite spectra are similar to those of the untreated phases (data not shown).

TIR spectra of allophane samples have broad bands from Si-O stretching and bending vibrations and from Al-O-Si and Al-OH deformation vibrations (Fig. 2A). Sulfate- and phosphate-adsorbed allophane spectra have shoulders at ~1050-1200 cm^{-1} from S-O and P-O stretching vibrations, respectively. TIR spectra of ferrihydrite samples have broad bands from Fe-O stretching and bending vibrations, and spectra of ion-adsorbed ferrihydrite have Christiansen features at higher wavenumbers than the untreated ferrihydrite (Fig. 2B). The position of the Christiansen feature of the sulfate-adsorbed ferrihydrite is similar to those of Fe-sulfate minerals reported by [16].

Discussion: Our analyses of sulfate and phosphate adsorbed onto allophane and ferrihydrite with laboratory instruments that correspond to those on martian orbiter and landed missions indicate a range in detectability of chemisorbed ionic species on nanophase weathering products on the martian surface. EGA measurements, which were implemented as a part of the Phoenix lander mission and the MSL SAM instrument package on the *Curiosity* rover, easily distinguish allophane and ferrihydrite from their forms chemisorbed with sulfate because the method directly detects evolved S-bearing species. Manifestations of chemisorbed sulfate and phosphate anions are also observed in TIR spectra. XRD powder patterns and VNIR and Mössbauer spectra show no apparent evidence for chemisorption at the concentration levels of our experiments.

References: [1] Rampe E. B. et al. (2012) *Geology*, *40*, 995-998. [2] Bishop J. L. and Rampe E. B. (2014) *LPS XLV*, #2068. [3] Clark B. (2005) *Earth Planet. Sci. Lett.*, 240, 73-94. [4] Ming D. W. et al. (2006) *JGR*, 111. [5] Morris R. V. et al. (2006a) *JGR*, 111. [6] Morris R. V. et al. (2006b) *JGR*, 111. [7] Bish D. L. et al. (2013) *Science*, 341. [8] Blake D. F. (2013) *Science*, 341. [9] Vaniman D. T. et al. (2014) 343. [10] Morris R. V. et al., this meeting. [11] Cichota R. et al. (2007) *Soil Sci. Soc. Am. J.*, 71, 703-710. [12] Jara A. A. et al. (2006) *Soil Sci. Soc. Am. J.*, 70, 337-346. [13] Willet I. R. et al. (1988) *J. Soil Sci.*, *39*, 275-282. [14] Schwertmann U. and Cornell R. M. (2000) Wiley-VCH. [15] Wada K. (1989) *SSSA Book Series*, no. 1. [16] Lane M. D. et al. (2015) *Am. Mineral.*, 100, 66-82.

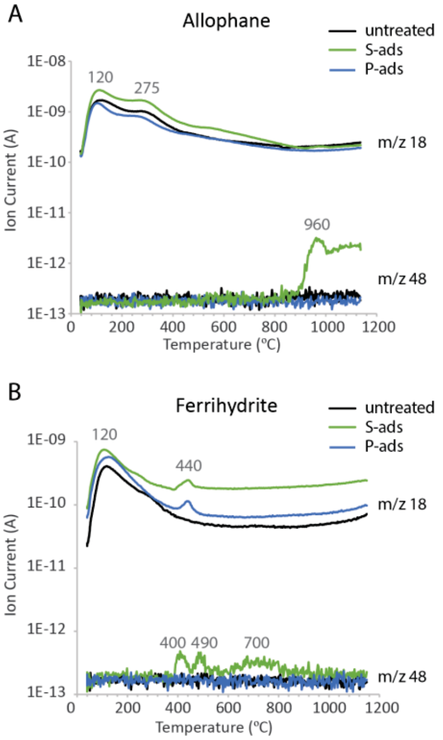

Figure 1. EGA data for untreated and ion-adsorbed A) allophane and B) ferrihydrite.

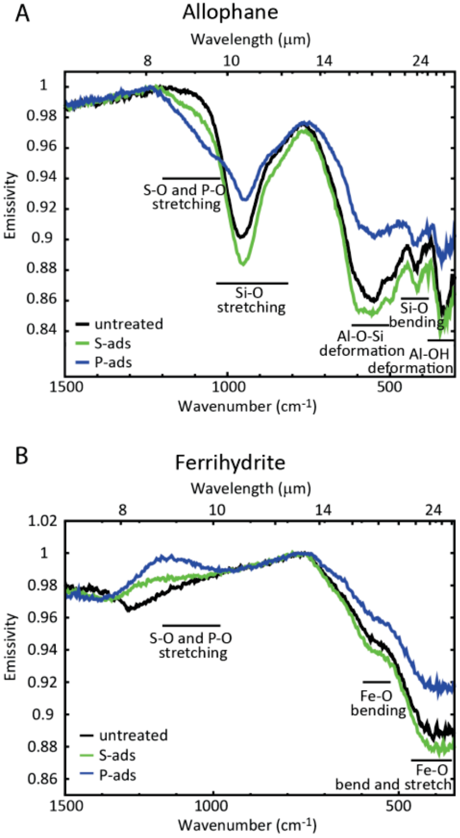

Figure 2. TIR emission spectra of untreated and ion-adsorbed A) allophane and B) ferrihydrite.