

CHARACTERIZING NANOPHASE MATERIALS ON MARS: SPECTROSCOPIC STUDIES OF ALLOPHANE AND IMOGOLITE. T.J. Jeute¹, L.L. Baker¹, Z. Abidin², J.L. Bishop³, and E.B. Rampe⁴, ¹Department of Geological Sciences, University of Idaho (Moscow, ID), ²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Bogor Agricultural University, Indonesia, ³SETI Institute & NASA Ames (Mountain View, CA), ⁴Jacobs-JETS at NASA-JSC (Houston, TX).

Introduction: The presence of allophane and other nanophase materials on Mars indicates a time when water was intermittent and short lived [1,2]. These materials likely represent partially altered or leached basaltic ash [3] and therefore, could represent a geologic marker for where water was present on the Martian surface. Further, they may indicate regions of climate change, where surface water was not present long enough to form clays [1]. Characterization of these materials is important for increasing spectral recognition capacities of our current Martian science array. Ongoing work suggests that variability in the Al:Si ratio of allophane can dictate the amount of both structural and adsorbed water in the crystalline structure.

Geologic Context: Allophane is an amorphous or poorly crystalline hydrous aluminosilicate material [3,4,5]. On Earth, allophane is typically associated with volcanic ash or fine-grained pumice-bearing soils and forms under neutral to mildly acidic pH regimes (5-7) [e.g. 3,4,5]. Allophane has been identified in clay-bearing regions on Mars using thermal emission spectroscopy (TES) [2]. Additionally, MSL Curiosity instruments have identified an X-ray-amorphous phase in soils that may contain allophane [6]. This evidence suggests allophane may be a common component of altered regions of Mars [2].

Methods: We created a suite of nanophase materials of varying compositions. These synthetic samples were then spectrally characterized using Fourier transformed IR (FTIR) spectroscopy, visible/near-infrared (VNIR) reflectance spectroscopy, thermal infrared emission spectroscopy (TIR), magic angle spin nuclear magnetic resonance (MAS NMR), and Fe K-edge X-ray absorption spectroscopy (XAS). Verification of compositions was carried out by supernatant analysis on an inductively-coupled plasma atomic emission spectrometer (ICP-AES), and by precipitant analysis using X-ray diffraction. Compositions of the nanophase materials range from high-Si allophane (molar Al:Si = 1:2) to protoimogolite (molar Al:Si = 2:1), while spanning a range of Fe³⁺ isomorphically substituted for Al from 0-10 mol%. These compositions span the range observed in natural terrestrial allophanes [4].

Synthesis Procedures. Synthetic allophane samples were created using an established method that has been modified to produce allophane with Fe isomorphically

substituted for Al in octahedral coordination [7,8]. Synthetic imogolite samples were created by Z. Abidin using a previously established method [9].

FT-IR. IR characterization was performed on a Perkin-Elmer Spectrum System 2000 FT-IR spectrometer. Samples were diluted to ~3 wt.% sample with optical KBr and measured as loose powder using a Perkin-Elmer diffuse reflectance accessory.

Emission spectroscopy. Thermal Infrared (TIR) emissivity spectra was collected from 5-50 μm at the Mars Space Flight Facility at Arizona State University as in past studies [2,10]. Samples were pressed into pellets and heated to 80 °C to increase the signal-to-noise ratio.

Reflectance spectroscopy. Reflectance spectra of undiluted, particulate samples were measured at the SETI Institute from 0.35 to 2.5 μm using an ASD spectrometer and are under measurement at RELAB, Brown University as in past studies [10]. FTIR spectra are measured from 1-50 μm relative to a rough gold surface and are scaled near 1.2 μm to bidirectional spectra measured from 0.3 to 2.5 μm relative to halon.

Nuclear Magnetic Resonance. ²⁷Al and ²⁹Si MAS NMR were collected at the University of Idaho Townsend NMR Suite. Spectra were collected at 12.6 kHz and processed using Bruker TopSpin analytical software.

X-Ray Absorption Spectroscopy. Fe K-edge X-ray absorption spectroscopic signatures of the allophane and imogolite samples were acquired at Stanford Synchrotron Radiation Laboratory (SSRL). Full EXAFS scans of the Fe K-edge range (6880-7874 eV) were collected at 10 K. The spectra were then processed using Demeter-Athena and fit using Demeter-Artemis.

Discussion: Differences in these spectra have been analyzed to show that changes in the chemical structure of allophane can be dictated by Al:Si ratio. VNIR reflectance spectra and FTIR transmittance spectra of Fe-bearing allophanes and imogolites indicate small changes in the OH features (Fig. 1), consistent with Fe in the structure. Allophane bands occur at 1.38, 1.40, 1.92 and 2.19 μm (Fig. 1a). Imogolite bands are similar, occurring at 1.39, 1.92 and 2.20 μm (Fig. 1b). Shifts towards longer wavelengths were observed with the addition of Fe for OH bands near 1.4 and 2.2 μm in both samples (Fig 1c). The OH band at 2.2 μm changes with the addition of Fe in the imogolite samples such that a shoulder forms at longer wavelengths (~2.22-2.23 μm)

and the reflectance maximum does not return as high following this band.

XAFS spectra indicate changes in octahedral sheet disorder due to the oxidation state of Fe (Fig. 2). XAFS spectra also indicate changes in local atomic structure when changes in Al:Si occur. ²⁷Al MAS NMR data show an increase in Si correlating with more tetrahedral Al as well as a correlation with increasing Fe resulting in increased tetrahedral Al.

Future Work: Loss on ignition (LOI) experiments are being conducted to confirm changes in water concentrations across varying sample compositions. Transmission electron microscopy will also be performed to look for varying degrees of crystallinity in the sample suite.

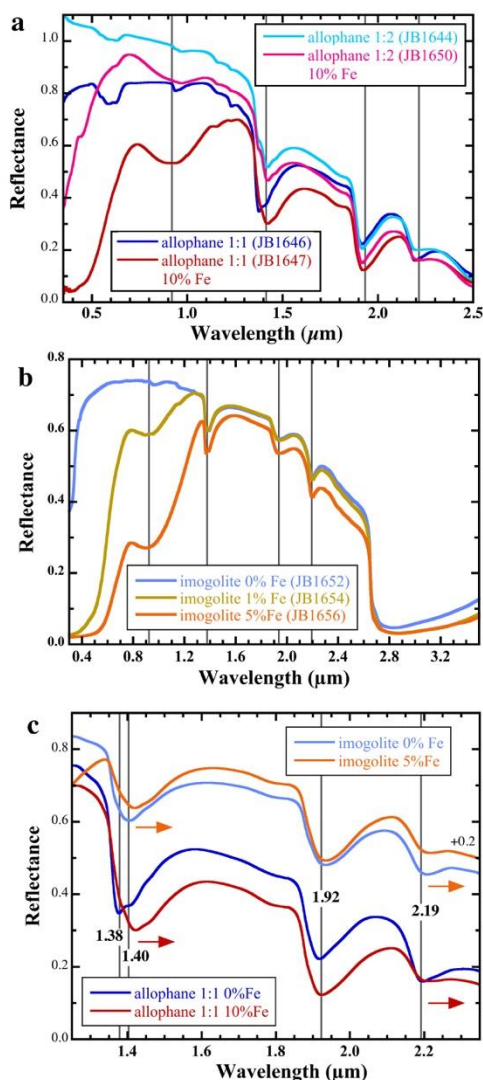


Figure 1. VNIR reflectance spectra of several allophane and imogolite samples showing the effects of Fe on the spectra. a) synthetic allophanes, b) synthetic imogolites, and c) close-up view of low and high Fe allophanes and imogolites. Grey lines mark spectral features of interest.

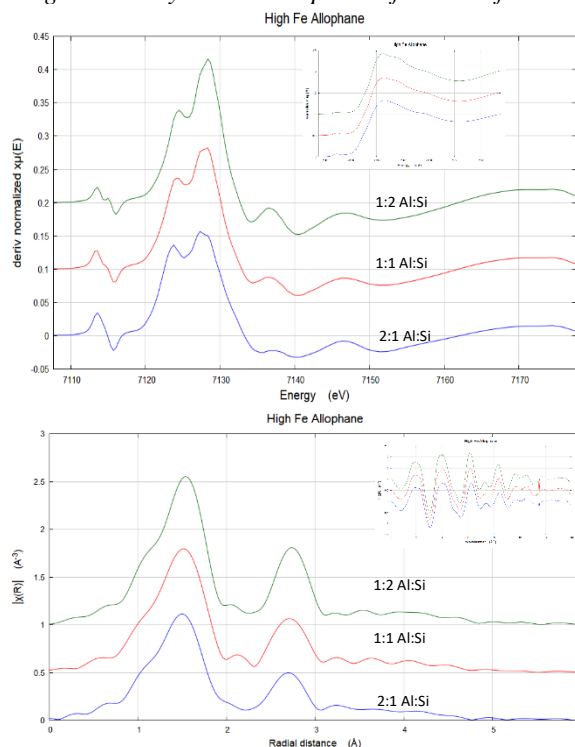


Figure 2. Fe K-edge X-ray absorption near edge structure for 10% Fe(III) allophane samples of 1:2, 1:1, and 2:1 Al:Si. Differences in the pre-edge region can be attributed to disorder introduced by increased Si content as well as changes in the edge shape. Fourier transformed Fe K-edge extended X-ray absorption fine structural spectra plotted in terms of R-space (radial distance from absorbing atom). Slight differences in magnitude and shape of the first and second shell structures indicate slight changes in bond distances, indicating a change in the local atomic structure.

References: [1] Bishop J.L. and Rampe E.B. (2016) *EPSL*, 448, 42-48. [2] Rampe E.B. et. al. (2012) *Geology* 40, 995. [3] Wada K. (1967) *Am. Miner.* 52, 690. [4] Farmer V.C. et. al. (1979) *Geochimica et Cosmochimica Acta* 43, 1417-1420. [5] Parfitt (2009) *ClayMin.*, 44, 135-155. [6] Bish D.L. et. al. (2013) *Science* 341. [7] Baker L.L. and Strawn D.G. (2012) *Physics and Chemistry of Minerals* 39, 675-684. [8] Baker L.L. et. al. (2014) *Clays and Clay Minerals* 62, 675-684. [9] Abidin Z. et. al. (2009) *Interdisciplinary studies on Environmental Chemistry-Environmental Research in Asia*, 331-341. [10] Bishop J. L. et al. (2013) *CCM*, 61, 57-74.

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