THERMAL INFRARED EMISSION SPECTROSCOPY OF SYNTHETIC ALLOPHANE AND ITS POTENTIAL FORMATION ON MARS.

E. B. Rampe[1], M. D. Kraft[1], T. G. Sharp[1], D. C. Golden[2], and D. W. Ming[2], [1]Arizona State University, School of Earth and Space Exploration (P.O. Box 871404, Tempe, AZ 85287, Liz.Rampe@asu.edu) for first author, [2]NASA-Johnson Space Center, Houston, TX.

Introduction: Allophane is a poorly-crystalline, hydrous aluminosilicate with variable Si/Al ratios ~0.5-1 and a metastable precursor of clay minerals. On Earth, it forms rapidly by aqueous alteration of volcanic glass under neutral to slightly acidic conditions [1]. Based on *in situ* chemical measurements and the identification of alteration phases [2-4], the Martian surface is interpreted to have been chemically weathered on local to regional scales. Chemical models of altered surfaces detected by the Mars Exploration Rover Spirit in Gusev crater suggest the presence of an allophane-like alteration product [3]. Thermal infrared (TIR) spectroscopy and spectral deconvolution models are primary tools for determining the mineralogy of the Martian surface [5]. Spectral models of data from the Thermal Emission Spectrometer (TES) indicate a global compositional dichotomy, where high latitudes tend to be enriched in a high-silica material [6,7], interpreted as high-silica, "K-rich" volcanic glass [6,8]. However, later interpretations proposed that the high-silica material may be an alteration product (such as amorphous silica, clay minerals, or allophane) and that high latitude surfaces are chemically weathered [9-11]. A TIR spectral library of pure minerals is available for the public [12], but it does not contain allophane spectra. The identification of allophane on the Martian surface would indicate high water activity at the time of its formation and would help constrain the aqueous alteration environment [13,14]. The addition of allophane to the spectral library is necessary to address the global compositional dichotomy. In this study, we characterize a synthetic allophane by IR spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM) to create an IR emission spectrum of pure allophane for the Mars science community to use in Martian spectral models.

Methods: Allophane with an approximate Si/Al ratio of 1 was synthesized at Johnson Space Center using a modification of *Ohashi et al.* (2002) [15] procedure. We mixed 0.1 M Na-orthosilicate and aluminum chloride solutions, stirred them rapidly at room temperature for one hour, placed them in a 95° C oven for 90 hours. Clear supernatant was decanted and each sample was washed twice with deionized water by repeated dispersion and centrifugation (3000 RPM for 10 minutes) to remove NaCl byproduct. The gelatinous solids were freeze dried to obtain the final product.

Compressed-pellet samples were prepared for mid-IR emission spectroscopy. We prepared pellets similarly to the clay minerals that are in the spectral library [16]. Emission spectra were collected at the Mars Space Flight Facility at Arizona State University using a Nicolet Nexus 670 spectrometer configured to measure emitted energy [17,18]. Spectra were scanned 270 times over the course of ~5 minutes, from 200-2000 cm^{-1} with 2 cm^{-1} spectral resolution.

XRD patterns of random powder mounts were measured using a PANalytical X-Pert Pro with a CuKa radiation source at the LeRoy Eyring Center for Solid State Sciences at Arizona State University (LE-CSSS).

Transmission IR spectra were measured at the LE-CSSS. Allophane powders (0.005 g of sample) were compressed into KBr (0.150 g of KBr) pellets using the same pressing methods as above and measured using a Bruker IFS 66 spectrometer. Spectra were measured over the wavelength range 6000-400 cm^{-1} with 2 cm^{-1} spectral resolution.

Bright field TEM images and diffraction patterns were collected with a Philips CM200-FEG high-resolution TEM/STEM and a 200 kV accelerating voltage in the John M. Cowley Center for High-Resolution Electron Microscopy at Arizona State University.

Results: TEM images, X-ray and electron diffraction patterns, and transmission IR spectroscopy of the material synthesized are all consistent with allophane. A TIR emission spectrum of the compressed allophane was prepared for the TIR spectral library.

XRD. XRD patterns show three broad peaks at 24, 41, and 66 degrees 2?, which is consistent with patterns measured by *Ohashi et al.* (2002).

TEM. Bright field TEM images display characteristic allophane morphology with aggregates of nearly spherical particulates ~3.5-5 nm in diameter (Figure 1a). High-resolution images show no signs of clay-like structures. Electron diffraction patterns have a diffuse ring at ~0.35 nm (Figure 1b), which is consistent with previous studies [1] and indicates the material is amorphous or has short-range order.

Transmission IR spectroscopy. The transmission spectrum is consistent with an allophane structure (Figure 2) [15,19]. Broad absorptions ~3700-3000 cm^{-1} from O-H stretching vibrations in hydroxyl groups and adsorbed H_2O [1,20] and sharp, weak absorptions at ~1600 cm^{-1} from H-O-H deformation vibrations of adsorbed H_2O [1] indicate the material is hydrated. The strong absorption ~1050 cm^{-1} from Si-O-Si stretching vibrations and the shoulder at ~880 cm^{-1} from Al^{IV}-O stretching vibrations show the tetrahedral sites in allophane are Si-rich. The sharp, weak bands at ~700 and 565 cm^{-1} are from vibrations within alumina octahedral sheets, and the sharp, strong band at ~455 cm^{-1} is from Si-O and Al^{IV}-O bending vibrations [21].

TIR emission spectroscopy. The TIR spectrum of allophane has broad absorptions at 1200-1000 cm^{-1} and 550-400 cm^{-1} from Si-O stretching and M-O-Si (M = Si or Al) deformation vibrations, respectively (Figure 3) [1,22-24]. The Si-O stretching minimum at ~1050 cm^{-1} indicates the allophane is Si-rich with a Si/Al ratio ~1.

Discussion: Transmission IR spectroscopy, TEM images, and electron diffraction patterns indicate that our sample is Si-rich allophane, making the TIR emission spectrum an appropriate addition to the public spectral library.

Allophane on Mars. The TIR spectrum of synthetic allophane is similar to that of other Si-rich phases, including clay minerals, opaline silica, and especially K-rich volcanic glass (Figure 3). This suggests that high concentrations of K-rich glass in spectral models of high-latitude surfaces on Mars may represent allophane produced by chemical weathering. Further spectral modeling of Martian TIR data with allophane in the spectral library is necessary to resolve this compositional dichotomy issue.

References: [1] Wada K. (1989) *Soil Sci Soc. Am., no. 1,* 1051–1087. [2] Bibring J.-P. et al. (2005) *Science, 307,* 1576-1581. [3] Ming D. W. et al. (2006) *JGR,111,* E02S12. [4] Milliken, R. E. et al. (2008) *Geology, 36,* 847-850. [5] Ramsey M. S. and Christensen P. R. (1998) *JGR, 103,* 577-592. [6] Bandfield J. L. et al. (2000) *Science, 287,* 1626-1630. [7] Rogers A. D. and Christensen P. R. (2007) *JGR, 112,* E01003. [8] Bandfield J. L. (2002) *JGR, 107,* 5042. [9] Wyatt M. B. and McSween H. Y. (2002) *Nature, 417,* 263-266. [10] Kraft M. D. et al. (2003) *GRL,* 30, DOI10.1029/ 2003GL018848. [11] Michalski, J. R. et al. (2006) *EPSL, 248,* 822-829. [12] Christensen P. R. et al. (2000) *JGR, 105,* 9735-9739. [13] Parfitt R. L. and Kimble J. M. (1989) *Soil Sci. Am., 53,* 971-977. [14] Parfitt R. L. (1990) *Aus. J. Soil Res., 28,* 343-360. [15] Ohashi F. et al. (2002), *Clay Mins., 37,* 451-456. [16] Michalski J. R. et al. (2005) *Icarus, 174,* 161-177. [17] Christensen P. R. and Harrison S. T. (1993) *JGR, 98,* B11. [18] Ruff S. W. et al. (1997) *JGR, 102,* 14,899-14,913. [19] Childs C. W. et al. (1990) *Clay Mins., 25,* 329-341. [20] van der Marel H. W. and Beutelspacher H. (1976) *Elsevier,* pp. 396. [21] Farmer, V. C. et al. (1979) GCA, 43, 1417-1420. [22] Farmer V. C. (1968) *Clay Mins., 7,* 373-387. [23] Parfitt R. L. and Henmi T. (1980) *CCM, 28,* 285-294. [24] Parfitt R. L. et al. (1980) *CCM, 28,* 328-334.

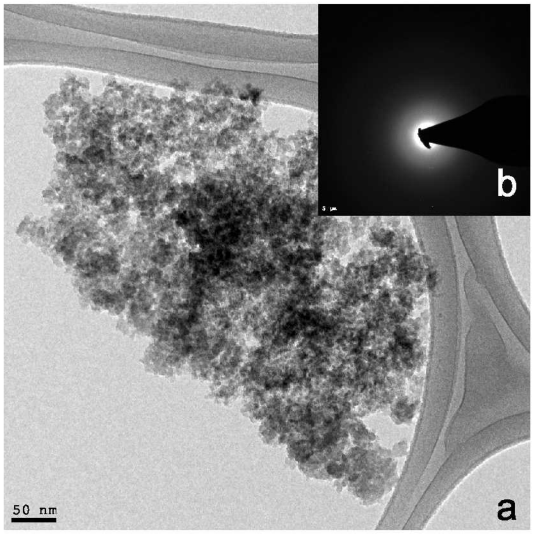

Figure 1. a)TEM bright field image of synthetic allophane, and b) electron diffraction pattern.

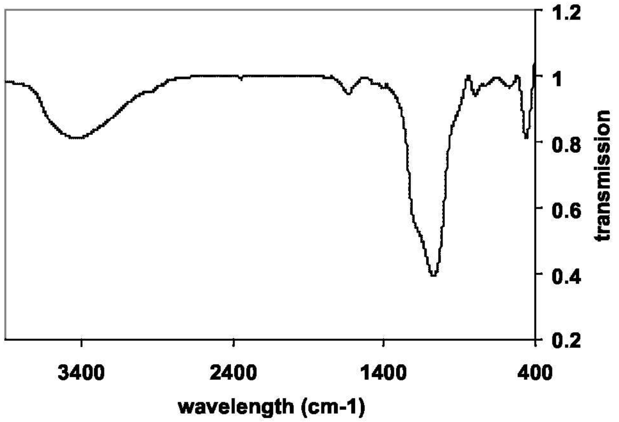

Figure 2. Transmission IR spectrum of synthetic allophane.

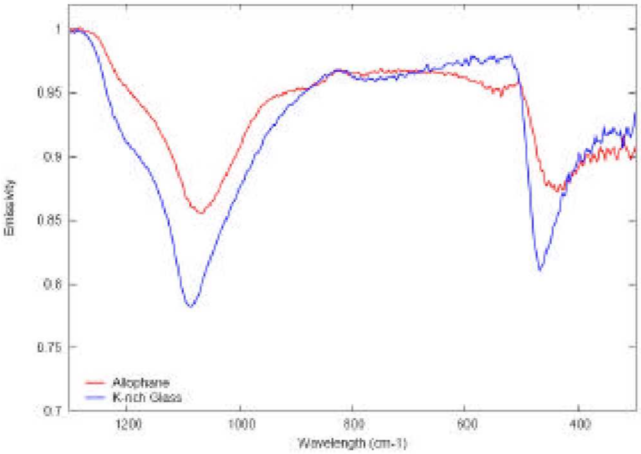

Figure 3. Emission TIR spectrum of allophane (red) and K-rich volcanic glass (blue).