DETECTION OF ALLOPHANE ON MARS THROUGH ORBITAL AND IN-SITU THERMAL-INFRARED SPECTROSCOPY. E. B. Rampe[1], M. D. Kraft[1], T. G. Sharp[1], D. C. Golden[2], D. W. Ming[3], P. R. Christensen[1], and S. W. Ruff[1], [1]School of Earth and Space Exploration, Arizona State University, Box 871404, Tempe, AZ 85287, Liz.Rampe@asu.edu; [2]ESCG-JE23, Houston, TX; [3]NASA-Johnson Space Center, Houston, TX.

Introduction: We have collected laboratory thermal IR spectra of the mineraloid allophane and aluminosilicate gels. Using those spectra to model regional TES spectra, we suggest that several areas of Mars contain significant amounts of allophane-like weathering products. The presence of allophane on Mars indicates that 1) significant Al sources, such as feldspar or glass, were weathered; 2) weathering on Mars produced poorly-crystalline aluminosilicates, rather than easily identifiable crystalline minerals; and 3) some Martian weathering proceeded under moderate pH environments, suggesting acid weathering is not the only major alteration mechanism on Mars.

Background: Allophane is a poorly-crystalline, hydrous aluminosilicate that forms by low-T aqueous alteration of feldspar and volcanic glass at near-neutral pH [1]. It is a clay mineraloid with variable composition (Si/Al ratios range from ~0.5-1) [1]. Aluminosilicates with greater Si/Al ratios can also precipitate, and, here, we refer to those products as “aluminosilicate gels.”

Allophane has been inferred for Mars from chemical models and thermal-infrared (TIR) spectroscopy [2-6]. It may be a significant constituent of light-toned soils in Meridiani and chemically weathered rock surfaces in Gusev crater, based on phase models of APXS data [2,3]. Allophane or other poorly-crystalline aluminosilicates may comprise the high-silica phases modeled in global Thermal Emission Spectrometer (TES) data; however, the lack of allophane in spectral libraries has impeded its detection in TES models. Consequently, high-silica materials have been modeled as phases with similar compositions and structures, including volcanic glass, phyllosilicates, zeolites, and amorphous silica [7-11], which have different geological implications than allophane. TIR spectra of allophanes were not previously available because natural allophanes are difficult to isolate. Thus, we synthesized allophanes and other aluminosilicate gels to acquire their TIR emission spectra and test for the presence of allophane on Mars by modeling TES and Mini-TES spectra.

Methods: Allophanes and gels were synthesized according to [12,13]. Compositions and structures were analyzed by atomic absorption spectroscopy, X-ray diffraction, transmission electron microscopy, and transmission FTIR spectroscopy. TIR emission spectra of compressed pellets were measured at the Mars Space Flight Facility at Arizona State University. Four distinct allophane and gel spectra were added to a spectral library commonly used to model TES spectra [14], and this library was used to model nine regional TES spectra identified by [15] using the same rigorous routine outlined by *Rogers and Christensen* (2007) [14]. The four allophane and gel spectra were added to spectral libraries used to model Mini-TES spectra of fresh and altered rocks from Gusev (Adirondack, Clovis, Wishstone, and Watchtower) [16].

Results: Laboratory analyses of our synthetic products are consistent with natural and synthetic allophanes and aluminosilicate gels [1]. Significant abundances of allophanes and gel were modeled in TES spectra from three regions of Mars. Mini-TES spectral models suggest some altered rocks in Gusev crater may contain allophane or another aluminosilicate weathering product.

TES Models. Significant abundances (>10 vol.%) of allophane and aluminosilicate gel were modeled in regional spectra of Northern Acidalia, Solis Planum, and Meridiani Planum, and the composition of the modeled allophanes and gel differ between each region. Models with allophane/gel have better RMS errors than models without. Allophane/gel components replace specific secondary silicates in models of each region. High-silica gel replaces phyllosilicates in models of Northern Acidalia; high-silica gel and Al-rich allophane replace phyllosilicates and volcanic glass in Solis; and high-silica allophane replaces aluminous opal in Meridiani. This confirms that some high-silica phases previously identified from TES spectral models, particularly phyllosilicates and amorphous silica, could be allophane [4-6].

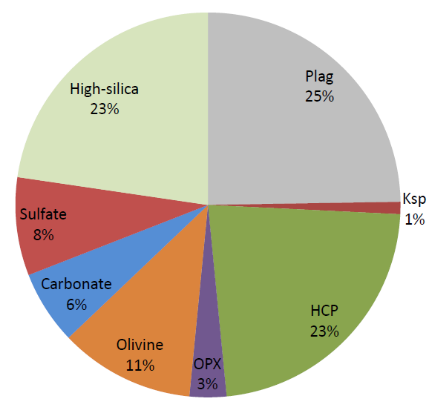
The identification of allophane in TES spectral models affects the modeled pyroxene mineralogy in Solis and Meridiani but does not affect the overall interpretation of major mineral groups. Models without allophane identify primarily orthopyroxene and high-calcium pyroxene in Solis and Meridiani, respectively [14]. The addition of allophane to the library results in the identification of pigeonite in models of both regions (Figure 1). Pigeonite has been identified in Meridiani from OMEGA visible/near-IR data and Mini-TES spectral models of the basaltic sand component [17,18]. We suggest that the addition of more accurate secondary phases to spectral libraries can improve modeled igneous mineralogy, therefore improving interpretations of aqueous alteration and petrologic histories.

Mini-TES Models. High-silica gel is identified in models of Clovis and high-silica gel and Al-rich allophane are identified in models of Wishstone; however, the addition of allophane does not improve RMS errors and the identification of allophane and gel are affected by small variations in the modeled wavelength range. Additionally, allophane and gel primarily replace plagioclase feldspar and minor amounts of high-silica phases in the models, including volcanic glass and zeolite. The iron mineralogy of Watchtower suggests that this sample is the most altered, and phase models of APXS data indicate it should have the most allophane [3], but our models of Watchtower do not identify allophane or gel. The replacement of igneous minerals by allophane, the dependence on modeled wavelength range, the lack of improvement of model fit, and the absence of allophane in models of Watchtower indicate 1) allophane may not be present in these rocks and the libraries may still lack the poorly-crystalline aluminosilicate phase(s) present in these samples, such as imogolite or hisingerite; or 2) allophane is present but weathering creates mineralogical and textural complexities that cause non-linear spectral mixing [5] so that allophane cannot be detected.

Implications for Aqueous Alteration on Mars: In-situ chemical data from APXS shows global variation in Fe and Mg abundances, which have been used as evidence for recent global acidic alteration at low water-to-rock ratios and the preferential dissolution of olivine [19]. Conversely, the identification of allophane and gel in TES spectral models of Northern Acidalia, Solis, and Meridiani suggest recent *near-neutral* aqueous alteration at low-T and low water-to-rock ratios. Furthermore, the presence of a secondary aluminosilicate requires the dissolution of an aluminum-rich phase, such as volcanic glass and/or plagioclase. Global acidic chemical weathering and the dissolution of olivine cannot account for the precipitation of allophane. We must reevaluate our ideas of global weathering mechanisms on Mars to explain the presence of allophanes and gels. We propose that distinct *regional* weathering mechanisms occur on Mars, resulting in the precipitation of different allophanes and gels in different Martian regions. Recent discoveries of carbonates in Gusev and at the Phoenix landing site further support regional weathering at near-neutral conditions [20,21].

References: [1] Wada K. (1989) *Soil Sci Soc. Am., no. 1*, 1051–1087. [2] Clark B. C. et al. (2005) *EPSL*, *240*, 73-94. [3] Ming D. W. et al. (2006) *JGR*, *111*, E02S12. [4] Hamilton V. E. et al. (2008) *JGR*, *113*, E12S43. [5] Kraft M. D. (2009) Ph.D. Thesis, Ariz. State Univ. [6] McDowell M. L. and Hamilton V. E. (2009) *JGR*, *114*, E06007. [7] Bandfield J. L. et al. (2000), Science, *287*, 1626-1630. [8] Wyatt M. B. and McSween H, Y. (2002) *Nature*, *417*, 263-266. [9] Kraft M. D. et al. (2003) *GRL*, 30, DOI10.1029/ 2003GL018848. [10] Ruff S. W. et al. (2004) *Icarus*, *168*, 131-143. [11] Michalski et al. (2005) *Icarus*, *174*, 161-177. [12] Ohashi F. et al. (2002), *Clay Mins.*, *37*, 451-456. [13] Wada S.-I. et al. (1979), *JSS*, *30*, 347-355. [14] Rogers A. D. and Christensen P. R. (2007) *JGR*, *112*, E01003. [15] Rogers A. D. et al. (2007) *JGR*, *112*, E02004. [16] Ruff S. W. et al. (2006) *JGR*, *111*, E12S18. [17] Glotch T. D. and Bandfield J. L. (2006) *JGR*, *111*, E12S06. [18] Poulet F. et al. (2009) *Icarus*, *195*, 106-130. [19] Hurowitz J. A. and McLennan S. M. (2007) *EPSL*, *260*, 432-443. [20] Morris R. V. et al. (2010) *Science*, *329*, 421-424. [21] Boynton, W. V. et al. (2009) *Science*, *325*, 61-64.

a



b

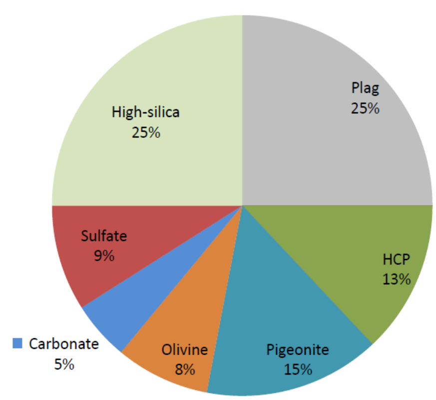


Figure 1. a) Grouped modeled mineral abundances in Meridiani from models without allophane by [13]. b) Grouped modeled mineral abundances in Meridiani from this study. Note the similarities between the two models, except for the identification of pigeonite in this study (b).