

ALLOPHANE IDENTIFIED AT MAWRTH VALLS IN CRISM AND TES DATASETS AND IMPLICATIONS FOR THE ANCIENT PHYLLOSILICATE-RICH ROCKS. J. L. Bishop¹ and E. B. Rampe², ¹SETI Institute & NASA-ARC (189 Bernardo Ave, Mountain View, jbishop@seti.org), ²NASA-JSC (Mail Code KR, Houston, TX 77058).

The Mawrth Vallis region contains thick phyllosilicate deposits [e.g. 1,2] including a variety of Al- and Si-rich phases in the uppermost units [3,4,5]. Recently, the nanophase mineral allophane was found to be a good match to TIR data of the Mawrth Vallis region [6]. Here we report identification of allophane (i) in this upper Al/Si-rich unit using CRISM data and (ii) across the Mawrth Vallis region at the ~10% level using TES data. The identification of allophane at Mawrth Vallis helps reconcile the NIR and TIR data of the region, and has important implications for understanding past pedogenic and igneous processes.

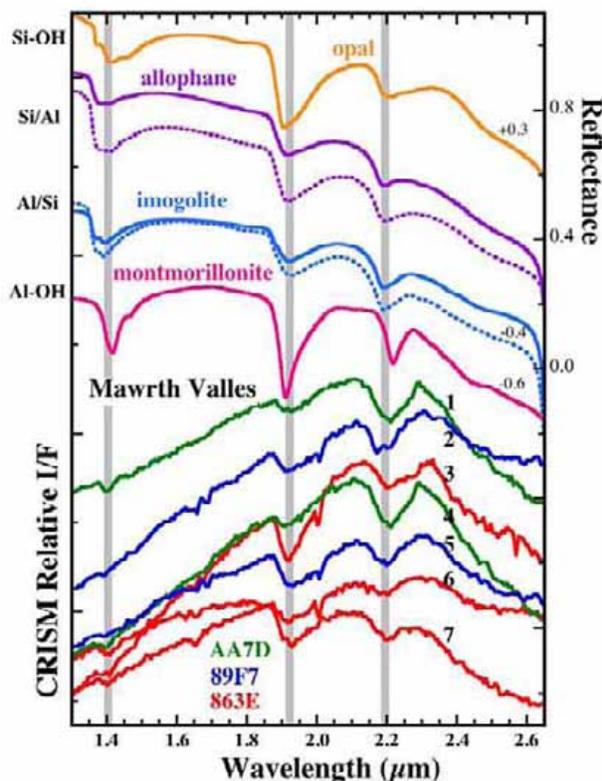


Figure 1 Selected CRISM spectra of Mawrth Vallis compared with reflectance spectra of Al/Si-phases (natural allophane and imogolite spectra in solid lines, synthetic spectra in broken lines).

Introduction: Allophane is an amorphous aluminosilicate mineral frequently found in well-drained soils derived from volcanic ash rich in feldspar and pyroxene [e.g. 7]. Continued weathering of allophane-rich soils can produce halloysite or montmorillonite [8], both of which have been observed at Mawrth Vallis [3]. The ideal mineral formula for allophane is $1-2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2-3\text{H}_2\text{O}$ with a molar Si/Al ratio be-

tween 0.5-1.0 [e.g. 8]. A related mineral imogolite has an Si/Al ratio closer to 0.5 and forms in similar environments to allophane [8]. The primarily 4-fold coordinated Al in volcanic glass alters to 4- and 6-fold coordinated Al in allophane and then transforms to primarily 6-fold coordinated Al in imogolite [9]. The spectral and hydration properties of allophane and imogolite were investigated recently [10].

NIR Spectral Properties of Allophane: Allophane spectra exhibit a doublet near 1.37 and 1.41 μm due to OH 2ν , a broad band near 1.92 μm due to H₂O $\nu + \delta$ (stretch+bend), and a band near 2.2 μm due to OH $\nu + \delta$ (Fig. 1, [10]). A strong broad H₂O band was also observed near 3 μm . Imogolite spectra are similar near 1.9, 2.2, and 3 μm , but the OH overtone occurs at 1.37 and 1.39 μm (Fig. 1). In contrast, spectra of Al-smectites and opal have an H₂O $\nu + \delta$ combination band at 1.91 μm and an OH $\nu + \delta$ combination band at 2.21 μm . The latter is extended towards longer wavelengths for opal spectra.

CRISM Spectra of Al/Si Unit at Mawrth Vallis: CRISM spectra of the upper clay unit at Mawrth Vallis exhibit small variations in 1.9 and 2.2 μm band character indicating the presence of multiple minerals/phases [3,4,5,11]. Many spectra are consistent with allophane (Figs. 1-2, [11]). This upper Al/Si-rich unit is likely a combination of hydrated silica (opal, altered glass), Al-smectite, kaolinite/halloysite, allophane/imogolite and related Al/Si phases. Many regions exhibit spectra more consistent with allophane than other species indicating that allophane may be spectrally dominant in some regions.

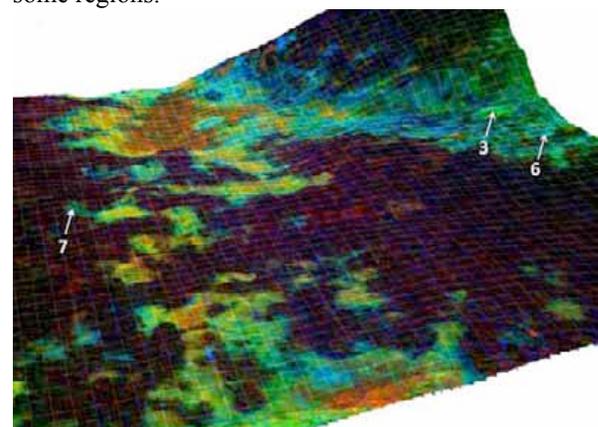


Figure 2 Sites of allophane type spectra in CRISM image FRT0000863E draped over MOLA elevations with 10X vertical exaggeration (Al/Si-OH minerals in blue/green, Fe/Mg-OH minerals in orange/yellow).

Mid-IR Spectral Properties of Allophane: Allophane reflectance and emissivity spectra exhibit an H₂O δ vibration near 6.1 μ m and several Si-O-Al vibrations in the infrared [10]. The Si(Al)-O ν vibration in emissivity spectra of allophane and imogolite (Fig. 3) occurs as a doublet with absorptions at \sim 1030 and 930 cm^{-1} (9.7 and 10.8 μ m). Additional Si(Al)-O δ vibrations are present near 530-550, 410-425, 310-325 cm^{-1} (\sim 18, 24 and 32 μ m). These features are readily distinguishable from montmorillonite and opal spectra (Fig. 3). Montmorillonite has an Si(Al)-O ν band near 1060 cm^{-1} (9.4 μ m) and Si-O-Si(Al) δ bands near 520 and 470 cm^{-1} (\sim 19 and 21 μ m). Opal has a doublet near 1250 and 1115 cm^{-1} (\sim 8 and 9 μ m) and an Si-O-Si δ band near 480 cm^{-1} (\sim 21 μ m).

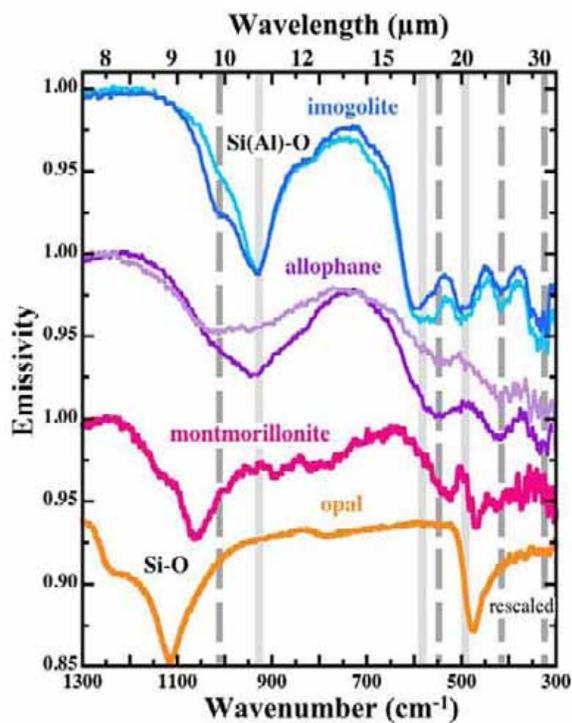


Figure 3 Thermal-infrared emissivity spectra of allophane and imogolite pellets (natural spectra in darker tones, synthetic spectra in lighter tones) plus montmorillonite (powder) and opal (pellet) for comparison.

TES Spectra of Mawrth Vallis: Models of TES data from some intermediate to high albedo areas in Mawrth Vallis identify \sim 10 vol.% allophane (Fig. 4). Modeled spectra fit well with TES data (Fig. 5), and the incorporation of allophane into the spectral library improves the fit. TES models also identify montmorillonite, Al/Si-gel, and zeolite in significant abundances ($>$ 10 vol.%) in these areas, further suggesting that there are a variety of secondary aluminosilicates in the upper units of Mawrth Vallis.

Acknowledgements: Thanks are due to the MRO/CRISM and MGS/TES teams for acquiring the data.

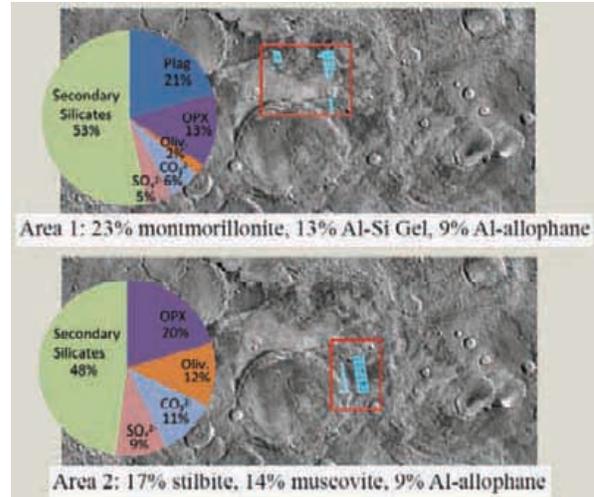


Figure 4 Modeling of TES data at Mawrth Vallis reveals that about half the material is secondary aluminosilicates. TES footprints (blue) indicate where allophane was identified through modeling in two regions.

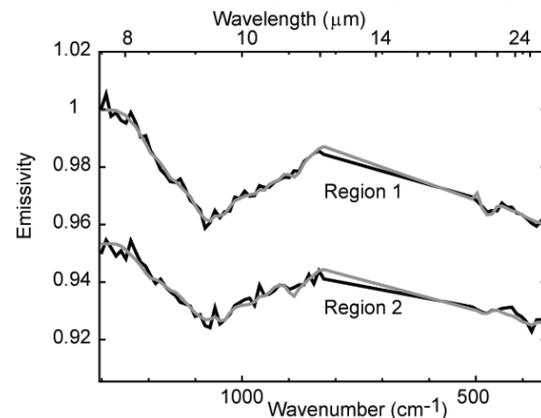


Figure 5 TES data (black) and modeled data (gray) for the two regions in Fig. 4

Summary and Applications to Mars: The presence of allophane and amorphous Al/Si phases at Mawrth Vallis suggests that aqueous alteration of volcanic ash deposits occurred under neutral to mildly acidic conditions. The variety of secondary aluminosilicates identified through NIR and TIR spectroscopy indicates multiple aqueous environments once existed at Mawrth Vallis. Models of regional TES data suggest allophane is present in other regions as well, including Northern Acidalia and Meridiani [12].

References: [1] Poulet et al. (2005) *Nature*, 438, 623-627. [2] Loizeau et al. (2007) *JGR*, 112, doi:10.1029/2006JE002877. [3] Bishop et al. (2008) *Science*, 321, 830-833. [4] McKeown et al. (2009) *JGR*, 114, doi:10.1029/2008JE003301. [5] Noe Dobrea et al. (2010) *JGR*, 115, doi:10.1029/2009JE003351. [6] Rampe et al. (2011) 5th MSL Landing Site wksp. [7] Wada (1967) *Am. Miner.*, 52, 690-708. [8] Wada (1987) *Chem. Geol.*, 60, 17-28. [9] Henmi & Wada (1976) *Am. Min.*, 61, 379-390. [10] Bishop et al. (2012) *Clays Clay Min.*, sub. [11] Bishop et al. (2012) *PSS*, sub. [12] Rampe et al. (2011) *LPS XLII*, #2145.