

THE PRESENCE OF NANOPHASE Al-Si-Fe COMPONENTS AT MAWRTH VALLIS INDICATE VARYING ENVIRONMENTAL CONDITIONS. J. L. Bishop¹ and E. B. Rampe², ¹SETI Institute & NASA-ARC (189 Bernardo Ave, Mountain View, CA, 94043, jbishop@seti.org), ²NASA-JSC (Mail Code KR, Houston, TX 77058).

Nanophase (*np*) materials are important components of the bright outcrops at Mawrth Vallis. Here we highlight the types and abundances of *np* components determined through joint analyses of CRISM and TES data. Allophane and silica-rich materials are present in many places in the upper phyllosilicate profile at Mawrth Vallis. Similar *np* materials containing high Fe levels (and may be precursor phases for phyllosilicates like nontronite and hisingerite) are a better match for the lower phyllosilicate unit dominated by nontronite. The presence of *np* Al-Si-Fe components in the clay-rich units at Mawrth Vallis is consistent with young soils derived from volcanic material. Variable mixing of these amorphous/*np* materials with opal, montmorillonite, and kaolinite/halloysite within the upper Al/Si-rich phyllosilicate unit suggests regionally different aqueous environments. Mixtures of allophane or Fe-rich *np* material with nontronite are more consistent with spectra of the lower Fe/Mg-rich phyllosilicate unit. Modeling of TES data indicates ~50-75% hydrated aluminosilicates and *np* materials are present in the bright units and ~50-60% in the intermediate units. Modeling of darker units includes lower phyllosilicate abundance and higher zeolite, imogolite and silica levels indicating a different alteration environment.

Introduction: Rampe et al. [1] identified allophane in several locations on Mars where phyllosilicates are present and Bishop et al. [2] identified allophane in CRISM spectra of Mawrth Vallis. CheMin on MSL recently discovered that 20-30 wt.% of the Rocknest soil and John Klein and Cumberland mudstones are composed of amorphous phases such as allophane or glass [3,4] along with another 20-30 wt.% smectite in the mudstones [4]. This indicates that these amorphous or *np* materials could be present in many locations other than Mawrth Vallis. Thus, understanding the orbital detections of these *np* Al-Si-Fe-OH materials at Mawrth Vallis where they are abundant could have important implications for aqueous alteration across the surface of Mars.

Background: Allophane and imogolite are *np* aluminosilicates commonly detected in well-drained soils derived from volcanic ash containing feldspar and pyroxene [e.g. 5]. Continued weathering of allophane-rich and imogolite-rich soils can produce kaolinite/halloysite or montmorillonite [6], which are also present at Mawrth Vallis [7]. The spectral and hydration properties of allophane and imogolite were investigated recently and shifts were observed in the NIR band centers with variable Al/Si/Fe [8,9].

NIR spectra of allophane include a doublet at 1.38 and 1.40 μm due to the OH stretching overtone, a broad H₂O band near 1.92 μm , and an OH combination (stretch+bend) band near 2.19 μm (Fig. 1, [8]). Fe-

bearing allophane has a broad shoulder on the 2.2 μm band [8] and was recently identified at Coprates Chasma [10]. Imogolite spectra have similar features at 1.92 and 2.19 μm , but the OH overtone occurs at 1.37 and 1.39 μm (Fig. 1, [8]). In contrast, spectra of Al-smectites and opal have an H₂O band at 1.91 μm and an OH band at 2.21 μm . The latter is extended towards longer wavelengths for opal spectra. The spectrum of

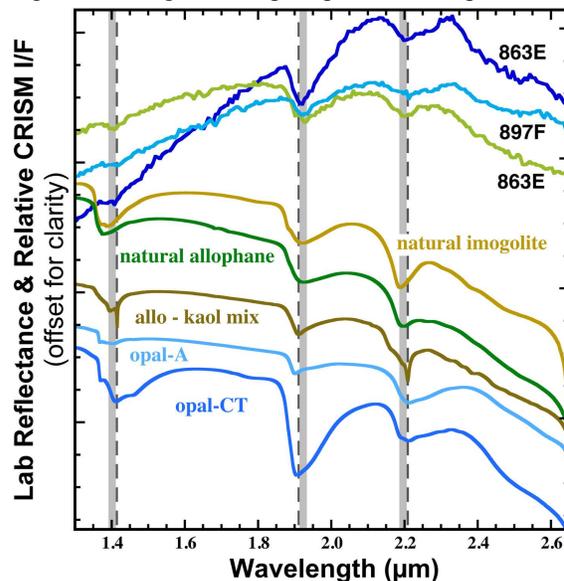


Figure 1. Selected Mawrth Vallis spectra compared with reflectance spectra of allophane, imogolite, opal, and an allophane-bearing mixture.

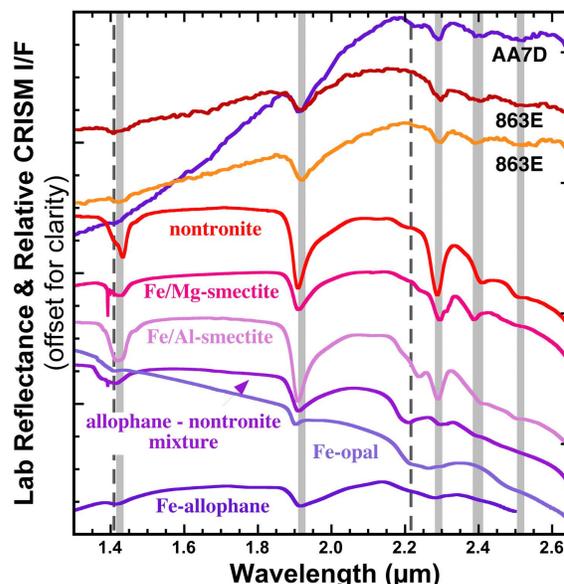


Figure 2. Selected Mawrth Vallis spectra compared with reflectance spectra of Fe-rich smectites and nano phase materials.

an Fe-bearing opal sample [9] exhibits features at 1.39-1.41 and 1.91 μm similar to those observed for opal-A (Fig. 1), but has a much broader 2.2-2.3 μm band due to OH bound to both Si and Fe. Spectra of a *np* Fe-rich allophane type material (Fig. 2) exhibits an OH overtone at 1.42 μm , similar to that of nontronite, a broad H₂O band at 1.92 μm , similar to that of allophane (Fig. 1), and a broad OH band near 2.29 μm with a shoulder at shorter wavelengths extending down below 2.2 μm . The OH combination band for the spectrum of this sample is attributed to OH bound to Fe, Si and Al.

Mid-IR spectra of allophane and imogolite exhibit an H₂O bending doublet near 6.0-6.2 μm and several Si-O-Al vibrations [1,8]. Bands occur in allophane spectra at ~ 1030 and 940 cm^{-1} (9.7, 10.6 μm), 610 cm^{-1} (16.4 μm) and 545 , 420 and 335 cm^{-1} (~ 18 , 24, 30 μm), and in imogolite spectra at ~ 1030 and 930 cm^{-1} (9.7, 10.8 μm), 595 cm^{-1} (16.8 μm) and 495 , 415 , and 335 cm^{-1} (~ 20 , 24, 30 μm). These features are readily distinguishable from bands in the spectra of montmorillonite and opal. The mid-IR spectrum of our Fe-rich *np* sample includes broad bands near 1030 cm^{-1} (9.7 μm) and 450 cm^{-1} ($\sim 22\text{ }\mu\text{m}$) [11], in contrast to nontronite spectra that have narrower bands near 1130, 1045, 500, 425 cm^{-1} (~ 8.8 , 9.6, 20, and 24 μm) [8].

CRISM Spectra of Phyllosilicate-bearing Units at Mawrth Vallis: CRISM spectra of the upper clay unit at Mawrth Vallis exhibit variations in the 1.9 and 2.2 μm bands indicating the presence of multiple minerals/phases [7]. Many spectra are consistent with allophane or imogolite (Fig. 1). This Al/Si-rich unit is regionally variable and includes hydrated silica (opal, altered glass), Al-smectite, kaolinite/halloysite, allophane/imogolite and related Al/Si phases [2]. CRISM spectra of the lower unit are characterized by a band near 2.29 μm similar to that of nontronite or Fe/Mg-smectite. This feature often includes a broader shoulder towards shorter wavelengths that could be explained by an Fe-rich *np* material that is structurally similar to allophane (Fig. 2).

TES Spectra of Mawrth Vallis: Models of TES data in phyllosilicate-rich regions at Mawrth Vallis identify ~ 10 -25 vol.% allophane and imogolite. TES models also identify montmorillonite, silica, and zeolite in significant abundances (>20 vol.%) in these areas (Table 1), confirming CRISM identifications of a variety of secondary aluminosilicates in the upper units of Mawrth Vallis. Nontronite is generally not selected in model fits. Ongoing modeling including spectra of our Fe-rich *np* sample will likely improve the fits for the Fe-phyllosilicate unit at Mawrth Vallis. The spectrum of the Fe-rich *np* sample has a single broad band near 450 cm^{-1} that is more consistent with the observed TES spectra than the doublet found in nontronite spectra.

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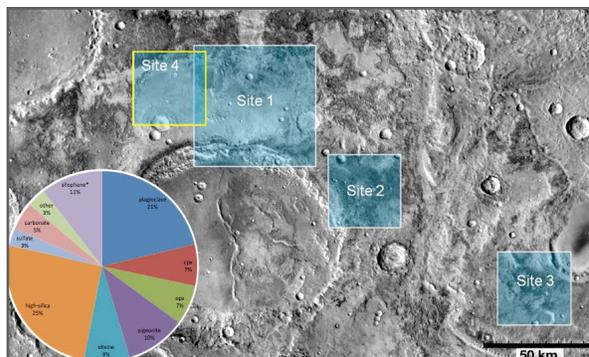


Figure 3. Modeling of TES data at Mawrth Vallis reveals that *np* Al-Si-Fe-bearing materials are abundant. TES footprints (blue) indicate where they were identified through modeling in these regions.

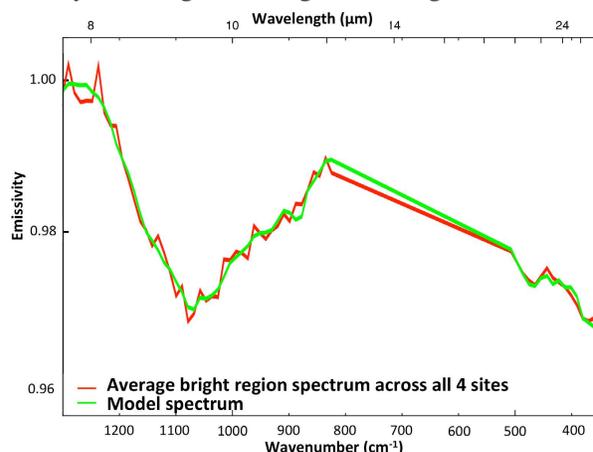


Figure 4. Average bright region TES spectrum (red) and modeled spectrum (green) for all 4 sites at Mawrth Vallis in Fig. 3. This model contains the abundances listed in Table 1 for bright regions.

Table 1. Modal Abundances from TES Analyses

	bright	intermediate	intermediate w/ imogolite
plagioclase	21	17	9
pyroxene	15	12	19
allophane	27	14	21
Al-phyllo	20	7	8
zeolite	7	9	8
imogolite	-	-	14
opal/Si-rich	0	23	4
other	2	12	16
total	100	100	99

References: [1] Rampe E. et al., (2012) *Geology*, 40, 995. [2] Bishop J. et al. (2013) *PSS*, 86, 130. [3] Blake D. et al. (2013) *Science*, 341, doi:10.1126/science.1239505. [4] Vaniman D. et al. (2013) *Science*, 343, doi: 10.1126/science.1243480. [5] Wada K. (1967) *Am. Miner.*, 52, 690. [6] Wada K. (1987) *Chem. Geol.*, 60, 17. [7] Bishop J. et al. (2008) *Science*, 321, 830. [8] Bishop J. et al. (2013) *Clays Clay Min.*, 61, 57. [9] Baker L. et al. (2011) LPS XLII, Abstract #1939. [10] Weitz C. et al. (2014) LPS XLV, Abstract #1386. [11] Davis A. et al. (2014) LPS XLV, Abstract #2699.