

Emission spectroscopy of smectites: Implications for the TES andesite-weathered basalt

debate. Joseph. R. Michalski¹, Michael D. Kraft¹, Thomas G. Sharp¹, Lynda B. Williams², and Philip R. Christensen¹

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Introduction: Mars Global Surveyor Thermal Emission Spectrometer (TES) data have revealed two major surface types on Mars [1]. Surface type-1 (ST1) is interpreted as basalt [1-4] and surface type-2 (ST2) as basaltic andesite [1,3] or altered basalt [4-6]. If the ST2 represents andesitic materials, it would have major implications for petrologic evolution of the Martian crust [7]. If ST2 represents weathered basaltic materials, it could provide key insight for understanding surface processes.

The geological interpretation of ST2 is dependent on which materials are used to model the ST2 spectrum. The ST2 spectrum can be modeled with spectra of plagioclase feldspars, pyroxene, and spectrally amorphous material [1-4]. Interpretations of the spectrally amorphous material include obsidian glass [1,3], smectite clays [4], palagonite [6], zeolites [8], or silica-rich rock coatings [5]. In this study, we consider the hypothesis that ST2 may represent smectite clays. One of the reasons for controversy on this subject is the difficulty in characterizing clay minerals, both spectrally and mineralogically.

In this study, we perform a new analysis of the emission spectral features of smectite clays, with detailed preparation and characterization. We relate the spectral features of smectite clay minerals to their structure and crystal chemistry. We provide further mineralogical constraints for the spectrally amorphous component observed by TES. Mineralogical constraint of potential alteration materials is important for understanding the alteration history on Mars.

Methods: Clay minerals were obtained from the Clay Minerals Society (CMS) source clay repository. The CMS source clays contain variable amounts of mineral impurities. To minimize the amount of impurities, a physical size separation was performed. The bulk sample was split into $> 2 \mu\text{m}$, $2\text{-}0.2 \mu\text{m}$, and $< 0.2 \mu\text{m}$ size fractions. Most of the impurities are contained in the $> 2 \mu\text{m}$ sizes, and the clay mineralogy becomes purer with finer size fractions [9].

Approximately 0.5 g of material from each size fraction was pressed into a pellet using a hydraulic press at an estimated maximum pressure of 91 MPa, creating a pellet 1 cm in diameter by approximately 3 mm thickness. In general, the pellets all have nearly specular surfaces as indicated by their reflective character at visible wavelengths. Some of the pellets have a mat-like surface. High-resolution emission spectra of clay

(pellet) samples were recorded at the Arizona State University Mars Spaceflight Facility at 2 cm^{-1} spectral resolution over the spectral range from $200\text{-}2000 \text{ cm}^{-1}$.

Transmission spectra of the $< 0.2 \mu\text{m}$ size fractions were obtained by the KBr pellet technique over the spectral range $5000\text{-}400 \text{ cm}^{-1}$, at 2 cm^{-1} spectral resolution. Transmission spectra contain similar information to emission spectra, but band shapes and the placement of bands is slightly shifted between the two because emission spectra depend on both the absorption coefficient (k) and index of refraction (n), whereas transmission spectra depend only on k . Analysis of transmission spectra is important for two reasons. First, transmission spectroscopy is sensitive to small amounts of impurities ($< 1\%$), which allows for additional spectral characterization. Secondly, analysis of the transmission spectra allows for discussion of the spectral features in terms of accepted band assignments [10-11]. The transmission spectra can be compared to emission spectra and the band assignments from transmission may be extrapolated to the emission spectra.

Results and Discussion: The transmission spectra indicate that the $< 0.2 \mu\text{m}$ size fractions are pure, with the exception of trace amounts of carbonate in the saponite and trace amounts of oxyhydroxides in Nau-2. A summary of the emission spectral features is listed below. Emission spectra are shown in Figure 1.

450-950 cm^{-1} : An absorption related to Si-O bending in the tetrahedral sheet is present between $450\text{-}475 \text{ cm}^{-1}$ in all of the samples. An absorption between $450\text{-}540 \text{ cm}^{-1}$ is related to Si-O-M deformations between the dioctahedral and tetrahedral sheets (where "M" = Al^{3+} , Fe^{3+} , Fe^{2+} , or Mg^{2+}). The exact placement of this absorption is a linear function of the ionic radius of the octahedral cation [10]. Absorptions related to the M-OH deformation occur between $550\text{-}915 \text{ cm}^{-1}$.

In previous work by [8], a spectral ratio was applied to TES data in the spectral range between $500\text{-}550 \text{ cm}^{-1}$ to determine if there is evidence for a clay absorption in this region. The results [8] indicate no evidence of this absorption in the putative clay-rich ST2 areas [4]. The spectral ratio applied by [8] is sensitive to the Si-O-M deformation absorption in the spectral range where $\text{M} = \text{Fe}^{3+}$ or Al^{3+} . The larger ionic radius of Mg^{2+} causes the Si-O-M absorption to occur at lower wavenumbers in Mg-smectites so that it overlaps with the Si-O bending absorption near 450

cm^{-1} . Therefore, we suggest that the results of [8] are evidence against the high abundance of dioctahedral ferric or aluminous smectites such as montmorillonite, nontronite, beidellite, or any smectite-like clay with octahedral Al^{3+} or Fe^{3+} . The results from [8] do not suggest an absence of Mg-bearing smectites.

950-1200 cm^{-1} : All of the smectites exhibit a broad absorption from 950-1200 cm^{-1} related to Si-O stretching in the tetrahedral sheet. The position of the absorption minimum between 1037-1072 cm^{-1} is shifted to smaller wavenumbers for trioctahedral clays relative to dioctahedral, and the exact placement for each subgroup is a function of the amount of Al^{3+} and Fe^{3+} substitution for Si^{4+} in the tetrahedral sheet.

One of the reasons for the conflicting interpretations of TES ST2 spectrum is the spectral similarity between clays and volcanic glasses in the 950-1200 cm^{-1} region. The ST2 spectrum is best modeled by incorporating an obsidian glass component [1]. Dioctahedral smectites can be ruled out from the low wavenumber observations discussed above. Trioctahedral smectites are allowable based on spectral similarity to Mars in the 450-550 cm^{-1} region, but tetrahedral absorptions of trioctahedral clays in the 950-1200 cm^{-1} region are shifted to lower wavenumbers by approximately 50 cm^{-1} relative to obsidian glass and are unlikely to be confused with obsidian in a deconvolution model.

In the 950-1200 cm^{-1} region, the placement of the emissivity minimum for all silicates is a function of the Si/O ratio of the tetrahedral network. The Si/O ratio ranges from 0.25 for nesosilicates to 0.5 for quartz; The Si/O ratio for clay minerals is between 0.3 and 0.4. As the Si/O ratio of the tetrahedral network decreases, the location of the Si-O stretching absorption shifts to lower wavenumbers. The Si/O ratio for obsidian is approximately 0.42 and obsidian glass has an emissivity minimum near 1087 cm^{-1} , which is higher than the emissivity minima of smectites. Therefore, crystal chemical substitutions in the tetrahedral sheet of a clay can only serve to lower the Si/O ratio, and shift the emissivity minimum to lower wavenumbers. Crystal chemical substitutions can never make a clay mineral look more obsidian-like in the thermal infrared. Structural differences that could allow the Si/O ratio of alteration materials to be higher than 0.4 would imply that the material has a tectosilicate structure.

Conclusions: Based on our analysis of smectite clay spectra and the spectral ratio results of [8], we conclude that TES results are not consistent with large abundances of Fe- or Al-bearing clay minerals on Mars. Mg-rich trioctahedral clays, which are expected from SWIR observations [12], may be a minor component of TES surface spectra. If Mg-clays are

present, they might be detected from the Mg-OH stretching absorption near 657 cm^{-1} , which is observable with Mini-TES, but is obscured by atmospheric CO_2 from orbit. The spectrally amorphous material thought to be significant component of TES ST2 must be a tectosilicate, not a phyllosilicate. Potential alteration materials that could satisfy the TES observations include certain silica-rich zeolites, or silica-rich mineraloids, such as Fe- or Al-bearing opal. The existence of such materials on Mars could be indicative of palagonitization-like weathering processes.

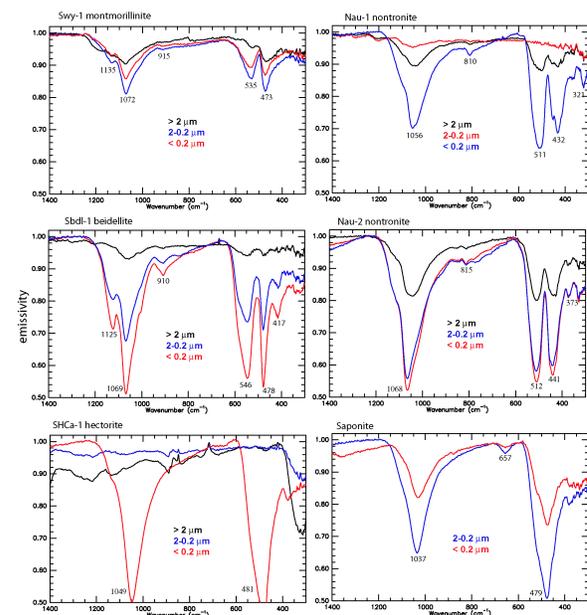


Figure 1: Thermal emission spectra of smectite clays.

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