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Thermal Emission Measurements (5-25 μm) of Palagonite/Fe-substituted Montmorillonite Intimate Mixtures: Applications to Mars: Ted L. Roush¹ and James B. Orenberg², ¹San Francisco State Univ. and NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035-1000, ²Dept. Chemistry & Biochemistry, San Francisco State Univ., 1600 Holloway Ave., San Francisco, CA 94132

Background: Based on Viking Lander x-ray fluorescence analyses Si and Fe are the two most abundant elements constituting 44% and 19%, respectively, of the martian soil when recast as their oxide equivalents [1-3]. Simulations of the relative elemental abundances have included smectite clays, iron oxides, sidromelane, chlorides, and sulfates [1-3]. The Viking Landers also performed experiments designed to address the question of biological activity on Mars [e.g. 4]. Mineralogical interpretation of these results include smectites [5-8] and palagonite/smectite mixtures [9]. However, since the Viking Landers did not carry any instruments capable of determining mineralogy, the exact mineralogical form of the surface materials remains uncertain.

Interpretations of continuing visual and near-infrared spectroscopic observations of Mars from the Earth and spacecraft over the past 20 years [10,11] have revealed that the ferric mineralogy occurs in two distinct forms: (1) nanophase or amorphous Fe^{3+} -bearing materials [12,13] that spectrally resemble terrestrial palagonites [e.g. 14-18]; and (2) well-crystalline ferric oxides [13,19-23]. The available data indicate that the poorly-crystalline "palagonite-like" phases are spectrally dominant [e.g. 10,11] and that the well crystalline ferric oxides cannot constitute an abundance of more than about 4-8 wt. % [22].

Spectral analyses of the 2.2 μm Al-OH absorption feature suggests that Al-OH-bearing materials have abundances ≤ 0.008 wt.% if they are present as the pure phase [24]. Fe-substituted montmorillonites (FeM), smectite clays where the interlayer cations have been chemically replaced by Fe, have also been suggested as a mineralogical analog for martian bright soils [5-9]. Since these smectites all exhibit the 2.2 μm feature, the extreme constraint imposed for Al-OH materials is likely applicable to the pure FeM. Spectral analyses of physical mixtures of palagonite and FeM suggest that up to 15 wt. % FeM may be present on Mars and remain undetected [25]

In the middle infrared (5-25 μm), spectral features arise from vibrational motions of atoms and molecules which compose the materials. These fundamental modes are much more intense than associated combination and/or overtones of these modes occurring at shorter wavelengths. Hence, remote sensing in the infrared is extremely sensitive to minor concentrations of these absorbing species. FeM transmission spectra exhibit typical clay absorption features in the mid-infrared (2.5-25 μm) [26]. Palagonites also have absorptions in the mid-infrared although they appear less complex than the clay features [11,27]. The research presented here represents a portion of a broader project that is intended to investigate the detectability limits for the minerals containing the biogenic elements. Such information can be used in the interpretation of past and future thermal observations of Mars.

We have measured the emissivity of a Mauna Kea palagonitic soil mixed with an Fe-substituted montmorillonite. The emission spectra of all samples were measured at the TES spectroscopy laboratory [28] at Arizona State University with the cooperation of Dr. Phil Christensen. The data were converted to emissivity using blackbody measurements combined with measurements of each sample at different temperatures [29].

Results: Emissivity spectra for the two pure end members and two mixtures are shown in Figure 1. The spectrum of the FeM sample exhibits greater emissivity variations than the palagonite sample spectrum. Several emissivity peaks are present in the FeM sample near 500, 1130, and 1880 cm^{-1} , indicated by arrows, that are not present in the palagonite spectrum. These peaks may serve to identify the presence of FeM when mixed with palagonite. For example, the spectrum of the 85% palagonite, 15% FeM mixture exhibits the 500 cm^{-1} peak and a hint of the 1130 cm^{-1} feature. In the spectrum of the 75% palagonite, 25% FeM mixture both of these features are more pronounced and an additional feature near 1880 cm^{-1} is also present. We had planned to measure mixture of 90% palagonite and 10% FeM as part of this study. However, the sample was destroyed during shipping.

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This preliminary study has demonstrated that both naturally-occurring palagonites, thought to be good visible to near-IR spectral analogs for Mars, and FeM exhibit complex emissivity spectra at thermal wavelengths. FeM exhibits greater emissivity variations than palagonite, and emissivity peaks observed in the FeM spectrum allows its identification for abundances $\geq 15\%$ when mixed with palagonite. Smaller abundances of FeM are potentially identifiable when mixed with palagonite, but this remains to be determined.

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Figure 1. Emissivity spectra (top two curves) of Hawaiian palagonitic soil (dotted line) and an Fe-substituted montmorillonite (FeM), solid line) and mixtures of palagonite and FeM (bottom two curves). The spectra are offset for obscurity. For the mixtures, the dotted line is 85% palagonite and 15% FeM while the solid line is for 75% palagonite and 25% FeM. The vertical line shows the frequency of the strong H-O-H bending fundamental caused by molecular water associated with these samples, while the arrows indicate emissivity features associated with the FeM.

