

## VISIBLE AND INFRARED REFLECTANCE SPECTROSCOPY OF PHYSICAL AND CHEMICAL FERRIC-SMECTITE MIXTURES AS MARS SOIL ANALOGS;

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**INTRODUCTION.** Subtle visible and near-infrared spectral variations in the bright regions on Mars have been observed due to heterogeneity in the ferric mineralogy and the presence of phyllosilicates. Ferric band minima in the range 0.85-0.92  $\mu\text{m}$  [1] have been observed and variations in the weak 2.2  $\mu\text{m}$  band [2] have been observed in martian bright regions. These spectral features observed on Mars could result from physical mixing of multiple components in the soil, or rather from chemical mixing as ferric component(s) form within/around the silicate grains, or both. Natural samples containing mixtures of hematite and pyroxene have shown a range of ferric band minima from 0.84-1.0  $\mu\text{m}$  [3]. Chemical mixtures have been prepared by forming ferric oxyhydroxide and oxyhydroxysulfate phases in between the smectite layers and around smectite grains; ferrihydrite- and ferric sulfate-bearing montmorillonites resulted from this chemical treatment that have ferric band minima ranging from 0.88-0.92  $\mu\text{m}$  [4,5].

Physical mixtures of fine-grained carbon and montmorillonite were performed [4] in order to observe the influence of mixing on band strengths in reflectance spectra of Mars analogs. Reflectance spectra of these mixtures, measured in a controlled, dry environment, exhibited significant suppression of the NIR montmorillonite features. Spectroscopic analyses of mixtures of smectites and palagonitic soils with hematite powder showed marked suppression of the 2.2  $\mu\text{m}$  band of the silicates due to the highly absorbing fine-grained hematite component [6]. The physical mixtures included in the current study contain fine-grained hematite and ferric sulfate-bearing montmorillonite, as well as ferrihydrite and ferrihydrite-bearing montmorillonite.

**METHODS AND SAMPLES.** Bi-directional reflectance spectra and bi-conical reflectance spectra were measured from 0.3-1.2  $\mu\text{m}$  and 1.2-25  $\mu\text{m}$ , respectively, at Brown University. Preparation of the chemically-treated montmorillonites and spectral measurement procedures can be found in [4,5]. One physical mixture (57) was prepared with 25 wt.% ferrihydrite (46) and 75 wt.% ferrihydrite-bearing montmorillonite (11). This mixture contains  $\text{Fe}^{3+}$  as ferrihydrite, as well as in the montmorillonite structure and interlayer regions. The two ferric sulfate-bearing montmorillonite samples used as end-members for the mixtures with hematite have 12 and 23 wt.%  $\text{Fe}_2\text{O}_3$ , of which ~4 wt.% is structural Fe from the SWy montmorillonite starting material. These physical mixtures were prepared by adding 5 and 10 wt.% hematite (<5  $\mu\text{m}$  p.s.  $\text{Fe}_2\text{O}_3$ , Aldrich). The amount of the Fe in these samples is shown in Table 1. The iron occupying octahedral sites in the montmorillonite structure is indicated by  $\text{Fe}_{\text{str}}$  in Table 1 and the iron located in the interlayer regions or along grain surfaces in the chemically-treated montmorillonites is indicated by  $\text{Fe}_{\text{int}}$ .

**RESULTS: VISIBLE REGION.** Spectra of montmorillonite-ferrihydrite mixtures are shown in Fig. 1. The influence of the ferrihydrite in the chemical and physical mixtures is observed most strongly in the extended visible region in Fig. 1a. Spectra of hematite-montmorillonite mixtures are shown in Fig. 2. The fine-grained hematite powder influences the intensity and the position of the ferric band minimum non-linearly. The wavelength of the local reflectance maxima near 0.7-0.8  $\mu\text{m}$  and the ferric band minima near 0.9  $\mu\text{m}$  were measured by taking first derivatives of the spectra and are summarized in Table 1 for the hematite-montmorillonite mixtures.

**RESULTS: NEAR-INFRARED REGION.** Mixing ferrihydrite with montmorillonite resulted in mild suppression of the NIR features and an increase in the 3  $\mu\text{m}$  water band strength (Fig. 1a). Band depths were determined at 1.41, 1.91 and 2.21  $\mu\text{m}$  for reflectance spectra of the hematite-smectite mixtures [7]. The 5 wt.% hematite powder mixtures exhibited band strengths reduced by ~1/2 relative to those of the smectite analogs alone for these NIR features and the NIR albedo was darkened from ~85% to ~50% [7].

**RESULTS: MID-INFRARED REGION.** Reflectance spectra of the ferrihydrite-montmorillonite mixtures and hematite-montmorillonite mixtures are shown from 7-24  $\mu\text{m}$  in Figs. 1b and 2b, respectively. In general, mixing of both ferrihydrite and hematite tends to dampen the montmorillonite features in the mid-infrared region. The Christiansen feature occurs near 7.9  $\mu\text{m}$  in natural montmorillonite and is shifted towards longer wavelengths as ferrihydrite and hematite are admixed. The Christiansen feature occurs at ~8.05  $\mu\text{m}$  for the ferric sulfate-bearing montmorillonites and at ~8.15 and ~8.20  $\mu\text{m}$ , respectively, for the mixtures containing 5 and 10 wt.% hematite powder. The physical mixtures of montmorillonite with Fe oxides have a greater influence on the Christiansen feature than the chemical Fe oxide mixtures. The relatively strong montmorillonite bands near 19 and 21  $\mu\text{m}$  are reduced in intensity in both physical mixing experiments.

**CONCLUSIONS.** These experiments indicate that chemically-formed and physically-formed mixtures of fine-grained ferric oxides and smectites produce different kinds of materials and that the method of incorporating ferric species into a smectite mineral has an important influence on the spectral properties. A few wt.%  $\text{Fe}_2\text{O}_3$  can be present in the smectite structure without giving visible ferric features, whereas as few wt.%  $\text{Fe}_2\text{O}_3$  as hematite contributes significantly to the visible and NIR spectral properties of the sample. The NIR spectral brightness and NIR band strengths of the chemically-treated montmorillonites containing ferrihydrite and ferric sulfate species are relatively similar to those of natural montmorillonite. In contrast, the NIR spectral brightness

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and NIR band depths are both significantly reduced when small amounts of fine-grained hematite are mixed with these smectites. Physical mixtures with ferrihydrite and hematite produced shifts in the montmorillonite Christiansen feature towards longer wavelengths and decreased the intensity of the montmorillonite features near 20  $\mu\text{m}$ . Chemical and physical mixtures of smectites with ferrihydrite and fine-grained hematite are good models for the bright region material on Mars because of the chemical and mineralogical compositions of these samples, as well as their visible and infrared region spectral properties.

Table 1 The amount and form of the ferric iron (wt.%  $\text{Fe}_2\text{O}_3$ ) and selected reflectance features.

sample	total $\text{Fe}^{3+}$	$\text{Fe}_{\text{str}}$	$\text{Fe}_{\text{int}}$	hematite	max. ( $\mu\text{m}$ )	min. ( $\mu\text{m}$ )
13	3.6	3.6	--	--	--	--
117	12.0	3.3	8.7	--	0.746	0.885
132	16.4	3.1	8.3	5.0	0.767	0.860
133	20.7	3.0	7.8	9.9	0.769	0.855
129	100			100	0.777	0.850
120	22.9	2.9	20.0	--	0.751	0.886
126	26.9	2.7	18.9	5.3	0.763	0.862
127	30.4	2.6	18.0	9.8	0.767	0.858

Figure 1 Reflectance spectra of montmorillonite (13), ferrihydrite (46) and mixtures of these minerals.

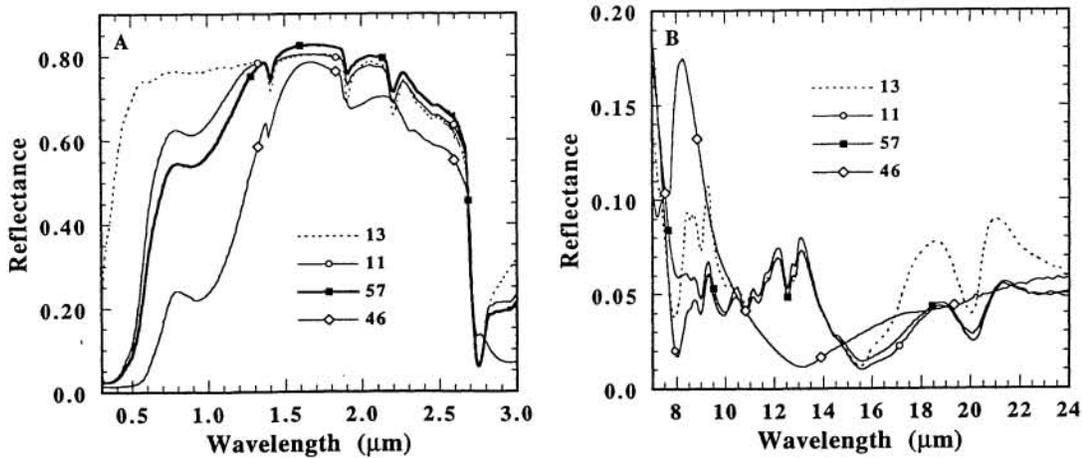
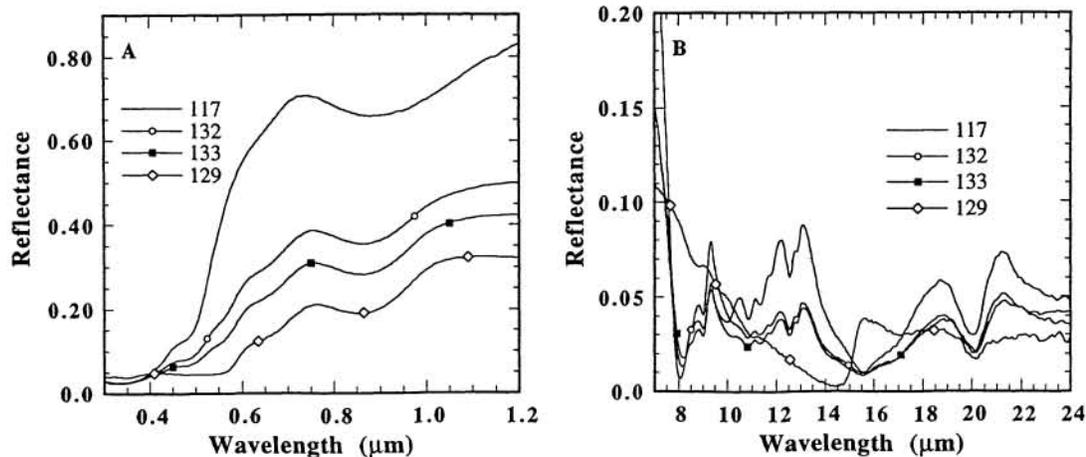


Figure 2 Reflectance spectra of hematite - montmorillonite mixtures.



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