

Fig. 1. Thermoskan thermal (top) and visible (bottom) images centered approximately upon 1°S, 39°W. North is top. In the thermal image, darker is cooler. Shalbatana, Simud, and Tiu Valles all continue for several hundred kilometers north of this image. Note the cool and generally uniform floors of all channels except the eastern (and rough floored) end of Ravi Vallis. The thermal boundaries closely match the boundaries of the channel floors and depart significantly from albedo boundaries seen in the visible image. Note also the dark, presumably colian deposits localized within the southern portions of Shalbatana Vallis and the southwestern portion of Hydraotes Chaos and spreading onto the surrounding plains in both cases. Buttes within the channels appear similar in temperature and appearance to the surrounding plains, not the channels. See, for example, the butte in the northeast corner of the image.

ting morphologies such as wide, flat floors and steep, scalloped walls. Therefore, we favor fretting processes over catastrophic flooding for explaining the inertia enhancements. Fretting may have emplaced more blocks on channel floors or caused increased bonding of fines due to increased availability of water. Alternatively, postchannel formation water that was preferentially present due to the low, flat fretted floors may have enhanced bonding of original fines or dust fallout.

Extended areal coverage from future missions will determine whether fretting is globally associated with enhanced channel floor inertias. In addition, future missions will be able to distinguish between our hypotheses for the small-scale causes of the inertia enhancements. Finally, we note that thermally distinctive channel floors represent interesting locations for future landers due to their

unique history and the probable surface presence of material from various stratigraphic layers and locations.

References: [1] Murray B. C. et al. (1991) *Planetary and Space Science*, 39, 112, 237–265. [2] Selivanov A. S. et al. (1989) *Nature*, 341, 593–595. [3] Betts B. H. (1993) Ph.D. thesis, Caltech. [4] Betts B. H. and Murray B. C. (1993) *LPS XXIV*, 103–104. [5] Christensen P. R. and Kieffer H. H. (1979) *JGR*, 84, 8233–8238. [6] Zimbelman J. R. (1986) in *Symposium on MECA*, 112–114, LPI. [7] Zimbelman J. R. and Leshin L. A. (1987) *Proc. LPSC 17th*, in *JGR*, 92, E588–E596. [8] Craddock R. A. et al. (1988) *LPSC XIX*, 215–216. [9] Pleskot L. K. and Miner E. D. (1981) *Icarus*, 45, 179–201. [10] Clifford S. M. et al. (1987) Lunar and Planetary Institute.

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THE IMPORTANCE OF ENVIRONMENTAL CONDITIONS IN REFLECTANCE SPECTROSCOPY OF LABORATORY ANALOGS FOR MARS SURFACE MATERIALS.

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Reflectance spectra are presented here for a variety of particulate, ferric-containing analogs to martian soil (Fe³⁺-doped smectites and palagonites) to facilitate interpretation of remotely acquired spectra. The analog spectra were measured under differing environmental conditions to evaluate the influence of exposure history on water content and absorption features due to H₂O in these samples. Each of these materials contains structural OH bonded to metal cations, adsorbed H₂O, and bound H₂O (either in a glass, structural site, or bound to a cation). Previous experiments involving a variety of Mars analogs have shown that the 3- μ m H₂O band in spectra of palagonites is more resistant to drying than the 3- μ m H₂O band in spectra of montmorillonites [1]. Other experiments have shown that spectra of ferrihydrite and montmorillonites doped with ferric sulfate also contain sufficient bound H₂O to retain a strong 3- μ m band under dry conditions [2,3]. Once the effects of the environment on bound water in clays, oxides, and salts are better understood, the hydration bands measured via reflectance spectroscopy can be used to gain information about the chemical composition and moisture content of real soil systems. Such information would be especially useful in interpreting observations of Mars where subtle spatial variations in the strengths of metal-OH and H₂O absorptions have been observed in telescopic [4] and ISM [5,6] spectra.

Experimental Procedures: We measured bidirectional reflectance spectra of several Mars soil analogs under controlled environmental conditions to assess the effects of moisture content on the metal-OH and H₂O absorptions. The samples analyzed include chemically altered montmorillonites, ferrihydrite, and palagonites from Hawaii and Iceland. Procedures for preparation of the cation-exchanged montmorillonites, ferric-salt doped montmorillonites, and ferric oxyhydroxides are described in detail elsewhere [2,3].

One set of experiments involved desiccating the samples by heating. Reflectance spectra were measured initially for these samples under humidified conditions and under N₂ purged of H₂O and CO₂. The samples were then heated in an oven to 175°C at a rate of 1°C/min, cooled in a desiccator and measured again. This procedure was repeated for heating the samples to 275°C. Water contents for these samples were measured independently using thermal gravimetric analysis.

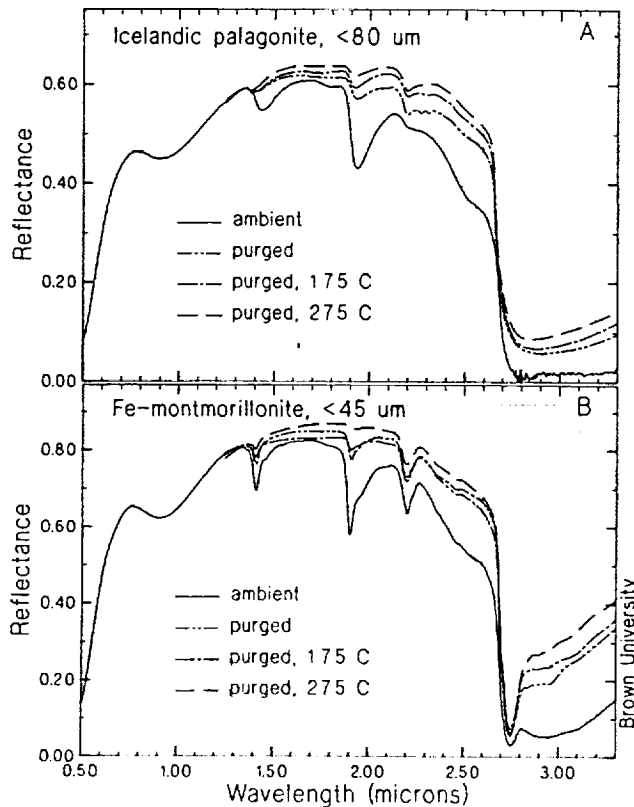


Fig. 1. Reflectance spectra 0.5–3.3 μm . (a) Icelandic palagonite; (b) Fe^{3+} -doped montmorillonite.

A second set of experiments involved drying the samples by reducing the atmospheric pressure in an environment chamber. Reflectance spectra were measured first for each sample under ambient pressure, and then under successively reduced atmospheric pressures to as low as $\sim 10 \mu\text{m Hg}$ (10^{-5} bar).

Results: Reflectance spectra from 0.5 to 3.3 μm are shown in Fig. 1 for Icelandic palagonite and Fe^{3+} -doped montmorillonite. These spectra were measured under humidified conditions, after exposure to dry N_2 , and after heating to 175°C and 275°C. The H_2O and structural OH absorptions in palagonites and montmorillonites are affected differently by drying in this manner. The broad 3- μm band observed in the montmorillonite spectra measured under humid conditions changes upon desiccation to a sharp feature at 2.75 μm , due to structural OH, and weaker features in the 2.8–3.3- μm region due to bound interlayer water. Most of the adsorbed water in montmorillonites is removed by flowing dry N_2 over the samples or by heating to less than 175°C. The overall band shape in the palagonite spectra does not change significantly with drying, although the strength of the 3- μm band continued to decrease with heating up to 275°C.

The montmorillonite spectra show absorptions at 1.41 μm and 1.91 μm under humid and arid conditions; however, the shoulders at 1.45 μm and 1.96 μm due to adsorbed water are only observed in the ambient spectrum. The intensity of these H_2O features near 1.4 μm and 1.9 μm are greatly subdued after desiccation in the

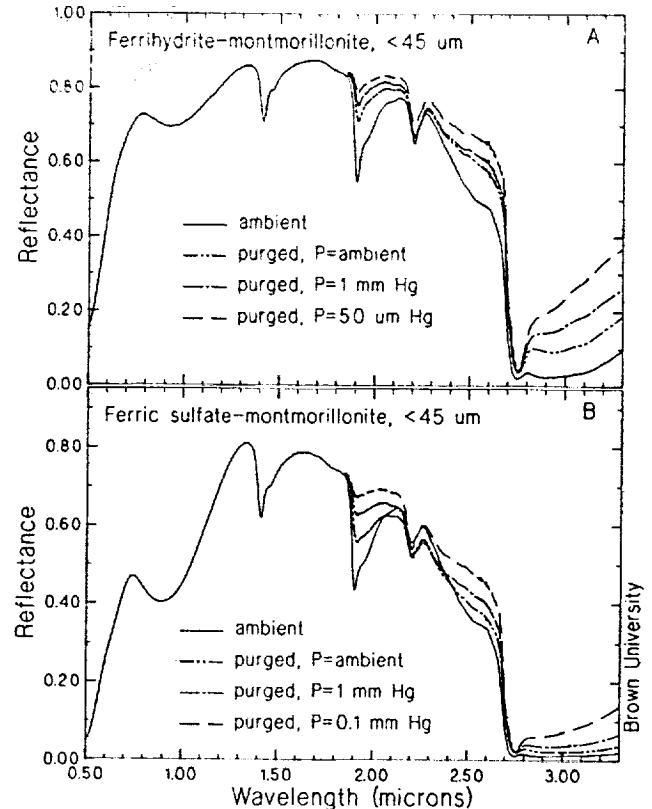


Fig. 2. Reflectance spectra 0.5–3.3 μm . (a) Ferrihydrite-doped montmorillonite; (b) ferric-sulfate-doped montmorillonite.

spectra of smectites and palagonites. The water combination band occurs at 1.93 μm in the ambient palagonite spectrum and at 1.91 μm in the spectrum after heating to 275°C. A shift toward shorter wavelength upon drying is also observed for the absorption near 1.4 μm in the palagonite spectra.

Reflectance spectra are shown in Fig. 2 from 0.5 to 3.3 μm for ferrihydrite-doped montmorillonite and ferric-sulfate-doped montmorillonite. The spectra shown were measured under ambient conditions, and purged of H_2O and CO_2 under dry N_2 at 1-bar pressure and finally under successively reduced atmospheric pressures. The broad 3- μm H_2O feature in the reflectance spectra of the ferric-sulfate-doped montmorillonite and ferrihydrite (not shown) remains strong after exposure to extremely drying conditions, while this band is suppressed under the same drying conditions in the spectra of the ferrihydrite-doped montmorillonite and other montmorillonites (not shown). Suppression of the 1.9- μm feature is observed for each of these samples upon desiccation.

Discussion and Conclusions: As seen in Figs. 1 and 2, reflectance spectra of each of these analog materials measured under humid conditions exhibit prominent infrared absorptions due to molecular H_2O . However, analog materials studied under more Mars-like environmental conditions tend to fall into two groups: those that retain a strong 3- μm band, and those that do not. This depends on the type of bonding of the H_2O in these materials. Those that lose a large proportion of the 3- μm band intensity upon mild heating or drying

contain H₂O physisorbed on grain surfaces or interlayer surfaces in smectites (see Figs. 1b and 2a). Other materials that retain a large amount of water, as seen by a strong 3- μ m band under dry conditions (e.g., at temperatures above \sim 150°C, or pressures below \sim 1 mm Hg) contain H₂O that is bound in the structure (see Figs. 1a, 2b, and ferrihydrite spectrum [3]). In the ferric-sulfate-doped montmorillonites water forms strong bonds to the sulfate ions because of its highly polarizing nature [7].

The hydration feature near 1.9 μ m is a combination of the H₂O vibrations at \sim 3 μ m and \sim 6 μ m, and is also affected by the environmental conditions and the type of H₂O bonding. The band strength and energy of this feature in spectra of smectites is dependent as well on the interlayer chemistry [3]. An important application to Mars is that a ferric montmorillonite in a dry environment would have a relatively weak 1.9- μ m feature that is difficult to observe in Mars spectra.

In conclusion, we would like to stress the importance of considering environmental conditions when measuring infrared spectra of laboratory samples as analogs for Mars surface materials. The strength and character of features due to molecular water (\sim 1.4, \sim 1.9, \sim 3, and \sim 6 μ m) in the spectra of clays, palagonites, and hydrated minerals are especially sensitive to the moisture environment of the samples. These features are influenced by the exposure history (atmospheric temperature, pressure, and composition) of the samples, as well as the environmental conditions at the time of measurement.

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References: [1] Bruckenthal (1987) M.S. thesis, Univ. of Hawaii. [2] Bishop et al. (1993) *LPS XXIV*, 115–116. [3] Bishop et al. (1993) *GCA*, in press. [4] Bell and Crisp (1993) *Icarus*, in press. [5] Murchie et al. (1993) *Icarus*, in press. [6] Bibring et al. (1989) *Nature*, 341, 591–592. [7] Bishop et al., this volume.

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FERRIC SULFATE MONTMORILLONITES AS MARS SOIL ANALOGS. J.L. Bishop¹, C.M. Pieters¹, and R.G. Burns², ¹Brown University, Providence RI 02912, USA, ²Massachusetts Institute of Technology, Cambridge MA 02139, USA.

Spectroscopic analyses have shown that Fe³⁺-doped smectites prepared in the laboratory exhibit important similarities to the soils on Mars [1,2]. Ferrihydrite in these smectites has features in the visible to near-infrared region that resemble the energies and band-strengths of features in reflectance spectra observed for several bright regions on Mars [3]. Ferric-sulfate-montmorillonite samples have been prepared more recently because they are a good compositional match with the surface material on Mars as measured by Viking [4]. Reflectance spectra of montmorillonite doped with ferric sulfate in the interlayer regions include a strong 3- μ m band that persists under dry conditions [5,6]. This is in contrast to spectra of similarly prepared ferric-doped montmorillonites, which exhibit a relatively weaker 3- μ m band under comparable dry environmental conditions. Presented here are reflectance spectra of a suite of ferric-sulfate-exchanged montmorillonites prepared with variable ferric sulfate concentrations and variable pH conditions.

Experimental Procedures: The Na and Ca interlayer cations in SWy-1 montmorillonite (Clay Mineral Society, Source Clays Repository) were exchanged with 0.5 N ferric sulfate solution in the clay suspension at pH 1.6–1.8 after titration with dilute HCl. The pH was raised dropwise with dilute NaOH to at least 3.0 in order to retain the ferric sulfate in the montmorillonite interlayer regions. The suspensions were then centrifuged and lyophilized to form a fine powder, which was dry sieved to $<$ 45 μ m.

Biconical reflectance spectra were measured relative to a rough gold surface using a Nicolet 740 FTIR in a H₂O- and CO₂-purged environment. A PbSe detector was used from 0.9 to 3.2 μ m and a DTGS detector from 1.8 to 25 μ m. Bulk powdered samples are measured horizontally in this system. Spectra are averaged from two locations on each of two replicates for each kind of sample.

Additional bidirectional spectra were measured relative to Halon from 0.3 to 3.6 μ m using an InSb detector under ambient conditions with the RELAB (reflectance experiment laboratory) spectrometer at Brown University. A detailed description of this instrument is provided elsewhere [7].

Results: Reflectance spectra (0.3 μ m–3.5 μ m) of natural and chemically altered SWy montmorillonite and ferrihydrite measured under dry (H₂O- and CO₂-purged) conditions are shown in Fig. 1.

The spectra of each of these ferric-bearing materials exhibits absorptions in the visible region near 0.5 μ m and 0.9 μ m, an inflection near 0.6 μ m, and a reflectance maxima near 0.74 μ m, although physical and chemical constraints on the Fe³⁺ sites in each mineral structure influence the exact energy of the crystal field transitions. The strengths of these electronic transitions are stronger in the ferric-sulfate-exchanged montmorillonites than in the other ferric-bearing materials shown in Fig. 1.

The spectra of each of these samples contain an absorption near 2.75 μ m due to OH bound to cations in the structure, and an absorption near 3.0 μ m due to H₂O bound to Fe³⁺ in the interlayer regions, H₂O bound to sulfate anions, or H₂O adsorbed on the grain surfaces. The ferric-sulfate-containing samples exhibit a much stronger absorption near 3 μ m and a much stronger 1.96- μ m shoulder than both the ferrihydrite and the ferrihydrite-montmorillonite.

Reflectance spectra are shown in Fig. 2 (0.3 μ m–1.1 μ m) for telescopic spectra of Mars [8], ferrihydrite-montmorillonite, and ferric sulfate-montmorillonite. This ferric sulfate-montmorillonite spectrum is that with the weakest 0.9- μ m and 3- μ m absorptions from Fig. 1. The spectra are scaled at 0.75 μ m to facilitate comparison of the spectral features.

Room-temperature Mössbauer spectra of the ferrihydrite-montmorillonite and ferric sulfate-montmorillonite are very similar; a doublet is observed with quadrupole splitting less than 1 mm/s. However, the Mössbauer spectra measured at 4.2 K exhibit a field strength of \sim 46 T for the ferric sulfate-montmorillonite and a field strength of \sim 48 T for the ferrihydrite-montmorillonite. The differences in field strengths of these two samples are sufficient to distinguish among them. The ferric sulfate species in the ferric sulfate-montmorillonite is also distinct from jarosite, which has a field strength of \sim 49 T. Asymmetry in the peaks of the sextet in the low-temperature Mössbauer spectra of the ferric sulfate-montmorillonite may indicate that multiple ferric phases are present.

Discussion: The intensity of the 0.9- μ m absorption increased with ferric sulfate concentration as expected, but tends to be stronger in general than the 0.9- μ m absorption in the ferrihydrite-montmorillonite. The band center for the ferric sulfate-montmorillonite occurs