Reflectance spectra of the surface of Mars exhibit a strong, broad feature at ~3 μm, which has been attributed to water and/or ice in the surface regolith material (e.g. 1,2). Additional, weak features in the martian surface spectra near 2.3 μm are difficult to interpret, but have been attributed to hydration as structural OH in phyllosilicate-like materials (e.g. 2). The strength and character of the hydration bands in spectra of the Martian surface are important to understanding the physical and compositional character of the surface and may also provide clues about the Martian environment. Spectral features due to hydration in clays have been discussed recently with an interest in understanding the hydration features on Mars (2,3,4). Sources of hydration in clays include structural OH in the octahedral layers, as well as strongly cation-bonded water and strongly self-bonded water in the interlayer region.

The wavelengths at which NIR and Mid-IR absorption features occur are related to the vibrational energy of molecular bonds in the material examined. The wavelengths of OH and H2O absorption in clays are influenced by the octahedral and interlayer cations, respectively (4). The strength of clay hydration bands in reflectance spectra is influenced as well by the type of cation in these sites. Variability in the strength of hydration features also depends on the packing pressure and particle size of the clay. Although the grain size of clays is usually very small, these grains cluster together and form larger aggregates. Absorption strength, and how light scatters in and around and through particles, is a complex function of grain size and aggregate size. As a result of the sensitivity of clays to these factors constant sample preparation techniques are essential for quantitative analysis of the spectral features.

Mixing with even a small amount of an opaque material can induce significant suppression of the hydration features in clays (5). The effects of an opaque component are demonstrated with mixtures of fine-grained SWy montmorillonite (~1.2 μm particle size) and small quantities of finely ground LCA101 carbon lampblack (< 0.23 μm particle size). Both materials form larger, physical aggregates which were greyed to < 125μm. Shown in Figure la (0.3 - 3.5 μm) and 1b (3.5 - 25 μm) are reflectance spectra of pure SWy montmorillonite, pure carbon and mixtures containing 0.1, 0.5, 2.0, and 5.0 wt % carbon. Spectra from 1.27 μm to 25 μm were measured in an H2O and CO2-purged environment relative to a rough gold standard using a Nicolet 740 FTIR. The infrared data were scaled to spectra measured with the RELAB spectrometer under ambient conditions using halon as a standard. Carbon darkens the clay spectra non-linearly: 0.1 wt % reduces the reflectance by about 40 %, and 5.0 wt % drops the reflectance to < 10 %. The clay hydration features at ~1.4, 1.9, 2.2 and 2.8 μm are substantially reduced with the addition of only 0.1 wt % carbon, and become no longer discernable with 5 wt % carbon (Figure 1a). The Mid-IR spectral character, including the 6 μm hydration feature, is increasingly diminished with increasing carbon content at wavelengths below the Christiansen feature, ~8 μm (Figure 1b). Although the reststrahlen features remain fairly weak in all of the spectra, they are slightly stronger for the 2 and 5 wt % C samples.

Hydration band intensity is also dependent on the kind of interlayer cation (4), since the size and polarizability of the cation affect the nature of the O-H bonds. The type of interlayer cation primarily influences the absorptions due to strongly cation-bonded interlayer H2O vibrations (4). The water stretching vibrations (νw, ~3 μm) overlap structural OH stretching vibrations (νOH, 2.75 μm) making resolution of either feature difficult. Fortunately, absorptions due to the water bending mode (δw, 6 μm) and the water combination (νw + δw, 1.9 μm) can be readily distinguished under low humidity conditions. Similarly, the 2.2 μm structural OH combination (νOH + δOH) can be readily determined when minimal adsorbed water is present.

Figure 2 shows both the 1.9 μm H2O combination and the 2.2 μm OH combination for natural (Na/Ca) SWy and Fe3+-, Ca- and Mg- exchanged forms of the clay. Fe3+, Ca and Mg were exchanged in the laboratory for the interlayer cations in SWy montmorillonite (4). The relative strengths of the 1.9 μm and 2.2 μm absorptions vary depending on the type of exchangeable cation. A correlation between the 1.9 μm absorption and the amount of adsorbed water is shown in Figure 3. A correlation of 0.85 is observed for the 1.9 μm band depth vs. amount of removable water for several cation-exchanged montmorillonites. Given the same low humidity environment, Fe- and Na-exchanged montmorillonite contain less removable water than do the Ca- and Mg- clays. This results in suppression of the interlayer water feature (1.9 μm) relative to the structural OH feature (2.2 μm) in the Fe-rich clay. Figure 4 illustrates the relative band depths of the 1.9 and 2.2 μm features for low moisture montmorillonites with several different interlayer cations. Ca- and Mg- samples give stronger interlayer H2O (1.9 μm) absorptions, while Fe- and Na- samples give stronger structural OH (2.2 μm) absorptions.

Conclusions. Hydration features in reflectance spectra of clays are dependent on the chemical environment of H2O and OH in the clay. Since clays have no other prominent features in the NIR past 1.3 μm, these hydration absorption features are readily discernable in pure clays. However, mixing masks the clay hydration features, especially mixing with materials that absorb strongly in the NIR. For this reason if clays are present on Mars, hydration features other than the ~3 μm absorption may be difficult to resolve.

Due to the ferric composition of Mars, clays formed there would be likely to have Fe3+ interlayer cations. Under low humidity conditions Fe3+-montmorillonite exhibits stronger hydration absorption features at 2.2 μm than at 1.9 μm. Thus a ferric montmorillonite in a low humidity environment, and with reduced spectral contrast, would show a 2.2 μm hydration feature preferentially to a 1.9 μm hydration feature. Recent detailed ISM spectral analyses of the bright regions on Mars reveal hydration features related to clays at 2.2 μm and probably at ~3 μm, but not at 1.9 μm (6,7).
HYDRATION BANDS: APPL. TO MARS;

J. L. Bishop & C. M. Pieters

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Figure 1a: SWy Montmorillonite-Carbon Mixtures

Figure 1b: SWy Montmorillonite-Carbon Mixtures


Figure 2: Variably exchanged SWy montmorillonite

Figure 3: Water Absorption vs Sample Moisture Content

Figure 4: Relative Hydration Band Depths

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