INFRARED SPECTROSCOPIC ANALYSES ON THE NATURE OF WATER IN MONTMORILLONITE

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Abstract—Interlayer cations and moisture content greatly influence the molecular vibrations of H_2O in montmorillonite as shown through reflectance spectroscopy in the infrared. The absorptions due to H_2O have been studied in montmorillonites exchanged with H, Na, Ca, Mg and Fe^{3+} interlayer cations under variable moisture environments. Band assignments have been made for absorptions in the 3 μm region due to structural OH vibrations, symmetric and asymmetric H_2O stretching vibrations and the H_2O bending overtone. Changes in the energies of the absorptions due to H_2O stretching vibrations were observed as the samples were dehydrated by reducing the atmospheric pressure. Absorptions near 3620 cm^{-1} and 3550 cm^{-1} have been assigned to water bound directly to cations (inner sphere) and surface-bonded H_2O and absorptions near 3450 cm^{-1} and 3350 cm^{-1} have been assigned to additional adsorbed water molecules. Band assignments have been made for combination bands in the near-infrared as well. Absorptions near 1.41 μm and 1.91 μm are assigned to bound H_2O combination bands, while the shoulders near 1.46 μm and 1.97 μm are assigned to combinations of additional H_2O molecules adsorbed in the interlayer regions and along grain surfaces.

Key Words—Montmorillonite, Spectroscopy, Water.

INTRODUCTION

These experiments were initiated to develop an understanding of the spectroscopic properties of smectites under variable environmental conditions that is necessary for the near infrared (NIR) and mid-range infrared (Mid-IR) geologic mapping of the Earth and Mars. Remote sensing measurements are made on these planets under a range of environmental conditions, requiring laboratory studies to determine the effects of environmental conditions on spectroscopic features in minerals and soils. The spectroscopic features due to water in smectites are sensitive to the cations present in the interlayer sites, as well as to the relative humidity of the sample environment, and are examined in detail in this study. Parallel laboratory studies of the influence of atmospheric pressure on the spectroscopic properties of montmorillonites containing hydrated ferric oxides, oxyhydroxides and sulfates prepared under a variety of chemical conditions (Bishop *et al* 1994) and the influence of atmospheric pressure and temperature on a few representative soils and chemically altered montmorillonites (Bishop and Pieters 1994) have been performed as well. Once the effects of the chemical environment on the interlayer water in model clays are better understood, it will possible to use the hydration bands measured via reflectance spectroscopy to gain information about the chemical composition and moisture content of clays in real systems. Developing a procedure for obtaining chemical and moisture information about surface soils from a remote perspective is especially useful in remote sensing of the Earth and Mars.

Reflectance spectroscopy is an effective tool, commonly used to study and characterize clay minerals (e.g., Lyon and Green 1975; Clark *et al* 1990; Bishop *et al* 1993; Post and Noble 1994). Many researchers have studied isolated spectroscopic features or either the near-infrared region or the mid-infrared region of smectites. However, as mentioned by Clark *et al* (1990), differences in the spectrometers or sample preparation often make it difficult to compare the spectral features from one study to another. For this reason spectra are measured here in the near-infrared to mid-infrared regions allowing the study of the spectroscopic features due to fundamental, overtone and combination vibrations in the same samples under the same environmental conditions with the same spectrometer.

Previous spectroscopic research on clays supports a complex system of interlayer water in montmorillonites (Fripiat *et al* 1960; Grim and Kulbicki 1961; Russell and Farmer 1964; Mortland *et al* 1963; Poinsignon *et al* 1978; Sposito and Prost 1982), including water that is bound to the interlayer surface, bound to interlayer cations, bound to other water molecules and adsorbed on the grain surfaces. The purpose of the study presented here is to examine several montmorillonite samples with different interlayer cations under variable moisture environments. The effects of these cations on the water molecules have been analyzed through infrared reflectance spectroscopy from 1–25 μm (10,000–400 cm^{-1}). By measuring the H_2O fundamental vibra-

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tions, as well as their combinations and overtones, correlated cation-water behavior has been observed. These absorptions due to water were measured in two experiments (a) where all samples were contained together in the same controlled, low-moisture environment and (b) where each sample was measured singly under reduced pressures, which resulted in dehydrating the samples. These experiments provide insights about the effects of cations and moisture on the vibrations of interlayer water in montmorillonite.

The focus of this work is on the infrared spectral features due to interlayer water in smectites and how these absorptions are influenced by cations in the interlayer sites. The infrared features near 1.4 μm ($\sim$7100 cm^{-1}), 1.9 μm ($\sim$5250 cm^{-1}), 2.7–3.0 μm (3700–3300 cm^{-1}) and 6.0 μm ($\sim$1630 cm^{-1}) are examined in detail here for cation-exchanged montmorillonite samples under variable moisture conditions. In order to study the effects of the interlayer cations on the energy and bandstrength of these molecular water features SWy-1 montmorillonite was exchanged with H^+, Na^+, Ca^{2+}, Mg^{2+} and Fe^{3+} cations.

BACKGROUND

Water in montmorillonite

Spectral hydration features in montmorillonite have been attributed to structural OH in the octahedral layer, water adsorbed on grain surfaces and water adsorbed or bound in the interlayer regions. The character of these interlayer water molecules is greatly dependent on the moisture level and the interlayer cations (Russell and Farmer 1964; Farmer and Russell 1971; Prost 1975, 1976; Cariati et al 1981, 1983a, 1983b; Sposito et al 1983; Bruckenthal 1987; Bishop et al 1993). These experiments suggest at least two kinds of interlayer water in smectites: water that is readily removable through drying or heating to $\sim$105°C, and water that is held more firmly. The firmly bound water molecules are thought to form the inner hydration sphere of the interlayer cations (water bound directly to cations), while the readily removable water consists of outer sphere water molecules H-bonded to each other in the interlayer region (Farmer and Russell 1971). The water molecules bound to the interlayer surfaces in montmorillonite have been predicted to have higher H-O-H stretching vibrations than bulk water (Low 1979, 1981), but it is not uniformly accepted that these "surface" bonded water molecules have significantly different H-O-H stretching vibrations than other highly H-bonded interlayer water molecules (Sposito et al 1983).

Molecular water vibrations

Infrared spectroscopy can be a useful tool for studying bonding of water molecules on surfaces. Water exhibits three vibrational modes: a symmetric stretch, an asymmetric stretch and an H-O-H bend. Eisenberg and Kauzmann (1969) assigned $\nu_1 \sim$ 3439 cm^{-1} (strong, broad), $\nu_3 \sim$ 3600 cm^{-1} (weak) and $2\nu_2 \sim$ 3200 cm^{-1}, where ν_1, ν_2 and ν_3 are distinct vibrational modes and $2\nu_2$ is the bending overtone. They explain the relatively weak absorption for ν_3 as a result of "intensity borrowing" by the $2\nu_2$ absorption, a process called Fermi resonance. Schultz (1957) studied H_2O vibrational modes through the use of D_2O and concentrated aqueous solutions of alkali halides. He observed molecular H_2O absorptions at ν_1 = 3460 cm^{-1}, ν_3 = 3612 cm^{-1} and $2\nu_2$ = 3261 cm^{-1} respectively. He found that ions affected these modes by polarization of the water molecules and distortion of the H_2O structure. Factors influencing these effects include ionic size, the magnitude of the ionic charge and other properties of the ion. Schultz (1957) also observed a decrease in the stretching frequencies corresponding to an increase in H-bonding of the H_2O molecule. Schultz and Horning (1961) found variations in the vibrational energies of the ν_1 and ν_2 H_2O modes as a function of type and concentration of several cations and anions. A shift toward lower energy with increasing water content has been observed in a H_2O stretching mode at 3420 cm^{-1} in Na-montmorillonite (Sposito and Prost 1982). This implies that H-bonding in H_2O of the montmorillonite system increases with increasing water content and that H-bonding is reduced in the interlayer H_2O of dehydrated montmorillonite. Bertie et al (1989) have also shown that the intensity of the H_2O stretching vibrations increases with increasing H-bonding.

The way that ions and H-bonding affect water molecules may be applied to clays to assist in assigning and deconvolving the complex interlayer water system. Poinsignon et al (1978) observed variability in the charge on the water proton as a function of polarizing power of the cation and the number of water molecules in the hydration shell. The influence of the polarizing power and adsorption isotherms of several cations on the spectral features due to water in montmorillonite are explored in this manuscript.

Molecular H₂O and structural OH absorptions

Infrared absorptions due to water in smectites were assigned by Russel and Farmer (1964) as follows: 3415 cm^{-1} to the H-O-H stretching vibration of H_2O readily lost upon heating, 3610 cm^{-1} to the H-O-H stretching vibration of firmly bonded H_2O, and 1630–1640 cm^{-1} to the H-O-H bending vibration. The infrared absorptions due to structural OH in montmorillonite include the O-H stretching vibration at 3632 cm^{-1} and in-plane librations at 915–950, $\sim$890 and $\sim$840 cm^{-1} due to Al_2OH, $Fe^{3+}AlOH$ and MgAlOH (Farmer 1974, pp. 335, 339, 349). Infrared spectroscopic studies of smectites having variable octahedral site compositions have shown related shifts in the spectral features at 2.2 μm ($\sim$4500 cm^{-1}) and 10–12 μm (950–850 cm^{-1}) due to

structural OH species (Bishop *et al* 1993). Although spectral features near 2.2 μm, 2.7 μm and 11 μm are diagnostic of structural OH in aluminous clays and can be observed remotely, they are not the focus of this manuscript.

Prost (1975, 1976) studied the character of smectite hydration features using transmission infrared spectroscopy on thin films of hectorite. Farmer and Russell (1971) found the infrared absorptions of molecular water in montmorillonite and hectorite to be remarkably similar. They attributed this to the fact that both have octahedral cation replacements, rather than tetrahedral cation replacements as in saponite and vermiculite. These smectites have slightly different infrared absorptions from those of montmorillonite and hectorite as a result of a difference in the distribution of negative charge on the interlayer siloxane surfaces (Farmer 1974, 1978). Spectral analyses of water features in hectorite thus provide a good background for understanding the spectral features due to water in montmorillonite.

Prost (1975) measured infrared spectra in the fundamental region of several cation-exchanged hectorites with a variety of water contents for each sample. These spectra show multiple absorptions between 3630 cm^{-1} and 3400 cm^{-1} due to H-O-H stretching vibrations for interlayer water and an absorption at ~3290 cm^{-1} which has been assigned to an overtone of the H$_2$O bending vibration (Eisenberg and Kauzmann 1969; Schultz 1957). There is also evidence for two H$_2$O bending vibrations, which vary depending on the interlayer cation (Prost 1975, 1976). An absorption occurs near 1625–1630 cm^{-1} in the very dry hectorites of his study and near 1635 cm^{-1} for some samples containing more water. In another study Prost and Chaussidon (1969) reported bands at 3630, 3545, 3460, 3405 and 3290 cm^{-1} for K-hectorite cooled to −95°C.

Both symmetric and asymmetric H$_2$O stretching vibrations are predicted in this region (3700 to 3300 cm^{-1}, ~3 μm) from group theory and vibrational symmetry (Schultz 1957). Based on these theories two stretching vibrations (ν_3 and ν_1) should be observed for each kind of H$_2$O in the clay system. Further analyses of published hectorite spectra (Prost 1975) coupled with new spectral experiments on montmorillonite should provide additional information about the symmetric and asymmetric H$_2$O modes in the 3 μm region.

The interlayer cations and the moisture content have been shown to influence the H$_2$O bending mode ν_2 near 6 μm in smectites (Prost 1975, 1976; Johnston *et al* 1992). Prost (1975) observed a spectral absorption centered near 1625 cm^{-1} for thin films of hectorite at 0% relative humidity and an absorption near 1635 cm^{-1} for thin films of hectorite at 0 to 50% relative humidity. Johnston *et al* (1992) observed a shift in this vibration from 1640 cm^{-1} to 1630 cm^{-1} in films of Na-montmorillonite as the water content was decreased from 7 to 2 H$_2$O molecules per Na$^+$ cation. Prost (1975) and

Johnston *et al* (1992) also observed an increase in the intensity of this ν_2 band as the water content in the smectite films increased.

Reflectance spectroscopy has also been used to study the near infrared combination bands in montmorillonite by varying the interlayer cations and the sample moisture content. Cariati *et al* (1981) noticed differences in the shape of the absorptions at ~7100 cm^{-1} (1.4 μm) and ~5250 cm^{-1} (1.9 μm) for montmorillonites with low and high moisture contents. Further work by Cariati *et al* (1983a, 1983b) supports the hypothesis of distinct vibrational energies for two kinds of interlayer water. They assigned the absorptions at 1.41 μm and 1.91 μm to combinations of the stretching and bending fundamental modes for H$_2$O with weak H-bonding, and the absorptions near 1.46 μm and 1.97 μm to combination modes for H$_2$O with stronger H-bonding. Cariati *et al* (1981, 1983a, 1983b) have assigned a combination of the stretching mode plus two bending modes for the absorptions observed near 1.4 μm, and a combination of the stretching mode plus one bending mode for the absorptions observed near 1.9 μm. Cariati and co-workers based their band assignments on those for water by Herzberg (1945). Sposito *et al* (1983) assigned absorptions at 1.41 μm and 1.46 μm to overtones of the stretching modes for adsorbed H$_2$O. Sposito and co-workers based their band assignments on those for water by Buijs and Choppin (1963), who assigned a band at 7040 cm^{-1} (1.42 μm) to a combination of $\nu_1 + \nu_3$ for H$_2$O in NaClO$_4$ solutions. Based on analyses of band shifts with H-bonding, Buijs and Choppin (1963) stated that all strong bands below 2.5 μm in the spectrum of liquid water are combination bands, not overtones. Many spectroscopic studies of clay minerals have assigned the 1.4 μm feature to an overtone of the H$_2$O stretching mode, perhaps because they have confused this feature with the structural OH overtone, also near 1.4 μm.

Coyne *et al* (1990a) applied near infrared reflectance analysis (NIRA), which involves correlating % H$_2$O with absorbance and second derivative absorbance values. Coyne and coworkers (Coyne *et al* 1990b) confirmed the concept of two kinds of interlayer water by showing a good statistical correlation for % H$_2$O with spectral absorbance and second derivative absorbance at ~1.91 μm for a suite of low humidity montmorillonites, while a good correlation occurs at ~1.96 μm for the same group of samples in a high humidity environment. Both the low moisture and high moisture correlations are dependent on the type of interlayer cation.

EXPERIMENTAL METHODS

Cation exchange procedure

H$^+$-, Na$^+$-, Ca^{2+}-, Mg^{2+}- and Fe^{3+}-montmorillonites have been prepared by chemically exchanging the

natural mixture of Na^+ and Ca^{2+} interlayer cations in SWy-1 montmorillonite obtained from the Clay Minerals Society, Source Clay Minerals Repository. The exchange reactions are based on a procedure developed by Banin (Banin and Rishpon 1979) and are described in detail elsewhere (Bishop 1994). In summary, the montmorillonite samples were washed with dilute HCl to exchange the naturally present interlayer cations with H^+, which is readily replaced by other cations when a dilute metal chloride solution is added in the presence of anion exchange resin in OH^- form. Moisture is removed from the clay solutions through centrifugation and then lyophilization. The dried clay is then ground gently using a mortar and pestle. Observations under a microscope showed tiny clay particles ~0.5–2 μm clustered together in variably-sized aggregates. Each sample was dry sieved to <45 μm aggregate size. Compositional data determined through XRF analyses for these exchanged montmorillonites is given in Bishop (1994).

Spectral measurements

Reflectance spectra were measured relative to a rough gold surface using a Nicolet 740 FTIR in a H_2O- and CO_2-purged environment. A PbSe detector was used from 0.9 μm–3.2 μm and a DTGS detector from 1.8 μm–25 μm. A triangular apodization function was used in both regions. The sample chamber is an Auto-COLLECTOR *Intelligent Controller* (Version 1.00), including a remotely controlled sample train with multiple sample positions, and was purchased from Spectra-Tech. The spectral resolution was 2 cm^{-1} for the spectra measured in the SpectraTech sample chamber. 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 spectra were measured relative to Halon from 0.3–3.6 μm using an InSb detector under ambient conditions with the bi-directional RELAB (reflectance experiment laboratory) spectrometer at Brown University. A detailed description of this instrument is provided in Mustard and Pieters (1989). The bi-directional spectrometer allows for variable illumination (i) and emergence (e) angles. Spectra included here were measured at i = 30° and e = 0°. The sample dish is rotated during the measurement to eliminate orientation effects.

Samples were dried over Drierite, then prepared in sample dishes (diameter = 12 mm, depth = 3 mm) (a) with constant packing texture and (b) with constant density for comparison. Constant density samples were prepared by forcing 0.28 g clay into sample dishes of the same volume. This caused variable degrees of alignment and orientation of the clay particles among the different samples because the force required to fit 0.28 g in the dishes varied. Constant packing texture samples were prepared by filling the dish with sifted clay,

tapping the dish gently on the counter and repeating until the dish remained full. These samples were also weighed.

The spectral differences as a result of constant density and constant packing texture preparations are shown in Figure 1 for the absorptions at 1.9 and 2.2 μm in natural Swy montmorillonite for three aggregate sizes: <45 μm, (45 μm–75 μm), (75 μm–125 μm). The spectra of samples prepared according to the constant packing texture method (Figure 1a) show a regular pattern of increasing band depths with increasing aggregate size. This is the expected result, since absorption bands in minerals are known to increase and broaden with particle size (e.g., Pieters 1983). As seen in Figure 1b spectra of samples prepared with constant density for the three size fractions showed variable band strengths, different from the expected order. Therefore, the constant packing texture procedure is recommended for quantitative analysis of band strengths in reflectance spectra of particulate samples. This technique was used for sample preparation in the reflectance experiments presented here.

Variable moisture experiments

Reflectance spectra were also measured under controlled atmospheric pressure conditions using an environmental chamber attachment (for the Nicolet 740 FTIR) built by Connecticut Instruments. Reflectance spectra were measured for each sample under ambient pressure and then again at several increments under reduced atmospheric pressures. Care was taken to deflect the IR beam during pressure adjustment to avoid additional heating of the sample. Dry conditions (i.e., most of the unbound water was lost) were achieved under pressures in the range 10 mm Hg to 0.1 mm Hg. The spectral resolution was 4 cm^{-1} for the spectra measured in the environmental sample chamber.

Thermal gravimetric analyses

Thermal gravimetric analyses were performed to examine the influence of interlayer cations on the character of interlayer water in montmorillonite. To ensure the presence of the more readily removable water the montmorillonite samples were placed in a desiccator over a saturated $Ca(NO_3)_2$ solution (~50% RH) for several weeks prior to measurement. Thermal gravimetric analysis (TGA) using a DuPont 951 Thermogravimetric Analyzer involved placing ~20 mg montmorillonite in a small Al basket in the apparatus. The sample mass was then recorded as the temperature was increased with a scan rate of 1°C/min.

RESULTS

Band assignments

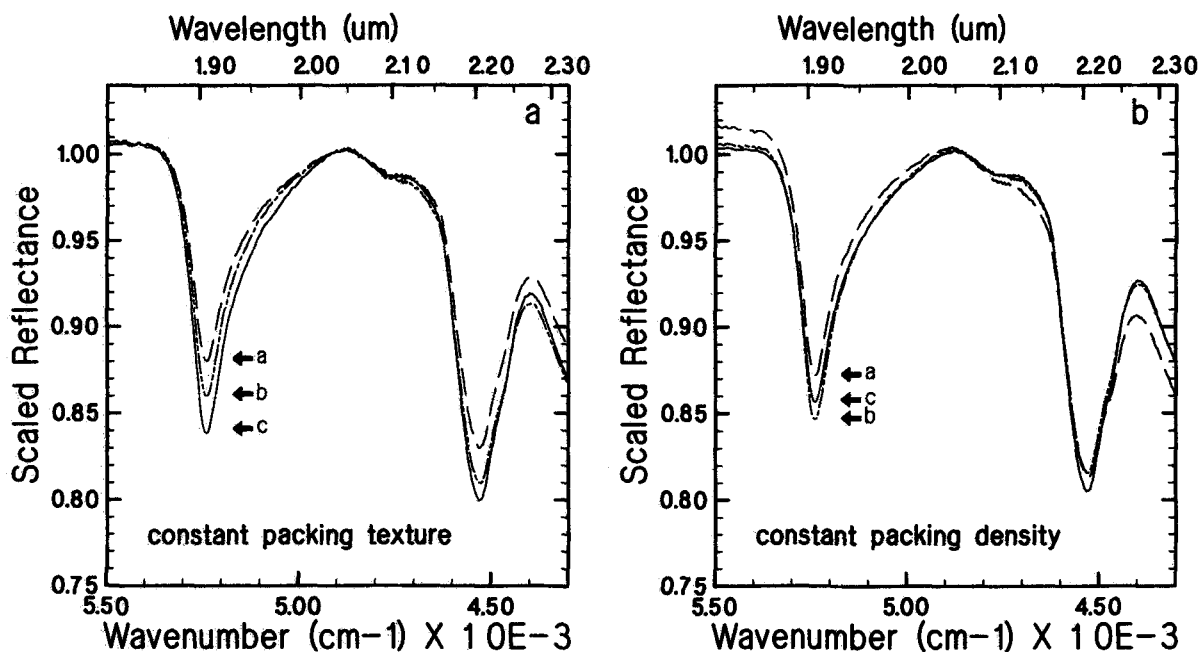The reflectance spectrum of natural SWy montmorillonite is shown in Figure 2 from 0.3–25 μm. The

Figure 1.   Reflectance spectra of SWy montmorillonite: 5500 cm^{-1} to 4300 cm^{-1} ($\sim$1.8–2.3 μm): a) constant packing texture, b) constant packing density. Samples prepared in dishes according to either the constant packing texture or the constant packing density method. These spectra are for samples dry sieved to (a) <45 μm, (b) 45–75 μm and (c) 75–125 μm. The constant packing texture preparation gives spectral bands that increase with increasing aggregate size, while the constant packing density preparation gives variable, unrelated spectral band depths.

portion of the spectrum from 0.3–1.2 μm was measured under ambient conditions using the bi-directional spectrometer. The portion of the spectrum at wavelengths longer than 1.2 μm was measured under CO$_2$- and H$_2$O-purged conditions using the Nicolet FTIR. Fundamental vibrations for H$_2$O in montmorillonite are shown at $\sim$3 μm (ν_w) and 6 μm (δ_w), and combination bands are shown near 1.4 μm and 1.9 μm. Spectral absorptions due to structural OH are labeled ν_{AlOH} for stretching and δ_{AlOH} for bending vibrations. The fundamental OH bands were assigned by Farmer (1974) and the combination and overtones by Cariati *et al* (1981) and Sposito *et al* (1983).

Fundamental vibrations of interlayer water

The 3 μm spectral region for smectites is crowded with a number of overlapping features. The absorptions due to H$_2$O stretching vibrations are labelled ν_w and those due to H$_2$O bending vibrations are labelled δ_w in Figure 2. These vibrations correspond to the ν_1, ν_2 and ν_3 assignments commonly used in spectroscopic analyses of water. In order to study the features due to fundamental stretching vibrations of interlayer water it is necessary to isolate the feature due to structural OH (labelled ν_{AlOH} in Figure 2). One method of distinguishing the features due to interlayer water involves varying the quantity of interlayer water molecules. Reflectance spectra spanning the 3 μm region are shown

in Figure 3 for montmorillonites with variable amounts of interlayer water molecules. Spectra of SWy montmorillonite exchanged with Mg^{2+}, Ca^{2+}, Na$^+$, H$^+$ and Fe^{3+} are displayed together in Figure 3 to facilitate comparison of the influences these cations have on the spectral features near 3 μm. The bottom spectrum in each set was measured under 1 bar atmospheric pressure conditions and shows the strongest water features. The spectra having progressively weaker water features were measured under reduced atmospheric pressures, down to $\sim$1 mm Hg.

There are also multiple absorptions comprising the 6 μm spectral absorption in smectites. Reflectance spectra are shown in Figure 4 of the bending fundamental vibrations of interlayer water near 6 μm for the homoionic Mg^{2+}-, Ca^{2+}-, Na$^+$-, H$^+$- and Fe^{3+}-exchanged SWy montmorillonite. The spectra measured under 1 bar atmospheric pressure ("moister" conditions) show a broad asymmetric absorption with a band minimum near 1635 cm^{-1} (6.12 μm). A shift in the band center toward lower energies (longer wavelengths) can be observed in the spectra of each sample as the sample is dehydrated. The spectra measured under dehydrated conditions (low atmospheric pressure) show two separate absorptions near 1730 cm^{-1} (5.78 μm) and 1625 cm^{-1} (6.15 μm). The band centers for this 6 μm feature are listed in Table 1 for each of the exchanged montmorillonite samples under moist and dry conditions.
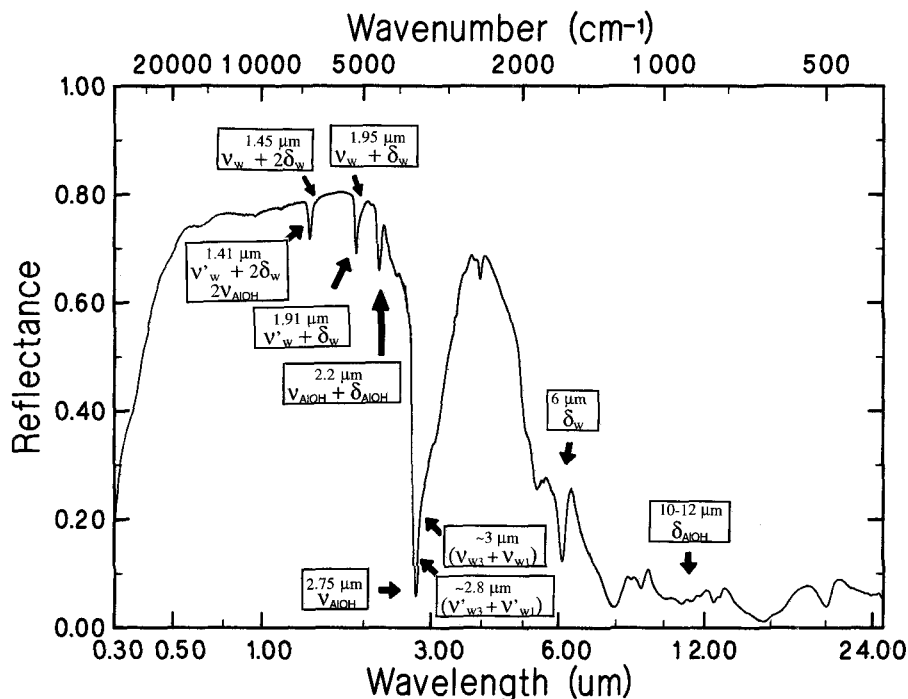
Figure 2. Reflectance spectrum of SWy montmorillonite (0.3–25 μm). Infrared reflectance spectra of montmorillonite exhibit absorptions due to interlayer H_2O and structural OH. Stretching vibrations are labeled with ν, bending vibrations with δ. The subscripts W and OH refer to molecular water in the interlayer region and structural OH respectively. Stretching vibrations due to inner sphere (bound) H_2O are indicated by ν' and those due to adsorbed H_2O are indicated by ν. The wavelength scale is nonlinear in order to display features throughout a broader range of the infrared spectrum. Both the strengths and energies of these absorptions are sensitive to the chemical environment of the H_2O molecules. For instance, the polarizing power of the interlayer cations influences the H_2O vibrational energies, and the adsorption isotherms for the interlayer cations influence the number of bound H_2O molecules per cation in the interlaminar spaces.

Near infrared vibrations of interlayer water

Figure 5 includes reflectance spectra from 1.3 to 3.3 μm measured both under dry, purged conditions using the Nicolet and under moist, ambient conditions using the bi-directional spectrometer. These spectra are presented here to illustrate the changes in both the intensity and shape of the hydration bands as a function of the sample moisture environment. The spectra measured under dry, purged conditions contain weak features at 1.41 μm, 1.91 μm and 2.2 μm, a strong feature at 2.75 μm, and a broad feature near 3 μm. The spectrum measured under ambient conditions exhibits more prominent features at 1.41 μm and 1.91 μm, and shoulders at 1.46 μm and 1.97 μm. The water features near 3 μm are also significantly stronger.

The band minima at 1.41 μm and 1.91 μm vary with the interlayer cation and moisture content of montmorillonite. The band centers of these features are listed in Table 2 for montmorillonites exchanged with Na, Ca, Mg and Fe^{3+} cations measured under ambient and H_2O-purged moisture conditions. For spectra measured under ambient moisture conditions the band center at 1.41 μm varies 17 cm^{-1} with these interlayer cations, while the spectra measured under H_2O-purged

conditions show only 6 cm^{-1} difference as a function of interlayer cation. Band center variation at 1.91 μm was about the same (12–14 cm^{-1}) for spectra measured under ambient and H_2O-purged conditions.

Thermal gravimetric analyses

Thermal analysis profiles are shown in Figure 6 for the Na-, Ca-, Mg- and Fe^{3+}-exchanged montmorillonites. Temperature is depicted across the horizontal axis and the amount of water lost during heating is indicated vertically. Water loss varied depending on the interlayer cation, producing a trend of increasing water content as follows: $Na^+ < Fe^{3+} < Ca^{2+} < Mg^{2+}$. This is comparable to adsorption isotherm trends observed for Na^+ and Ca^{2+} montmorillonites (Hall and Astill 1989) and for Na^+, Ca^{2+} and Mg^{2+} hectorites (Prost 1975), where the amount of water absorbed by a given smectite varies with the type of interlayer cation and the relative humidity.

Polarizing power of the interlayer cations

A rough estimate of the polarizing power of the cations was calculated by dividing the charge on the cation by the radius of the hexa-coordinated metals. This approximate polarizing power increases from Na^+ (0.86

Wavelength (um)
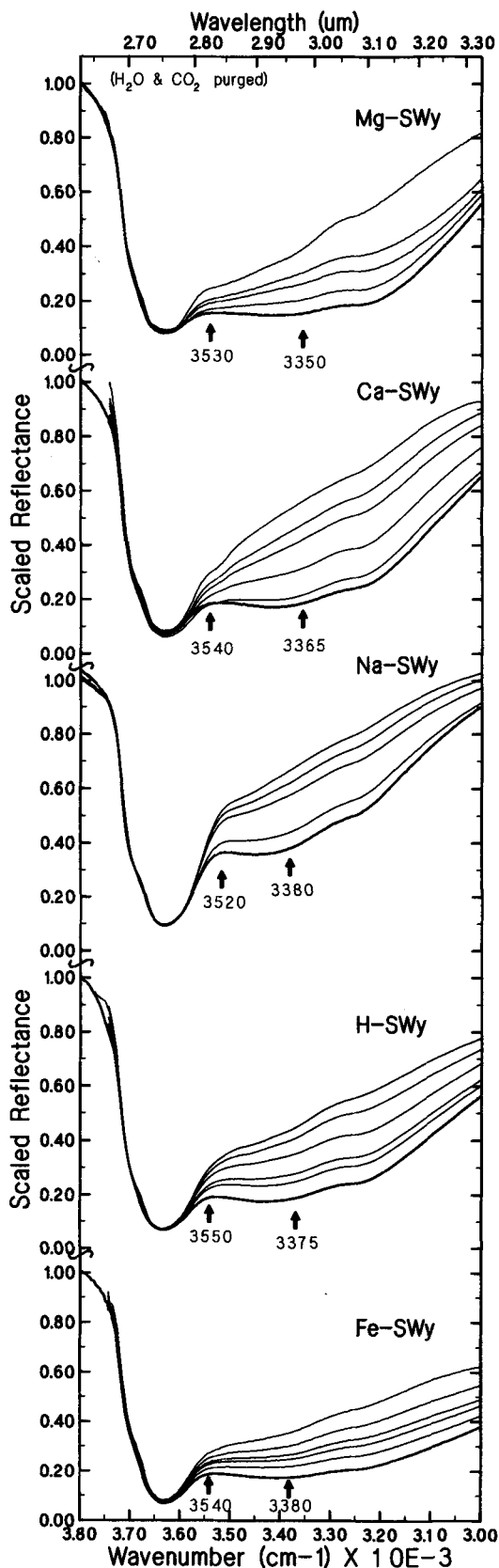
charge/Å) to Ca^{2+} (1.75 charge/Å) to Mg^{2+} (2.33 charge/Å) to Fe^{3+} (3.82 charge/Å). (H behaves in a different manner.)

DISCUSSION

Band assignments

Fundamental vibrations. Structural OH absorptions can be identified in Figure 3 at 3680 cm^{-1} (2.71 μm) and 3630 cm^{-1} (2.75 μm) because they are independent of the kind of interlayer cation or the amount of interlayer water. The shoulder near 3680 cm^{-1} is within the range 3680–3690 cm^{-1}, the value assigned for structural OH in hectorite (Prost 1975), and may be a result of OH bound to cations other than Al in the octahedral layers.

Based on the work of Schultz (1957), Cariati *et al* (1981) and Sposito and Prost (1982) qualitative reasoning about the relative vibrational energies of H_2O in montmorillonite can be made. Under dehydrated conditions, when most of the interlayer water is bound to cations or the interlayer surface, the spectral absorptions due to H_2O stretching vibrations in montmorillonite are expected at higher energies (shorter wavelengths) than similar absorptions when more water is present. The asymmetric H_2O stretching mode (ν_3) has been assigned at a higher energy (shorter wavelength) than the symmetric H_2O stretching mode (ν_1) for bulk water (Eisenberg and Kauzmann 1969) and for water containing alkali halides (Schultz 1957). A general trend can, therefore, be expected for the H_2O stretching vibrations in montmorillonite. The vibrational energy should decrease from the asymmetric bound H_2O stretch (ν_3') to the symmetric bound H_2O stretch (ν_1') to the asymmetric adsorbed H_2O stretch (ν_3) to the symmetric adsorbed H_2O stretch (ν_1), which would have the lowest energy vibration. Specific band assignments for these features are described in detail in this section and are summarized in Table 3.

Subtle variations along the long-wavelength (lower energy) shoulder of the 2.75 μm OH absorption are readily observable in Figure 3 as a function of moisture. A H_2O stretching mode has been assigned near 3610–3630 cm^{-1} in montmorillonite (Farmer and Russell 1971) and in hectorite (Prost 1975). Since the asymmetric stretching vibration in bulk water occurs near 3600 cm^{-1} (Eisenberg and Kauzmann 1969), the spectral features near 3610–3630 cm^{-1} in montmorillonite should be due to the asymmetric H_2O vibration as well.

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Figure 3. Reflectance spectra of variably cation-exchanged SWy montmorillonites: 3800 cm^{-1} to 3000 cm^{-1} (2.65–3.3 μm). Spectra are shown here as a function of sample moisture content for SWy montmorillonite exchanged with Mg, Ca, Na, H and Fe^{3+} cations in the interlayer regions. The bottom spectrum (bold) in each set was measured under 1 bar atmospheric pressure conditions and shows the strongest water features. The spectra having progressively weaker water features were measured under reduced atmospheric pressures.
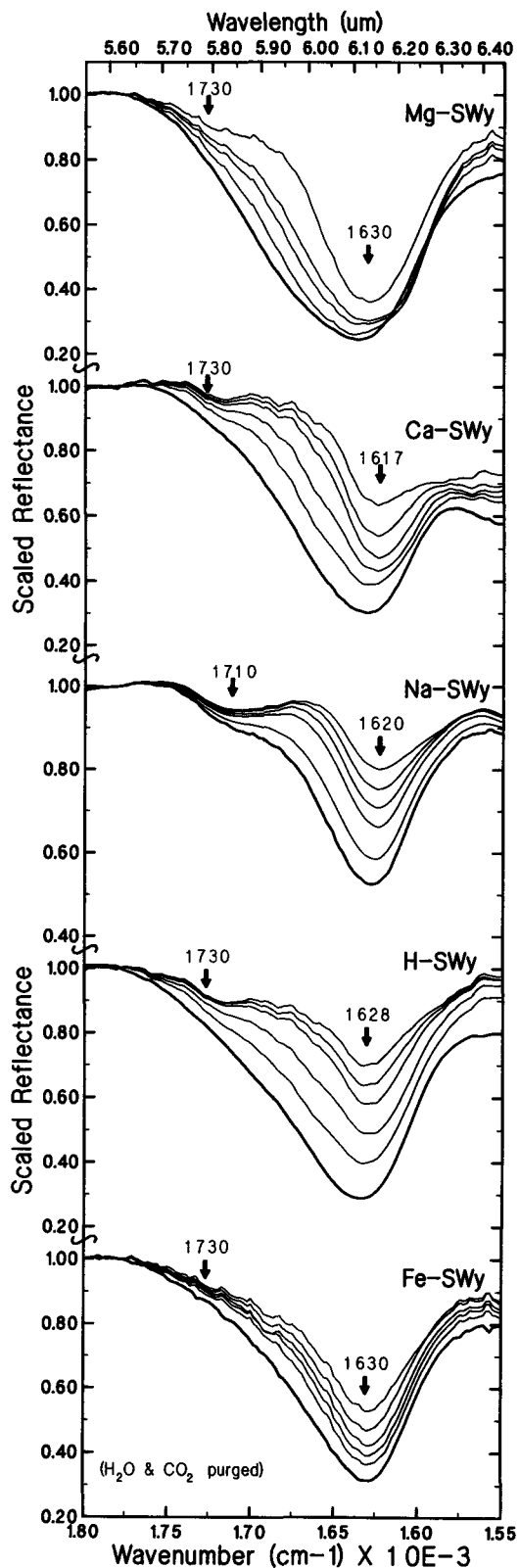
Table 1. ν_1 and ν_2 vibrational modes for interlayer water in montmorillonite.

Cation	ν_1 (cm^{-1})		ν_2 (cm^{-1})	
	Bound	Adsorbed	Dehydrated	Ambient
Na$^+$	3520	3380	1620	1630
Ca^{2+}	3540	3365	1617	1629
Mg^{2+}	3530	3350	1630	1640
H$^+$	3550	3375	1628	1636
Fe^{3+}	3540	~3380	1630	1633

The band centers for these spectral features were derived by finding the reflectance minimum from the data file and by taking first derivatives of the reflectance spectra. The bound ν_2 H_2O vibrations are near those listed under "dehydrated" and the adsorbed ν_2 H_2O vibrations occur at higher energies, shifting the band centers towards those listed under "ambient."

Poinsignon et al (1978) assigned an asymmetric H_2O stretching mode at 3620 to 3640 cm^{-1} for hectorites exchanged with several interlayer cations. They found no change in this band for Li$^+$-hectorite under low moisture conditions ranging from 1 to 3 H_2O molecules per Li$^+$ cation.

Analysis of the reflectance spectra shown in Figure 3 and the relative spectra shown in Figure 7 indicate that there are absorptions near 3550 cm^{-1} in montmorillonite under dry conditions and near 3400 cm^{-1} in montmorillonite under moist conditions. Prost (1975) observed a similar change for hectorite under low humidity and high humidity conditions. These are likely due to ν_1 absorptions of bound H_2O molecules (inner sphere and surface-bonded) near 3550 cm^{-1} and H_2O molecules in outer solvation shells near 3400 cm^{-1}. Under extremely dry conditions only the bound H_2O absorptions near 3550 cm^{-1} are observed, whereas under more moist conditions both absorptions are present. Poinsignon et al (1978) assigned a symmetric H_2O stretching mode at 3560 to 3580 cm^{-1} for hectorites exchanged with several interlayer cations under low moisture conditions. Under high relative humidity conditions (see Figure 5) the absorption near 3420 cm^{-1} (2.92 μm) becomes much more prominent. Eischens and Pliskin (1958) and Kiselev and Lygin (1962) found differences in the infrared spectra of physisorbed and chemisorbed molecules, which suggests that there should be differences between bound and adsorbed water in montmorillonite.

←

Figure 4. Reflectance spectra of variably cation-exchanged SWy montmorillonites: 1800 cm^{-1} to 1550 cm^{-1} (5.6–6.4 μm). Spectra are shown here as a function of sample moisture content for SWy montmorillonite exchanged with Mg, Ca, Na, H and Fe^{3+} cations in the interlayer regions. The bottom spectrum (bold) in each set was measured under 1 bar atmospheric pressure conditions and shows the strongest water features. The spectra having progressively weaker water features were measured under reduced atmospheric pressures.
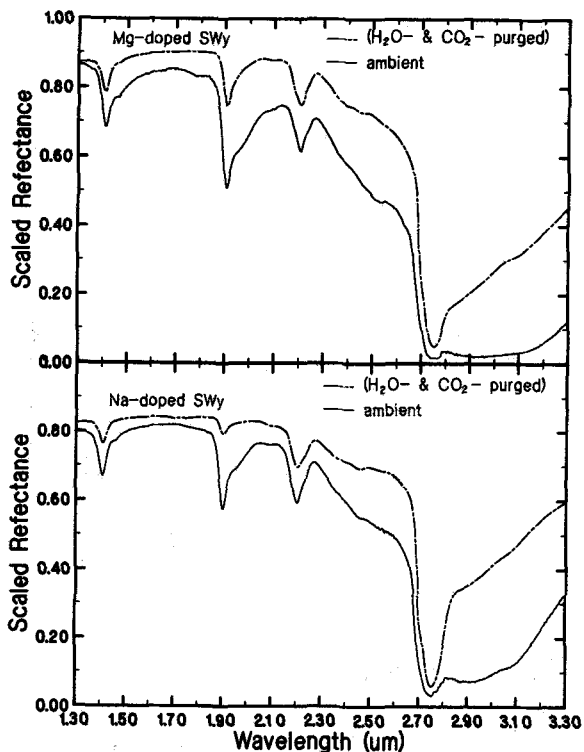
Figure 5. Reflectance spectra of SWy montmorillonites: 1.3 μm to 3.3 μm (7700–3000 cm⁻¹). Spectra are shown for (a) Mg-exchanged and (b) Na-exchanged SWy measured under ambient and dry (H_2O- and CO_2-purged) conditions.
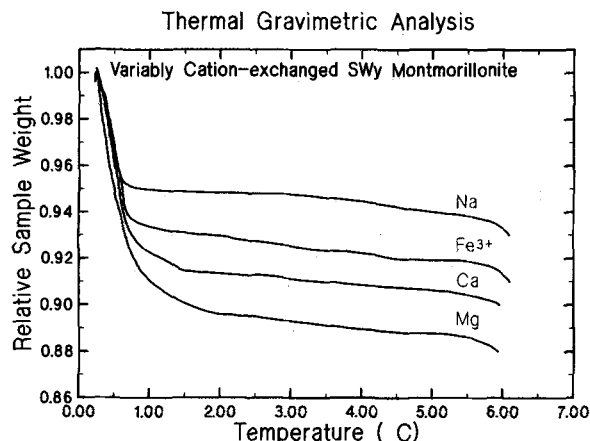

Figure 6. Thermogravimetric analyses of variably cation-exchanged SWy montmorillonites (relative sample weight versus temperature). The amount of water lost increased from Na- to Fe^{3+}- to Ca- to Mg-exchanged SWy.

The spectral absorptions due to ν_3 and ν_1 studied here exhibit changes in the region ~3600 cm⁻¹ to ~3300 cm⁻¹ depending on the type of interlayer cation in addition to the moisture conditions of the sample. To facilitate finding the band minima for these absorptions the spectra were examined in several forms. The ν_3 and ν_1 absorptions have been assigned by evaluating the reflectance spectra, relative reflectance spectra, first and second derivatives of these spectra, and also previous experiments (Farmer and Russell 1971; Prost 1975). There are absorptions near 3520–3550 cm⁻¹ and 3400–3350 cm⁻¹ in each sample, which have been assigned to ν_1 under dehydrated and moist con-

Table 2. Near-infrared band centers for homoionically exchanged montmorillonite.

| | 1.41 μm | | 1.91 μm | |
Cation	Ambient (cm⁻¹)	H_2O-purged (cm⁻¹)	Ambient (cm⁻¹)	H_2O-purged (cm⁻¹)
Na^+	7097	7092	5256	5246
Ca^{2+}	7092	7088	5249	5231
Mg^{2+}	7080	7086	5242	5234
Fe^{3+}	7087	7090	5247	5243

The band centers for these spectral features were derived by finding the reflectance minimum from the data file and by taking first derivatives of the reflectance spectra.

ditions, respectively. An additional absorption is observed near 3450 cm⁻¹ under moist conditions and has been assigned to ν_3 vibrations of outer sphere H_2O molecules.

The final absorption in this region occurs near 3230 cm⁻¹ (3.1 μm) and is assigned to an overtone of the water bending vibration, $2\nu_2$. A band in this region was previously observed near 3200 cm⁻¹ in thin films of saponite (Farmer and Russell 1971) and at 3290 cm⁻¹ in low temperature (−95°C) spectra of thin films of hectorite (Prost and Chaussidon 1969). In reflectance spectra of each of the homoionically-exchanged montmorillonites in Figure 3 a shoulder is observed near 3230 cm⁻¹ that decreases in intensity as the water content is decreased. The relative reflectance spectra of Ca-montmorillonite in Figure 7 illustrate more clearly the spectral changes near 3230 cm⁻¹ as a function of water content, indicating the presence of a vibrational mode near 3230 cm⁻¹.

Near-infrared vibrations. The absorptions near 1.9 μm in reflectance spectra of Mg-montmorillonite and Na-montmorillonite in Figure 5 exhibit significant differences as a result of the sample moisture environment. The samples measured under a H_2O-purged environment exhibit a slightly asymmetric peak centered at 1.91 μm. The same samples measured under moist conditions exhibit a much stronger feature at 1.91 μm and a strong shoulder at 1.97 μm. The peak at 1.91 μm in dehydrated montmorillonite is therefore due to H_2O that is most tightly bound in the montmorillonite (inner sphere and surface-bonded H_2O), while the shoulder near 1.97 μm is due to adsorbed H_2O that is present under moist conditions. Similar changes in this feature were observed by Cariati *et al* (1981) for reflectance spectra of Ca-bentonite measured under moist conditions and then after heating to 250°C. The spec-

Table 3a. Previous band assignments for water and structural OH in montmorillonite.

Wavenumber (cm^{-1})	Wavelength (μm)	Vibrations	Source
7090	**1.410**	H_2O stretch X 2	montmorillonite[7]
7087	**1.411**	H_2O stretch + 2 bend (H-bonded to surface)	hectorite[8]
6868	**1.456**	H_2O stretch + 2 bend (H-bonded to H_2O)	Ca-bentonite[8]
6872	**1.455**	H_2O stretch + 2 bend (H-bonded to H_2O)	hectorite[8]
6850	**1.460**	H_2O stretch X 2 (sh)	montmorillonite[7]
5076	**1.970**	H_2O stretch + bend (H-bonded to H_2O)	Ca-bentonite[8]
5236	**1.910**	H_2O stretch + bend (H-bonded to surface)	Ca-bentonite[8]
5130	**1.949**	H_2O stretch + bend (sh)	montmorillonite[7]
5250	**1.905**	H_2O stretch + bend	montmorillonite[7]
4533	**2.206**	OH stretch + bend	Ca-bentonite[8]
4535	**2.205**	OH stretch + bend (Al_2-OH)	montmorillonite[7]
4510	**2.217**	OH stretch + bend (AlFe-OH)	montmorillonite[7]
4480	**2.232**	OH stretch + bend (AlMg-OH)	montmorillonite[7]
3632	**2.75**	OH stretch	montmorillonite[4]
3640	2.75	asymmetric H_2O stretch	Li-hectorite[9]
3580-3610	~2.8	symmetric H_2O stretch	Li-hectorite[9]
3610	2.77	H_2O stretch (high-frequency)	montmorillonite[3]
3415	2.93	H_2O stretch (low-frequency)	montmorillonite[3]
~**3630**	2.75	H_2O stretch	hectorite[5]
~**3570**	2.81	H_2O stretch (0% RH)	hectorite[5]
3390-3420	~2.9	H_2O stretch (0 to 50% RH)	hectorite[5]
3630	2.75	H_2O stretch	montmorillonite ($-95°C$)[6]
3545	2.82	H_2O stretch	montmorillonite ($-95°C$)[6]
3460	2.89	H_2O stretch	montmorillonite ($-95°C$)[6]
3405	2.94	H_2O stretch	montmorillonite ($-95°C$)[6]
3439	2.91	ν_1	bulk H_2O[1]
3460	2.89	ν_1	alkali-saturated H_2O[2]
~**3600**	~2.78	ν_3	bulk H_2O[1]
3612	2.77	ν_3	alkali-saturated H_2O[2]
3290	3.04	2 X bend	montmorillonite ($-95°C$)[6]
~**3200**	~3.1	$2\nu_2$	bulk H_2O[1]
3261	3.07	$2\nu_2$	alkali-sat. H_2O[2]
1625-1630	~6.1	H_2O bend	hectorite (dehydrated)[5]
1635	~6.1	H_2O bend	hectorite (more water)[5]
1633-1653	~6.1	ν_2	alkali-saturated H_2O[2]
915-950	10.5-10.9	OH bend (Al_2-OH)	montmorillonite[4]
918	10.9	OH bend (Al_2-OH)	montmorillonite[7]
~**890**	11.2	OH bend (AlFe-OH)	montmorillonite[4]
885	11.3	OH bend (AlFe-OH)	montmorillonite[7]
~**840**	11.9	OH bend (AlMg-OH)	montmorillonite[4]
851	11.75	OH bend (AlMg-OH)	montmorillonite[7]

Note: band assignments in bold were reported, others were calculated from the reported value.

[1] Eisenberg and Kauzmann (1969), [2] Schultz (1957), [3] Russel and Farmer (1964), [4] Farmer (1974), [5] Prost (1975), [6] Prost and Chaussidon (1969), [7] Sposito *et al* (1983), [8] Cariati *et al* (1981, 1983a, 1983b), [9] Poinsignon *et al* (1978).

tral absorptions near 1.9 μm are assigned to a combination of the H_2O stretching and bending modes (Cariati *et al* 1981, Sposito and Prost 1982).

The spectra of Mg-montmorillonite and Na-montmorillonite in Figure 5 show that the feature at 1.41 μm becomes sharper and more symmetrical under dehydrated conditions and that the shoulder near 1.46 μm becomes much stronger under moist conditions. The spectral character of the features near 1.4 μm and 1.9 μm parallel each other as the relative humidity of the sample environment is increased from 4% to 98%: the shoulders at 1.46 μm and 1.97 μm become stronger, and eventually dominate the spectral absorptions near 1.4 μm and 1.9 μm for particulate montmorillonites that have adsorbed sufficient moisture to form a paste

(Bishop 1988). Because of this strong similarity in behavior of the features near 1.4 μm and 1.9 μm they should be assigned similarly to combinations of the H_2O stretching and bending modes, where the absorptions near 1.4 μm are due to a stretch plus two bends. This band assignment is in agreement with assignments by Cariati *et al* (1981, 1983a, 1983b), but in disagreement with Sposito *et al* (1983) and Clark *et al* (1990) for the 1.4 μm feature. An additional feature due to a combination of the symmetric and asymmetric H_2O stretching modes may be present as well at 1.41 μm (Buijs and Choppin 1963).

Clay minerals such as kaolinite exhibit spectral features near 1.4 μm due to an overtone of the structural OH stretching mode (e.g., Adams 1975; Hunt and Sal-

Table 3b.   Band assignments for water and structural OH in SWy montmorillonite.

Wavenumber (cm⁻¹)	Wavelength (µm)	Vibrations (montmorillonite)
7090	1.41	$2\nu_{OH}$
7000–7100	~1.41	$\nu'_w + 2\delta_w$
6800–6850	1.46	$\nu_w + 2\delta_w$
5230–5250	1.91	$\nu'_w + \delta_w$
~5100	1.97	$\nu_w + \delta_w$
4540	2.20	$\nu_{OH} + \delta_{AlMOH}$
3680	2.70	ν_{M2OH}
3630	2.75	ν_{AlMOH}
3600–3620	2.76–2.78	ν'_{w3}
3520–3550	2.82–2.84	ν'_{w1}
~3450	~2.90	ν_{w3}
3350–3400	2.94–2.99	ν_{w1}
~3230	~3.10	$2\delta_w$
~1650	~6.0	δ_w
1617–1630	6.1–6.2	δ'_w
925	10.8	δ_{Al2-OH}
885	11.3	$\delta_{AlFe-OH}$
845	11.8	$\delta_{AlMg-OH}$

Vibrations are labeled with ν (stretching) and δ (bending) as in Figure 2. The subscripts w and OH refer to molecular water and structural OH respectively. Stretching vibrations due to bound (inner sphere and surface) H_2O are indicated by ν'_w and those due to adsorbed H_2O are indicated by ν_w.
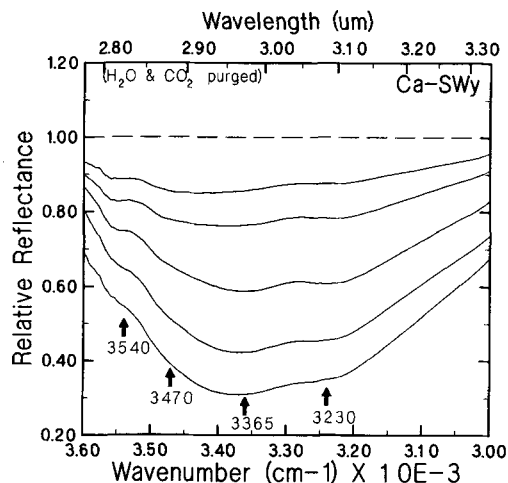

Figure 7.   Relative reflectance spectra of Ca-exchanged SWy montmorillonite: 3600 cm⁻¹ to 3000 cm⁻¹ (2.8 to 3.3 µm). The spectra shown are ratios relative to the reflectance spectrum with the weakest water features (measured under an atmospheric pressure of 30 µm Hg). The relative spectrum showing the strongest water features was measured under ambient atmospheric pressure.

isbury 1970). The structural OH overtone cannot be distinguished from the bound H_2O combinations in montmorillonite spectra because they both occur near 1.41 µm. However, in spectra of other smectites, such as saponite and hectorite, the structural OH overtone occurs at 1.39 µm and can be distinguished from the H_2O combinations (Clark *et al* 1990).

Cation influence on band position

Fundamental vibrations. The polarizing power of the interlayer cations forms a trend that is consistent in general to the vibrational energies of the 6 µm water bending vibrations. In both the 1 bar atmospheric pressure and reduced pressure (dehydrated) spectra the energies of the Na and Ca samples are lower than the energies of the Mg and Fe³⁺ samples. The stronger the polarizing power of the cation, the more the cation hinders the bending vibration. Therefore, higher vibrational energies are predicted and observed for ν_2 in the case of the Mg^{2+} and Fe^{3+}-exchanged montmorillonites relative to the Na^+ and Ca^{2+}-exchanged montmorillonites (Table 1).

The symmetric stretching modes involve motion along the H-bonding axes and in the direction of the cation-oxygen bond, which implies that H-bonding and bonding with the interlayer cation should influence this vibration (Bishop 1994). Variations in these ν_1 absorptions as a result of the interlayer cations are summarized in Table 1. Based on the increasing polarizing power from Na to Ca to Mg, the ν_1 energies are expected to decrease from Na to Ca to Mg. This is ob-

served for the ν_1 vibrational energies of the samples containing higher moisture contents. However, the ν_1 absorption under dry conditions for the Na sample has an absorption at lower energy than those for the Ca and Mg samples. This is probably due to adsorption isotherm effects. In order to better isolate the effects of the cations on the H_2O molecules, spectra should be compared for samples having identical H_2O contents rather than identical relative humidities. Measuring spectra of these samples at reduced temperatures may also provide more readily discernible features, as seen by Prost and Chaussidon (1969).

The symmetric stretching modes are much stronger and more sensitive to bonding with the interlayer cations than the asymmetric stretching modes. The asymmetric stretching mode requires forces of opposite directions along the H-bonding axes and motion lateral to the cation bound to the O atom, which implies that the cation may not have a strong influence on this vibration (Bishop 1994). Systematic variations in the ν_3 absorptions with the interlayer cations were not observed.

Near-infrared vibrations. Spectral absorptions are also observed in the infrared near 1.4 µm and 1.9 µm due to combinations of the stretching and bending vibrations of H_2O. The energy differences as a result of bound and adsorbed H_2O can be seen in these absorption features by comparing spectra measured under ambient and H_2O-purged conditions (Figure 5). Combination bands involving bound H_2O are observed at ~7090 cm⁻¹ (1.41 µm) and ~5240 cm⁻¹ (1.91 µm). The long-wavelength shoulders occur under more moist

conditions and are due to combination bands involving adsorbed H_2O. These are observed near 6820–6860 cm^{-1} (~1.46 μm) and 5040–5120 cm^{-1} (~1.97 μm), and depend on the type of interlayer cation and the sample moisture content. Adsorption isotherm effects play a prominent role in determining the adsorption energies at 1.41 μm and 1.91 μm because the adsorption isotherms determine the number of H_2O molecules per cation and hence the strength of the longer-wavelength shoulders. Cariati *et al* (1983a, 1983b) show the effects of both interlayer cation and amount of interlayer water on these 1.4 μm and 1.9 μm features in bentonites and hectorites.

The variations in the 1.41 μm and 1.91 μm band centers follow more closely the trends for adsorption isotherms (Na < Fe < Ca < Mg) than for polarizing power of the interlayer cation (Na < Ca < Mg < Fe). Since the stretching and bending modes of H_2O are influenced in opposite directions by the polarizing power of the interlayer cations the effects of polarizing power of these cations on the combination bands (stretch + bend) should be neutralized. This is observed at 1.41 μm and 1.91 μm, which supports combination band assignments for these features. The similar variation between Na- and Mg-montmorillonite under variable moisture conditions implies that the strength of the shoulder near 1.97 μm is influencing the 1.91 μm band center, and that subtle variation in the 1.91 μm band center depends primarily on the strength of this 1.97 μm shoulder, which depends (i) on the relative humidity of the sample environment and (ii) on the kind of interlayer cation.

The 1.41 μm band center behaves similar to the 1.91 μm band center as a function of moisture and interlayer cation, except under low moisture conditions. The spectra measured in a H_2O-purged environment show much less variation at 1.41 μm (only 6 cm^{-1} from Na to Mg). Under such low moisture conditions the 1.41 μm feature is therefore due primarily to structural OH. The shoulder near 1.46 μm due to a combination of a stretch plus two bends of H_2O is very weak and has very little influence on the 1.41 μm band center.

Low (1981) predicted that bonding to the interlayer cations plays a secondary role to surface bonding in influencing the vibrational energies of H_2O in montmorillonite, except under very dry conditions. Mulla and Low (1983) showed that Na^+ as an interlayer cation has little effect on the fundamental H_2O vibrations for moist films of montmorillonite (water content range: 1–15 g H_2O/g clay). Our study shows the influence of the interlayer cations on the vibrational energies of H_2O in montmorillonite under very dry conditions and the work of Prost (1975) shows the influence of the interlayer cations on the vibrational energies of H_2O in hectorite under very dry conditions. This implies that for smectites under dehydrated conditions more of the interlayer water is bound to cations and/or the
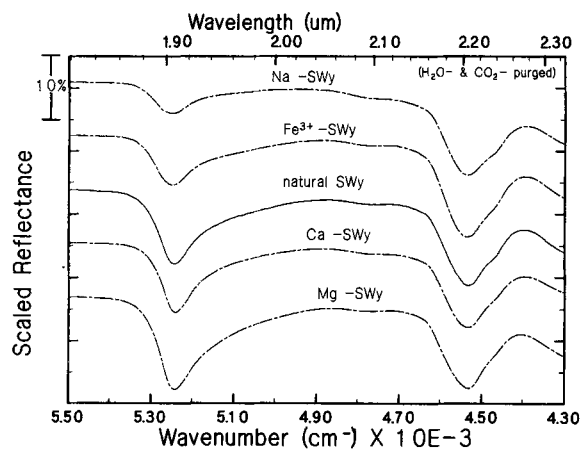

Figure 8. Reflectance spectrum of variably cation-exchanged SWy montmorillonites: 1.8 μm to 2.3 μm (5500–4300 cm^{-1}). These spectra are scaled to 1.0 at 1.78 μm and are offset by 10% for clarity. The strength of the 1.9 μm feature relative to the 2.2 μm feature is weakest for the Na sample and strongest for the Mg sample. The spectrum of the natural (Na, Ca) SWy is depicted by a solid line.

interlayer surface, and that the vibrational energies of this bound water are different from the vibrational energies of additional interlayer water in smectites.

Cation influence on band depth

The interlayer cation also plays a role in how much water is adsorbed in the interlayer regions of smectites. For the Na^+, Ca^{2+}, Mg^{2+} and Fe^{3+} montmorillonites studied here a range of moisture contents were observed. Although each of these samples was stored for weeks in a 50% relative humidity environment, the amount of moisture lost from each sample on subsequent heating to 500°C was 6% for Na^+, 8% for Fe^{3+}, 9.5% for Ca^{2+} and 11% for Mg^{2+}-exchanged samples. Prost (1975) also observed increasing water contents from Na^+ to Ca^{2+} to Mg^{2+} for a given relative humidity environment. The thermal analyses confirm that the interlayer cations influence the character of the interlayer water and that two or more forms of water exist in the interlayer region.

Johnston *et al* (1992) measured an increase in the basal spacing and an increase in the intensity of the ν_2 band depth as the water content was increased in thin films of Na-montmorillonite. Basal spacing of the natural SWy and cation-exchanged montmorillonites were measured by X-ray Powder Diffraction. These basal spacings were 11.6 Å for Na- and Fe^{3+}-, 11.8 Å for H-, 11.9 Å for the natural (Na/Ca) SWy, 12.7 Å for Ca-, and 13.9 Å for Mg-exchanged montmorillonites. The basal spacings in these samples increases for the interlayer cations: Na < Fe^{3+} < H < natural < Ca < Mg. This compares well with the amount of interlayer water present as shown in the TGA results in Figure 6 and the 1.9 μm band depths in Figures 8, 9 and 10.
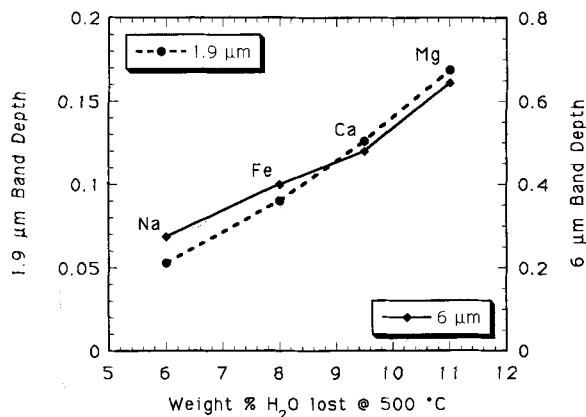
Figure 9. Spectral band depths at 1.9 μm and 6 μm in homoionically-exchanged SWy montmorillonites vs water loss. Band depths for the spectral features near 1.9 μm and 6 μm, measured by removing the continuum and scaling to unity on either side of the feature, for Na-, Fe^{3+}-, Ca- and Mg-exchanged montmorillonites correspond linearly to the amount of water lost upon heating to 500°C using TGA (Figure 6).

Reflectance spectra are shown in Figure 8 of natural (Na/Ca), Na-, Ca-, Mg- and Fe^{3+}-SWy montmorillonite from 1.8 to 2.3 μm. Although spectra of these samples were measured while all of the samples were enclosed in the same, controlled, low-humidity environment, an increase in intensity of the 1.9 μm band is observed from Na- to Fe- to Ca- to Mg-interlayer cations. Such changes are not observed for the 2.2 μm feature which is due to structural OH. The relative strengths of the 1.9 μm and 2.2 μm hydration features are due to two factors: (a) multiple forms of interlayer H_2O, depending on the moisture conditions;
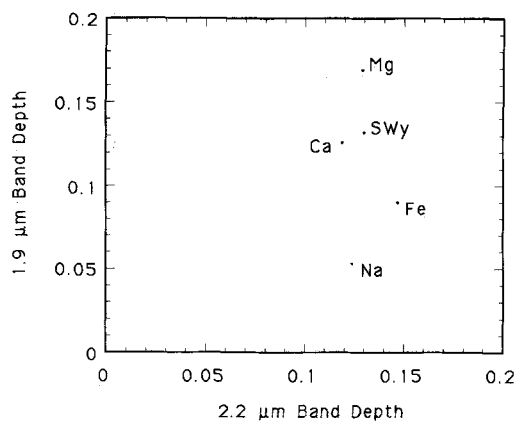

Figure 10. Band depths at 1.9 μm vs band depths at 2.2 μm in homoionically-exchanged SWy montmorillonites. Band depths measured by removing the continuum and scaling to unity on either side of the feature for Na-, Fe^{3+}-, natural (SWy), Ca- and Mg-exchanged montmorillonites show significant variability in the stength of the 1.9 μm feature and little change in the strength of the 2.2 μm feature as a result of exchanging the interlayer cations.

and (b) the ability of the interlayer cations to polarize the H_2O molecules to varying degrees, which shifts the stretching and bending vibrational energies of these H_2O molecules.

The percentage of water lost (by weight) up to 500°C is compared in Figure 9 with the band depths of the spectral features due to water. The band depths were calculated by removing the continuum and scaling to unity on either side of the feature. The amount of removable water in this suite of cation-exchanged clays correlates well with the 1.9 μm and 6 μm band depths. The strengths of these 1.9 μm and 6 μm hydration features thus depend on the kind of interlayer cation, as well as on the moisture environment, whereas the strength of the 2.2 μm feature is primarily due to structural OH and octahedral cations. A comparison of the band strengths of the 1.9 μm and 2.2 μm features in Figure 10 shows significant variation in the strength of the 1.9 μm feature with the type of interlayer cation, while the 2.2 μm feature is not affected by these changes.

CONCLUSIONS

Spectral features attributed to interlayer water molecules in smectites have been analyzed here as a function of water content and interlayer cation. H-O-H stretching vibrations have been assigned to ν_3 (asymmetric) bound H_2O at ~3620 cm^{-1} and adsorbed H_2O at ~3450 cm^{-1}. The ν_1 (symmetric) vibrations depend more strongly on the cation and have been assigned in the range 3520–3550 cm^{-1} for bound (inner sphere and surface-bonded) H_2O and 3400–3350 cm^{-1} for adsorbed H_2O. H-O-H bending vibrations (ν_2) have been observed in the range 1617–1630 cm^{-1} for bound H_2O and at shorter wavelengths for adsorbed H_2O. The bending overtone ($2\nu_2$) is observed at 3230 cm^{-1}. Increasing strength in polarizing power of the interlayer cations was found to produce, in general, higher energy bending vibrations (ν_2) and lower energy symmetric stretching vibrations (ν_1).

Energy differences are also observed in the near infrared combination features at 1.4 μm and 1.9 μm. The combination bands involving bound H_2O vibrations have higher energies (shorter wavelengths) and occur near 7090 cm^{-1} (1.41 μm) and 5240 cm^{-1} (1.91 μm). Also observed at 1.41 μm in spectra of montmorillonite is an overtone of the structural OH stretching mode. Shoulders on each of these features due to adsorbed H_2O combinations arise at 6820–6860 cm^{-1} (~1.46 μm) and 5040–5120 cm^{-1} (~1.97 μm) as the amount of interlayer water increases.

Spectral absorptions due to molecular water in montmorillonite are influenced by both the interlayer cation and the moisture environment. Since the absorptions near 1.4 μm, 1.9 μm and 3 μm are composed of multiple, overlapping molecular water features, the band shape, the individual band minima and the band

strengths are all important in laboratory spectral analyses and remote sensing of smectites.

ACKNOWLEDGMENTS

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