NOTE

WATER MOLECULES AND HYDROXYL GROUPS IN MONTMORILLONITES AS STUDIED BY NEAR INFRARED SPECTROSCOPY

Layer silicates are characterized by the presence of water molecules that interact with each other, with surface oxygen atoms, and with exchangeable cations. In montmorillonites the positive charge deficiency due to octahedral substitutions gives the surface oxygens weak electron-donor properties. Therefore, it has been proposed that they are linked to water molecules only through weak hydrogen bonds (Farmer, 1971; Farmer and Russell, 1971; Low, 1979). Infrared spectroscopy (IR) has been widely used to characterize water molecules and hydroxyl groups (Farmer and Russell, 1964; Farmer, 1974; Suquet *et al.*, 1977) and to study the acidic properties of laminar silicates (Mortland and Raman, 1968). In the near infrared (NIR) region also, absorptions due to the vibration modes (overtones and combination bands) of water molecules and lattice hydroxyl groups are clearly observable. However, the use of this technique is still limited, although its potential utility in the characterization of clays and other minerals has been recently emphasized (Lindberg and Snyder, 1972; Velghe *et al.*, 1977; Hunt, 1977, 1979). Proposed NIR assignments have been discussed only in a general manner without interpretation concerning their relations with molecular and intermolecular phenomena in the interlamellar space and without supportive experimental data on dehydration, dehydroxylation, and deuteration. It is the aim of the present study to provide information in this area in order to follow chemical and physical processes occurring in layer silicates.

EXPERIMENTAL

Materials

Natural bentonite from Uri, Sardinia, was used in this study. Pietracaprina *et al.* (1972) reported the structural formula of this material as $(Si_{7.878} Al_{0.122})(Al_{3.156} Fe^{3+}_{0.235} Mg_{0.561})(OH)_4O_{20}$ and its cation-exchange capacity (CEC) as 65 meq/100 g. Homoionic samples were obtained by saturating the <2-μm clay fraction with 1 N $CaCl_2$ or LiCl solutions and removing the excess salt by repeated washings with water.

Measurement techniques

Diffuse reflectance spectra in the 1300–2450-nm wavelength range were recorded with a Beckman Acta M IV spectrophotometer equipped with an integrating sphere coated by $BaSO_4$. $BaSO_4$ was used as a reference. IR spectra were taken with a Beckman 4250 spectrophotometer using the KBr-pellet technique. Dehydration and dehydroxylation temperatures were chosen on the basis of thermal analyses obtained on 100-mg samples using a Leeds & Northrup differential thermal analysis (DTA) apparatus operating at a heating rate of 10°C/min with calcined kaolinite as the inert material. The water content of the samples was checked by thermogravimetric analyses obtained on a Perkin-Elmer TGS-2 apparatus under a nitrogen stream at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Diffuse reflectance spectra of bentonites in the 1300–2450-nm wavelength region are shown in Figures 1 and 2. The spectroscopic assignments are reported in Table 1. The spectrum of the air-dried Ca-sample (H_2O content = 15.7%), reported in Figure 1, is characterized by a symmetric band at 2206 nm and two bands at 1910 and 1410 nm, with asymmetrical shapes due to shoulders at 1978 and 1456 nm, respectively.

Molecular water absorption bands

Because dehydration of the samples at 250°C resulted in the absence of the shoulders at 1978 and 1456 nm (Figure 1), the shoulders can be reasonably attributed to water molecules that were released during heating. The spectroscopic assignments were made following the scheme reported by Herzberg (1945) for the spectrum of water vapor. The comparison allowed the

Table 1. Near infrared absorption bands (nm) in Ca-montmorillonite.[1,2]

Sample	H_2O			OH			D_2O[3]	OD[3]
	$\nu_w + 2\delta_w$	$\nu'_w + \delta_w$	$\nu_w + \delta_w$	$2\nu_{OH}$	$\nu_{OH} + \delta_{AlOH}$	$\nu_{OH} + \delta_{MgOH}$	$\nu_{dw} + 2\delta_{dw}$	$2\nu_{OD}$
Ca-montmorillonite	1456 sh	1910 vs	1978 sh	1410 s	2206 s	—		
Ca-montmorillonite heated at 250°C	—	1910 w	—	1410 m	2206 s	2354 w		
Ca-montmorillonite treated with D_2O							1998 w	1884 m
Ca-montmorillonite treated with D_2O and heated at 250°C							—	1884 m

[1] ν_w, ν'_w, ν_{dw} = stretching frequencies of water (w) and heavy water (dw).
[2] s = strong; m = medium; w = weak; sh = shoulder; v = very.
[3] The other combination bands are shifted beyond the instrumental limits.
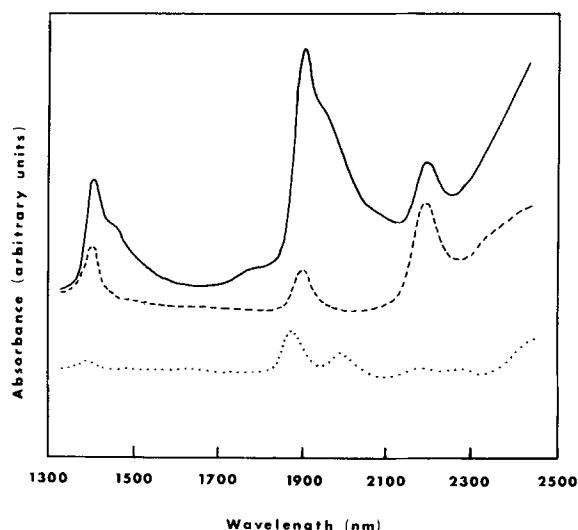
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Figure 1. Diffuse reflectance spectra of Ca-bentonite (solid line); Ca-bentonite heated at 250°C (dashed line); Ca-bentonite treated with D_2O (dotted line).

Figure 2. Diffuse reflectance spectra of Li-bentonite (solid line); Li-bentonite heated at 250°C (dotted line).

1978- and 1456-nm absorptions to be ascribed to the $(\nu_w + \delta_w)$ and $(\nu_w + 2\delta_w)$ combinations, respectively. A computation made assuming the ν_w (3420 cm^{-1}) stretching and δ_w (1635 cm^{-1}) bending frequency values found in the IR spectrum (see Figure 3) confirmed this hypothesis.

The spectra of samples dehydrated at 250°C (H_2O content <0.5%) showed notably weaker 1910-nm absorptions. To determine whether the 1910-nm absorption is due to water molecules, a Li-saturated bentonite was examined because of the ability of this ion (unlike calcium) to penetrate into lattice octahedral positions (Tettenhorst, 1962; McBride and Mortland, 1974). After heating the sample at 250°C (the water content was below the detection limit by thermogravimetric analysis), the absorption weakened considerably (see Figure 2). Therefore, this band could also be due to interlayer water molecules, but it can be explained only by taking into account a combination between the bending mode ($\delta_w = 1635$ cm^{-1}) and a high frequency stretching ($\nu'_w = 3620$ cm^{-1}) vibration. High frequency stretching modes, observed in hectorite (Farmer and Russell, 1971; Poinsignon *et al.*, 1978) and in D_2O-montmorillonites (Farmer, 1971; Farmer and Russell, 1971), were attributed to the OH groups of water directed at high angle to the plane of silicate sheet (Farmer, 1971) or to residual water molecules coordinated to cations in dehydrated smectites (Poinsignon *et al.*, 1978). The higher the ν_w value, the higher is the force constant of the OH bond. Thus, it is reasonable to assume that ν'_w is due to weak and extended intermolecular hydrogen bonds between the surface oxygens and the neighboring water molecules. On a statistical basis these molecules are peripherical and do not belong to the inner hydration shells of cations in hydrated samples. At very low water contents they are necessarily bound to the ions which perturb them according to a well-defined polarization order (Cariati *et al.*, 1981).

In both situations, OH groups of the "free" water molecules have coordination numbers lower than those in bulk liquid and may be characterized by properties different than those of the molecules that produce the 1978- and 1456-nm bands and that strongly interact through hydrogen bonds. In contrast to the sharp band at 1910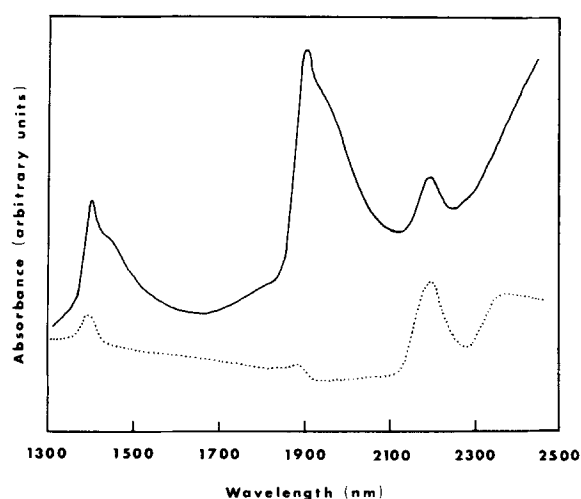 nm, the width of the bands at 1978 and 1456 nm suggests a certain distribution of intermolecular bonds slightly different from each other.

All observations substantiate the proposed presence of differently hydrogen-bound water molecules in layer silicates which give interlayer properties very different than those of ordinary solutions (Low, 1979). The weakly bonded water-OH groups should also produce a $(\nu'_w + 2\delta_w)$ combination band near 1400 nm. The weakening of this absorption after heating the sample at 250°C is the probable cause of the remarkable lowering of the absorbance in the composite band centered around 1410 nm. This behavior is more evident in Li-bentonite (see Figure 2) as would be expected.

Lattice-hydroxyl absorption bands

Lattice hydroxyls are responsible for bands at 1410, 2206, and 2354 nm in the spectrum of the sample heated at 250°C (Figure 1). These bands also can be explained on the basis of IR frequency values (see Figure 3) in the following way: (1) The 1410-nm absorption is due to a $2\nu_{OH}$ overtone ($\nu_{OH} = 3630$ cm^{-1}); (2) The 2206-nm band corresponds to the $(\nu_{OH} + \delta_{AlOH})$ combination ($\delta_{AlOH} = 915$ cm^{-1}); and (3) The weak absorption at 2354 nm is attributable to the $(\nu_{OH} + \delta_{MgOH})$ combination, as already reported (Hunt, 1979).
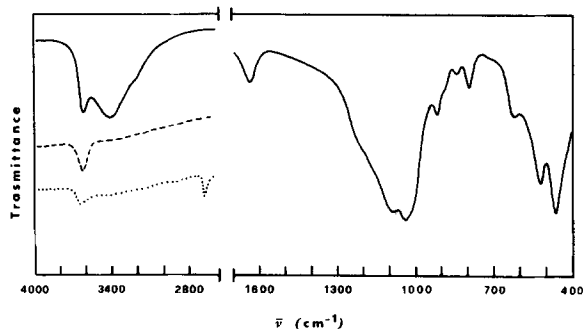

Figure 3. Infrared spectra (KBr phase) of Ca-bentonite (solid line); Ca-bentonite heated at 250°C (dashed line); Ca-bentonite treated with D_2O and heated at 250°C (dotted line).

Deuteration

To substantiate the above assignments, a sample dehydroxylated at 650°C was treated with boiling D_2O for two days under H_2O-free nitrogen and dried under nitrogen. The NIR spectrum of the sample exhibited two new bands at 1884 and 1998 nm (see Figure 1). By converting OD frequencies to the corresponding OH frequencies, the new bands were found to coincide with the above-mentioned absorptions at 1410 nm (shifted to 1398 nm after the dehydroxylation) and 1456 nm, respectively. On heating the deuterated sample at 250°C, the 1998 nm band disappeared, indicating its origin from interlayered, strongly linked D_2O molecules. On the other hand, the 1884-nm band was still present and, consequently, must be due to lattice-OD groups. OD groups were suggested also by the ν_{OD} stretching band at 2700 cm^{-1} in the IR spectrum (Figure 3).

CONCLUSIONS

This work shows that the NIR spectrum of montmorillonites is characterized by absorption bands due to both water molecules and lattice-hydroxyl groups. The results are in contrast with those of Lindberg and Snyder (1972) who ascribed all such bands to water. The results clarify also the different vibrational properties of water molecules in relation to the intermolecular bonding, a possibility not examined by Hunt (1977, 1979) who reported only general NIR spectral features of silicates.

The resulting spectral behavior agrees very well with the proposed existence in layer silicates of several intermolecular interaction mechanisms involving water molecules. These interactions impart to the interlayer distinctive features quite different from those of the simple ionic solutions. A uniform distribution of hydrogen bonded solvent molecules exists in the latter, whereas in interlamellar solutions, discrete populations are present including molecules either strongly coupled by hydrogen bonds or weakly interacting with the surfaces. The extent of such interactions may be different with different exchangeable cations and different hydration conditions. Indeed, at low water contents, all residual molecules are coordinated to ions and weakly interact with the smectite lattice. NIR spectra evidence and distinguish the several interaction mechanisms in all situations, whereas IR spectroscopy is useful only in some cases.

For this reason, the near infrared technique could be used to follow chemical and physical processes which modify intra- and inter-molecular bonds of water molecules and lattice-hydroxyl groups in phyllosilicates.

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