

NOTE

EFFECTS OF LAYER CHARGE ON THE NEAR-INFRARED SPECTRA OF WATER MOLECULES IN SMECTITES AND VERMICULITES

Key Words—Bentonite, Hectorite, Near-infrared spectroscopy, Nontronite, Vermiculite, Water.

Discrete populations of water molecules are present in the interlayer space of swelling layer silicates. Molecules involved in strong hydrogen bonds exhibit vibrational properties different with respect to those of molecules having protons weakly bonded to the oxygen silicate atoms. Such mechanisms have been revealed by infrared (IR) spectroscopy (Mortland and Raman, 1968; Farmer and Russell, 1971; Poinson *et al.*, 1978). Spectroscopic differences between the two types of water molecules as a function of the hydration state of the sample and the nature of the exchange cation, however, were well demonstrated in near-infrared investigations on bentonite, a montmorillonitic system consisting of (Al,Fe(III),Mg)-O₄(OH)₂ octahedral sheets sandwiched between (Si,Al)₄ tetrahedral sheets (Cariati *et al.*, 1981, 1983).

Because the interactions between water and silicate oxygens should also be sensitive to the charge density originating from cation substitutions, we have extended the near-infrared analysis to layer silicates characterized by different structures and compositions. In this paper hectorite, whose negative charge is due to octahedral replacement of Mg by Li, and nontronite and vermiculite, whose charge arises from substitutions of Al (and in some samples Fe(III)) for Si in tetrahedral positions, are examined.

EXPERIMENTAL

The following samples were examined: nontronite from Allentown, Pennsylvania [M⁺_{0.67}(Si_{7.42}Al_{0.58})(Fe(III)_{3.36}Mg_{0.08}-Al_{0.36})(OH)₄O₂₀], and vermiculite from Libby, Montana [M⁺_{1.53}(Si_{6.16}Al_{1.84})(Al_{0.36}Fe(III)_{1.20}Mg_{3.82})(OH)₄O₂₀], both obtained from Ward's Natural Science Establishment, Rochester, New York, and hectorite from Hector, California [M⁺_{0.91}(Si_{8.00})(Mg_{4.40}Al_{0.36}Li_{0.70}Fe(III)_{0.17})(OH)₄O₂₀], supplied by Lavisosa S.p.A., Italy. Bentonite (Uri, Sardinia), described by Pietracaprina *et al.* (1972) and Cariati *et al.* (1981, 1983) was also investigated.

Chemical analysis was performed with a Spectraspan IV emission spectrometer after HF-dissolution of the clays in a Perkin-Elmer mod. 3 digestion bomb. The dehydration and deuteration techniques and the instrumentation used in obtaining physical and spectroscopic data were previously described (Cariati *et al.*, 1981, 1983).

RESULTS AND DISCUSSION

The near-infrared spectra of homoionic samples of Li-hectorite, -vermiculite, and -nontronite are reported in Figure 1. For comparison, the spectrum of the Li-exchanged Uri bentonite is also shown. To assist in the identification of the main absorption bands, corresponding to overtone and combination modes of water molecules and hydroxyl groups, both dehydration and deuteration experiments were carried out, as described by Cariati *et al.* (1981). The spectral assignments are listed in Table 1.

Briefly, the structural hydroxyls are responsible for the $2\nu_{\text{OH}}$ overtone and the $\nu_{\text{OH}} + \delta_{\text{MgOH}}$ (in hectorite and vermiculite) and the $\nu_{\text{OH}} + \delta_{\text{FeOH}}$ (in nontronite) combination bands. On the other hand, the $\nu_{\text{w}} + \delta_{\text{w}}$, $\nu_{\text{w}} + 2\delta_{\text{w}}$, $\nu'_{\text{w}} + \delta_{\text{w}}$, and $\nu'_{\text{w}} + 2\delta_{\text{w}}$ combination bands are attributed to water molecules. As shown by Cariati *et al.*, (1981), the high-frequency stretch (ν'_{w}) can be attributed to the water OH-groups directed towards the surfaces and subjected to weak hydrogen bond, whereas lower frequency values (ν_{w}) characterize the stretches of the water OH-groups involved in strong hydrogen bonding with adjacent water molecules. Only hectorite, nontronite, and vermiculite show the absorption band attributed to the $\nu'_{\text{w}} + 2\delta_{\text{w}}$ mode, which was not distinguishable for montmorillonite due to strong overlapping of bands.

The overtone bands, $2\nu_{\text{OH}}$, involving the stretching vibrations due to the structural hydroxyl groups, further distinguish the phyllosilicates from each other. The structural differences connected with the type of cation linked to the OH groups in the octahedral position (Al in bentonite, Mg in hectorite and vermiculite, and Fe(III) in nontronite) influence the values of the $2\nu_{\text{OH}}$ band, which mainly depend on the varying degrees of polarization of the OH groups. The lower the wavelength value, the stronger is the bond order of the OH groups; hence, in the phyllosilicates herein examined the polarization order is Fe > Al > Mg, as suggested by Farmer and Russell (1964) on the basis of IR measurements.

Both the spectral position and the shape of the water absorption bands differentiate the phyllosilicates from one other. The observed wavelength values of the combination bands $\nu'_{\text{w}} + \delta_{\text{w}}$, involving the high frequency stretching bands, increase in the order hectorite, bentonite < nontronite, ver-

Table 1. Near-infrared absorption bands (nm) in Li-phyllosilicates.¹

Sample	H ₂ O				OH			
	$\nu'_{\text{w}} + 2\delta_{\text{w}}$	$\nu_{\text{w}} + 2\delta_{\text{w}}$	$\nu'_{\text{w}} + \delta_{\text{w}}$	$\nu_{\text{w}} + \delta_{\text{w}}$	$2\nu_{\text{OH}}$	$\nu_{\text{OH}} + \delta_{\text{AlOH}}$	$\nu_{\text{OH}} + \delta_{\text{FeOH}}$	$\nu_{\text{OH}} + \delta_{\text{MgOH}}$
Bentonite ²		1456	1910	1970	1410	2206		
Hectorite ³	1411	1455	1907	1954	1390			2302
Nontronite ⁴	1418	1466	1918	⁶	1432		2290	
Vermiculite ⁵	1418	⁶	1922	⁶	1396			2314

¹ Bentonite: $\nu_{\text{OH}} = 3630 \text{ cm}^{-1}$, $\delta_{\text{AlOH}} = 915 \text{ cm}^{-1}$; hectorite: $\nu_{\text{OH}} = 3670 \text{ cm}^{-1}$, $\delta_{\text{MgOH}} = 620 \text{ cm}^{-1}$; nontronite: $\nu_{\text{OH}} = 3560 \text{ cm}^{-1}$, $\delta_{\text{FeOH}} = 815 \text{ cm}^{-1}$; vermiculite: $\nu_{\text{OH}} = 3670 \text{ cm}^{-1}$, $\delta_{\text{MgOH}} = 620 \text{ cm}^{-1}$ (Farmer, 1974; Hunt, 1979).

² H₂O/Li = 14.6. ³ H₂O/Li = 9.3. ⁴ H₂O/Li = 13.7. ⁵ H₂O/Li = 3.3. ⁶ Broad absorption.

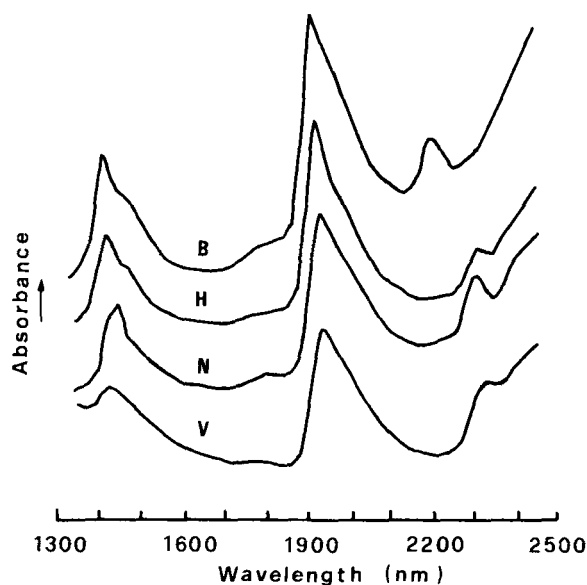


Figure 1. Near-infrared spectra of Li-bentonite (B), Li-hectorite (H), Li-nontronite (N), and Li-vermiculite (V). The water contents are listed in Table 1.

miculite. The same trend was observed for samples with lower water content and differing exchange cations where spectral shifts, whose origin was previously discussed (Cariati *et al.*, 1983), were observed (see Table 2).

The results indicate that the vibrational properties of the 'free' water molecules, which are directed toward the uncharged silicate oxygen atoms, depend on the composition of the structure. As variations in the combination values are related to variations in the OH bond order (Cariati *et al.*, 1983), the hydrogen bonds formed by interlayer water molecules with the surface oxygens must be stronger in nontronite and vermiculite than in hectorite and bentonite (see Table 1), suggesting that the Si-O-Si groups near aluminum-containing tetrahedra acquire induced charge and allow stronger hydrogen bonds to 'free' water molecules. This perturbation is still evident after dehydration, when the residual 'free' water mol-

Table 2. Spectral variations of the $\nu_w + \delta_w$ band for M(I)- and M(II)-phyllosilicates under conditions of variable hydration.

M	Hectorite		Vermiculite		
	H ₂ O/M	λ (nm)	M	H ₂ O/M	λ (nm)
Li	9.3	1907	Li	3.3	1922
	4.7	1903		1.6	1917
	1.3	1902		0.9	1917
K	7.0	1903	K	1.0	1915
	2.6	1903		0.8	1902
	1.3	1902		0.5	1902
Ca	20.2	1909	Ca	7.4	1924
	13.8	1908		2.5	1921
	6.5	1908		1.8	1918
Cu	22.0	1910	Cu	8.4	1926
	8.0	1908		4.8	1922
	5.2	1915		1.6	1922
	3.8	1918			

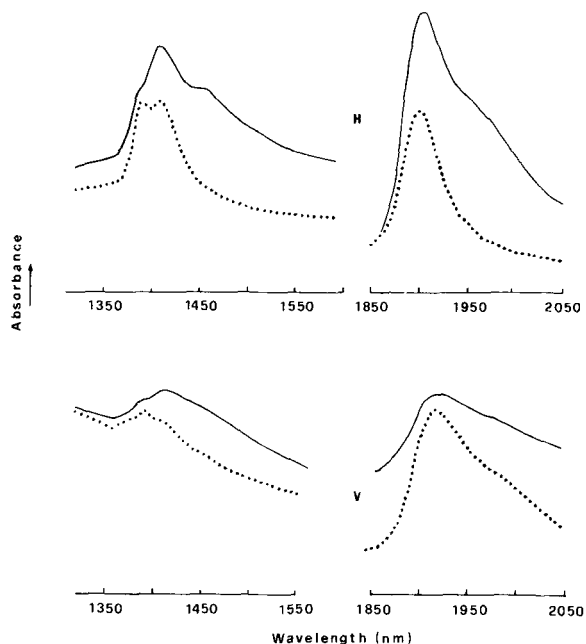


Figure 2. Near-infrared spectra: H,Li-hectorite [$H_2O/Li = 9.3$ (—) and 3.0 (····)]; V,Li-vermiculite [$H_2O/Li = 3.3$ (—) and 0.9 (····)].

ecules are coordinated and perturbed by the exchange cations (Table 2).

The $\nu_w + \delta_w$ and $\nu_w + 2\delta_w$ combination bands, assigned to water molecules involved in strong hydrogen bonds (such as water-to-water bonds), although never appearing as well-resolved absorptions, are more diffuse for vermiculite and nontronite than for hectorite and bentonite (see, e.g., Figure 2).

Differences among these bands are more pronounced in the spectra of partially dehydrated samples (Figure 2). The dehydration of phyllosilicates shortens the chains of water molecules and reduces the interlayer distance. Consequently, the residual water molecules are forced to interact with both the exchange cations and the surface oxygens, water-to-water bonds being rather unlikely. Accordingly, in the spectra of bentonite and hectorite ($H_2O/Li < 3$), the $\nu_w + \delta_w$ and $\nu_w + 2\delta_w$ water absorptions were not detected. In contrast, the spectra of nontronite and vermiculite ($H_2O/Li \sim 1$) exhibited remarkable tails due to strongly bound water. These latter findings can be explained only by assuming the presence of water molecules involved in hydrogen bonding with charged oxygens of Al-bearing tetrahedra.

These data illustrate well the effects of cation-substitutions in phyllosilicates. In hectorite and bentonite, where most replacements occur in the internal octahedral layer, the charge appears to be uniformly distributed on the oxygen atoms of the surfaces. Thus, the water molecules approaching the surfaces form weak hydrogen bonds with the silicate framework. On the contrary, in nontronite and vermiculite, due to Al for Si replacements in tetrahedral positions, oxygens carrying direct or induced charges are also present. Thus, in addition to 'free' water, molecules interacting with these oxygens and exhibiting stronger polarization of the OH bonds are expected. The distinctive spectral components, of broad shape, which were clearly apparent after partial dehydration of vermiculite and nontronite, allow for the water population approaching the surfaces and interacting with charged oxygens. Indeed, the

presence of either charged or uncharged oxygens on the surface and of water-to-water bonds in the interlayer, should produce a wide range of hydrogen bonding. In the limiting case, continuous rather than discrete absorptions should be expected for the water molecules, as is closely approached by vermiculite.

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