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.

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 $2\nu_{OH}$ overtone and the $\nu_{OH} + \delta_{OH\nu}$ (in hectorite and vermiculite) and the $\nu_{OH} + \delta_{OH\nu}$ (in nontronite) combination bands. On the other hand, the $\nu_{w} + \delta_{w}$, $\nu_{w} + 2\delta_{w}$, $\nu_{w} + \delta_{w}$, and $\nu_{w} + 2\delta_{w}$ combination bands are attributed to water molecules. As shown by Cariati et al. (1981), the high-frequency stretch ($\nu_{w}$) can be attributed to the water OH-groups directed towards the surfaces and subjected to weak hydrogen bond, whereas lower frequency values ($\nu_{w}$) 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 $\nu_{w} + 2\delta_{w}$ mode, which was not distinguishable for montmorillonite due to strong overlapping of bands.

The overtone bands, $2\nu_{OH}$, 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 $2\nu_{OH}$ 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 $\nu_{w} + \delta_{w}$, involving the high frequency stretching bands, increase in the order hectorite, bentonite < nontronite, ver-
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 molecules are coordinated and perturbed by the exchange cations (Table 2).

The $\delta_w + \delta_w$ and $\delta_w + 2\delta_w$ 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 $\delta_w + \delta_w$ and $\delta_w + 2\delta_w$ 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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