

POLARIZATION OF WATER MOLECULES IN PHYLLOSILICATES IN  
RELATION TO EXCHANGE CATIONS AS STUDIED  
BY NEAR INFRARED SPECTROSCOPY

Key Words—Bentonite, Exchangeable cations, Near infrared spectroscopy, Polarization, Water.

In the past, several contributions dealing with the effects of the exchange cations and the hydration status on infrared (IR) absorptions of water molecules in phyllosilicates have been published (e.g., Fripiat *et al.*, 1960; Farmer and Russell, 1971), although spectral resolution was hindered by the overlapping of many intense bands. The investigation of the near infrared (NIR) spectra of Ca-bentonites has enabled us to distinguish the absorptions due to water molecules from those of structural hydroxyl groups and to perform the spectral assignments of the overtone and combination bands observed in phyllosilicates (Cariati *et al.*, 1981). NIR spectra allow easier detection of the several types of water molecules simultaneously present in the interlayer. Thus we have made a comparative study on some M(I)- and M(II)-bentonites (M(I) = Li, Na, K; M(II) = Ca, Ba, Ni, Cu). The aim of this investigation is: (1) to seek confirmation of previous IR results; (2) to correlate changes in the vibrational properties of distinguishable water molecules with the nature of the exchange cations and the hydration status of the samples.

#### EXPERIMENTAL

Natural bentonite from Uri, Sardinia, was used in this study. Pietracaprina *et al.* (1972) reported a structural formula for this material of  $(\text{Si}_{7.878}\text{Al}_{0.122})(\text{Al}_{3.156}\text{Fe(III)}_{0.235}\text{Mg}_{0.561})(\text{OH})_4\text{O}_{20}$  and a cation-exchange capacity (CEC) of 65 meq/100 g. Homoionic samples were obtained by usual exchange procedures (Bart *et al.*, 1979) using metal chloride solutions. The exchanged samples were equilibrated over  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  solutions or dehydrated under *vacuum* to obtain different water/ion ratios. The final water content was monitored by thermogravimetric analysis using a Perkin-Elmer TGS-2 apparatus under a nitrogen stream and a heating rate of  $5^\circ\text{C}/\text{min}$ . NIR spectra were recorded with a Beckman Acta M IV spectrophotometer equipped with a reflectance unit.  $\text{BaSO}_4$  was the reference sample. The spectra were fitted to a sum of Gaussian-shaped bands in the 1360–2100-nm range using a least-squares program run on an Univac 1108 computer. The quality of the fit was judged from the agreement factor which indicated that the absorptions were reasonably described, as a first approximation, by Gaussian shape. It should be noted that the hydroxyl-group bands had almost the identical half-widths and positions in all samples, whereas the water absorptions were markedly different with varying conditions.

#### RESULTS

Typical spectra of bentonites (that of the Ca-exchanged sample is shown in Figure 1), show in the NIR region bands at 1409 and 2205 nm due to framework hydroxyl groups plus three main absorptions attributable to water molecules. Shoulders A and C (Figure 1) are due to water-OH groups engaged in strong hydrogen bonds (Cariati *et al.*, 1981) and band B (Figure 1) is due to "free" water molecules involved in weak interactions with the low-basicity oxygen ions of the silicate surfaces (Cariati *et al.*, 1981). Assignments of the NIR absorptions are listed in Table 1.

Spectral changes appeared by varying the exchange cation or dehydrating the samples. Representative results concerning several monoionic samples are listed in Tables 2 and 3 as a function of the water/ion ratio. With reference to band A in higher hydrates (see Table 2) the absorption value is remark-

ably constant within the series of samples containing mono-valent and divalent ions; however, for comparable  $\text{H}_2\text{O}/\text{M}$  ratios, higher wavelength values differentiate Ca-, Ba-, Ni-, and Cu-bentonites from Li-, Na-, and K-bentonites (cf., Cu- and K-exchanged samples at  $\text{H}_2\text{O}/\text{M} \approx 8$ ). In addition, irrespective of the exchange cation, with dehydration, band A progressively decreased in intensity and shifted to higher wavelength and ultimately disappeared at the lowest  $\text{H}_2\text{O}/\text{M}$  ratios (see Figure 2 for the results of a band analysis on Ca-bentonite). Although less clearly distinguished, band C showed a similar trend. In contrast, absorption band B occurred at almost the same wavelength for all the samples having  $\text{H}_2\text{O}/\text{M}$  ratios greater than  $\sim 10$ . On further dehydration, the absorption shifted and approached a distinct limit for the different cations (see Table 3). Indeed, as the band was still observed in the spectra of the most strongly dehydrated samples, it must be due to the residual water molecules associated with the exchange cation.

#### DISCUSSION AND CONCLUSIONS

The results obtained from spectral analysis of the NIR absorption spectra of water molecules are consistent with previous suggestions about the coexistence of discrete arrays of water molecules in phyllosilicates contrary to the normal ionic solutions (Farmer and Russell, 1971; Cariati *et al.*, 1981). In fact, in layer silicates, in addition to the water molecules strongly linked through hydrogen bonds, water molecules exhibiting higher stretching frequencies are always present. These "free" water molecules may exist in different states, depending on the water content of the samples.

From a statistical point of view, it is unlikely at high  $\text{H}_2\text{O}/\text{M}$  ratios that the "free" molecules, being interacting with the surfaces, belong to the inner hydration shell of the exchange cations. Several studies (e.g., McBride *et al.*, 1975a; McBride *et al.*, 1975b) suggest that in hydrated layer silicates exchangeable cations occur as aquo-ions freely tumbling as in aqueous solutions. After dehydration, the hydration shells of the ions progressively shrink, the interlayer distance decreases, and the water molecules associated with the cations approach the internal surfaces.

The experimental results enable us to evaluate the effects

Table 1. Assignments of near-infrared absorption bands in Ca-bentonite ( $\text{H}_2\text{O}/\text{Ca} \approx 32$ ).<sup>1</sup>

H <sub>2</sub> O			OH		
$\nu_w + 2\delta_w$ A	$\nu_w' + \delta_w$ B	$\nu_w + \delta_w$ C	$2\nu_{\text{OH}}$	$\nu_{\text{OH}} + \delta_{\text{AlOH}}$	
1456 sh	1911 vs	1978 sh	1409 s	2205 s	nm
6868	5233	5056	7097	4535	cm <sup>-1</sup>

<sup>1</sup>  $\nu_w$  = low-frequency stretching vibration ( $3420\text{ cm}^{-1}$  in the infrared spectrum);  $\nu_w'$  = high-frequency stretching vibration not resolved in the infrared spectrum and calculated at about  $3630\text{ cm}^{-1}$  from the combination band value;  $\delta_w$  = bending vibration;  $\delta_{\text{AlOH}}$  = bending vibration; sh = shoulder; vs = very strong; s = strong.

Table 2. Spectral variations of band A for higher hydrates of M(I)- and M(II)-bentonites.

M	H <sub>2</sub> O/M	λ (nm)	M	H <sub>2</sub> O/M	λ (nm)
Ca	31.8	1456	Li	14.6	1453
	13.0	1460		7.2	1456
	6.1	1461		5.0	1460
Ba	20.2	1456	Na	9.4	1456
	8.0	1463		7.0	1460
Ni	26.7	1454	K	7.8	1457
	12.2	1457		5.0	1458
	8.0	1464			
Cu	22.4	1453			
	12.9	1463			
	7.9	1464			

of the exchange cations on the distinguishable water populations as a function of the hydration state of the samples. As is expected, band A, derived from water that is hydrogen-bonded through either horizontal or vertical bridges (including also water molecules linked to the cations), is the first to be modified by dehydration. This band is a combination of the stretching and bending vibrations of the water molecules. Because the latter mode is found at almost the same value in the IR spectra of samples containing the same cation, significant variations of the H–O–H angle are unlikely. On the other hand, the decrease in the bending frequency noted by Fripiat *et al.* (1960), Russell and Farmer (1964), and Poinsignon *et al.* (1978) for dehydrated samples should make only a minor contribution to the overall frequency value of the combination band. Thus, the spectral changes of band A suggest that the ions perturb mainly the stretching properties of the surrounding water molecules by polarizing the OH-bonds. The fewer the water molecules, the higher the polarization of each bond, accordingly to the continuous shift to higher wavelength observed for band A.

Regarding band B, it is likely that at high water contents the "free" water molecules are not perturbed by the compensating cations and, therefore, have similar vibrational properties, in accordance with the experimental results. In lower hydrates the "free" water is, instead, directly coordinated to the ions.

Table 3. Spectral variations of band B for M(I)- and M(II)-bentonites under conditions of variable hydration.<sup>1</sup>

M	H <sub>2</sub> O/M	λ (nm)	M	H <sub>2</sub> O/M	λ (nm)
Cu	22.4	1912	Li	14.6	1911
	8.5	1912		3.0	1906
	1.7	1919		0.9	1906
Ni	26.7	1912	K	7.8	1905
	9.0	1911		3.4	1902
	3.0	1917		0.9	1901
Ca	31.8	1911	Na	9.4	1905
	13.0	1909		4.6	1902
	3.3	1907		0.5	1901
Ba	20.1	1911			
	13.1	1908			
	1.0	1902			

<sup>1</sup> Samples with H<sub>2</sub>O/M >7.8 and 9.4 were not obtained for K and Na, respectively.

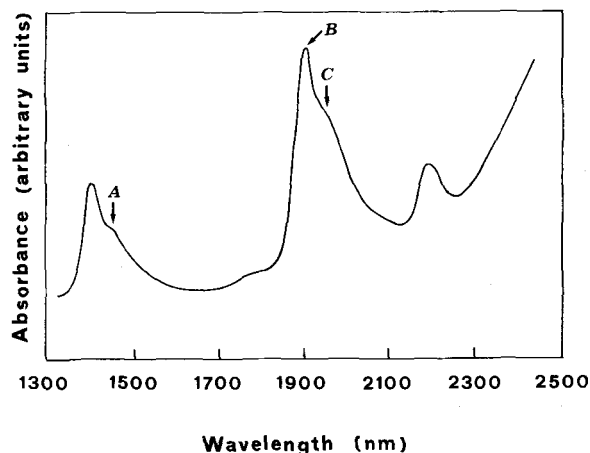


Figure 1. Near infrared spectrum of Ca-bentonite (H<sub>2</sub>O/M ~ 32).

Here the solvent molecules are subjected only to the cationic field, as strong hydrogen bonds are absent. Accordingly, band B is extremely sensitive to the nature of the exchange cation. Again, the more polarizing the cation, the weaker the water OH-bonds and the higher the wavelength of band B absorption. The polarizing order is almost the same as expected on the basis of the cationic charge/radius ratio. However, contributions from both geometrical and bonding properties can not be excluded.

In conclusion, several kinds of interactions are responsible for the vibrational properties of the water molecules in layer silicates. Moreover, these properties vary with the water content. The water absorptions, especially bands A and C, are broad, and all the above conclusions must be treated on a statistical basis. A continuous distribution of water molecules with hydrogen bond lengths around that associated to the maximum of each band seems more realistic.

Nevertheless, the data are consistent with the high dissociation degree of the water molecules as well as the acidic and catalytic properties, which themselves are dependent on the hydration conditions, found in phyllosilicates (Bart *et al.*, 1979; Fripiat *et al.*, 1964; Mortland and Raman, 1968).

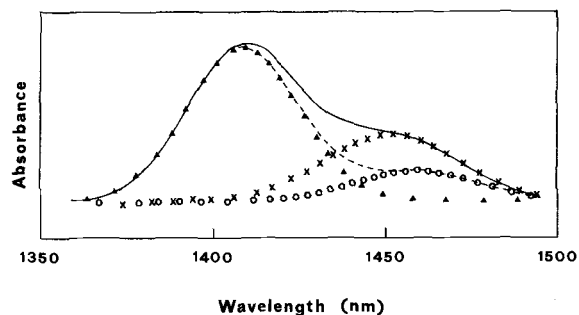


Figure 2. Part of near infrared reflectance spectra of Ca-bentonite after decomposition in Gaussian bands: (a) sample with H<sub>2</sub>O/M = 31.8: — total absorption; ▲▲▲ band at 1409 nm due to structural hydroxyl groups; ××× band 'A'. (b) sample with H<sub>2</sub>O/M = 13.0: - - - total absorption; ▲▲▲ band at 1409 nm due to structural hydroxyl groups; ○○○ band 'A'.

## ACKNOWLEDGMENTS

Thanks are due to Dr. P. Cocetta for her technical assistance and to C.N.R. for financial support.

*Istituto di Chimica Generale e  
Inorganica  
Università di Sassari  
Via Vienna 2  
07100 Sassari, Italy*

F. CARIATI  
L. ERRE  
G. MICERA  
P. PIU

*Istituto di Chimica Agraria  
Università di Sassari  
Via de Nicola  
07100 Sassari, Italy*

C. GESSA

## REFERENCES

- Bart, J. C. J., Cariati, F., Erre, L., Gessa, C., Micera, G., and Piu, P. (1979) Formation of polymeric species in the interlayer of bentonite: *Clays & Clay Minerals* **27**, 429–432.
- Cariati, F., Erre, L., Micera, G., Piu, P., and Gessa, C. (1981) Water molecules and hydroxyl groups in montmorillonites as studied by near infrared spectroscopy: *Clays & Clay Minerals* **29**, 157–159.
- Farmer, V. C. and Russell, J. D. (1971) Interlayer complexes in layer silicates: the structure of water in lamellar ionic solutions: *Trans. Faraday Soc.* **67**, 2737–2749.
- Fripiat, J. J., Chaussidon, J., and Touillaux, R. (1960) Study of dehydration of montmorillonite and vermiculite by infrared spectroscopy: *J. Phys. Chem.* **64**, 1234–1241.
- Fripiat, J. J., Helsen, J. A., and Vielvoye, J. (1964) Formation de radicaux libre sur la surface des montmorillonites: *Bull. Groupe Franc. Argiles* **10**, 3–10.
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M. (1975a) Electron spin relaxation and the mobility of manganese(II) exchange ions in smectites: *Amer. Mineral.* **60**, 66–72.
- McBride, M. B., Pinnavaia, T. J., and Mortland, M. M. (1975b) Electron spin resonance studies of cation orientation in restricted water layers on phyllosilicate (smectite) surface: *J. Phys. Chem.* **79**, 2430–2435.
- Mortland, M. M. and Raman, K. V. (1968) Surface acidity of smectites in relation to hydration, exchangeable cation, and structure: *Clays & Clay Minerals* **16**, 393–398.
- Pietracaprina, A., Novelli, G., and Rinaldi, A. (1972) Bentonite deposit at Uri, Sardinia, Italy: *Clay Miner.* **9**, 351–355.
- Poinsignon, C., Cases, J. M., and Fripiat, J. J. (1978) Electrical polarization of water molecules adsorbed by smectites. An infrared study: *J. Phys. Chem.* **82**, 1855–1860.
- Russell, J. D. and Farmer, V. C. (1964) Infrared spectroscopic study of the dehydration of montmorillonite and saponite: *Clay Miner. Bull.* **5**, 443–464.

(Received 22 January 1982, accepted 8 June 1982)