

NOTE

USE OF X-RAY POWDER DIFFRACTION AND LINEAR DICHROISM METHODS TO STUDY THE ORIENTATION OF MONTMORILLONITE CLAY PARTICLES

Key Words—Infrared spectroscopy, Linear dichroism, Montmorillonite, Orientation, X-ray powder diffraction.

X-ray powder diffraction (XRD) is a powerful technique widely used in the identification and analysis of clays. An important crystallographic value usually determined by this technique is the basal spacing of the clay. This parameter provides valuable information regarding processes which take place in the interlayer space, such as the intercalation of water and solute molecules, the adsorption and orientation of organic molecules on the clay surface, and the formation of pillared interlayer complexes (Brindley and Brown, 1980; Lahav *et al.*, 1978; Sterte, 1986; Theng, 1974). The intensity of the basal reflections is strongly enhanced in specimens having largely parallel orientation of the clay particles on their basal surfaces and perpendicular to the *c*-axis (in the context of this note these will be referred to as "oriented" samples) (Brindley and Brown, 1980; van Olphen and Fripiat, 1979). Conversely, it is usually assumed that if a distinct XRD peak corresponding to the basal reflections is observed for a clay sample, its particles are well oriented. Although the preparation of highly oriented samples is relatively easy for pure clays, it is not always so for heterogeneous materials, such as soils or clay-organic complexes. A peak corresponding to the basal spacing in the XRD pattern of a poorly oriented sample of such materials may be erroneously interpreted as representing the whole sample, whereas in fact it may arise from relatively small amounts of parallel platelets. This may lead to overestimation of the inter-platelet ("interlamellar") volume in the clay, which is used, for example, in calculations of molecular adsorption and intercalation.

Information regarding the orientation of clay platelets can be obtained using infrared linear dichroism (IRLD) spectroscopy, *i.e.*, the differential absorption of linearly polarized infrared light. This technique has been used in studies of clays mainly to determine the polarization of the lattice vibrations (Farmer, 1974) and to determine the orientation of organic molecules adsorbed on the clay surface (Margulies and Rozen,

1986; Nguyen *et al.*, 1987; Raupach *et al.*, 1975; Seratosa, 1966).

We report here an experiment in which a thick film of montmorillonite having low overall orientation (composed of a thin, highly oriented film covered with a much thicker, non-oriented film) showed almost the same XRD pattern as a thin, highly oriented film. The use of IRLD spectroscopy enabled a better evaluation of the sample orientation. We demonstrate how erroneous conclusions regarding the basal spacing of the clay sample in the bulk can be reached by the indiscriminate use of the XRD technique, and suggest that a combination of the two techniques, XRD and IRLD, might enable a more meaningful use of the diffraction data, especially for the calculation of interlamellar volumes of the clay.

MATERIALS AND METHODS

Preparation of oriented clay samples

Na-montmorillonite SWy-1 (Source Clays Repository of The Clay Minerals Society) was used as obtained. To prepare a highly oriented sample for XRD and IR absorption measurements, 2 ml of a 0.01% sonicated aqueous suspension of the clay was deposited on an IR transparent ZnS disk ("Irtan-2", 32 × 2 mm, Barnes Analytical) and kept in a covered Petri dish for 4 days at room temperature. The cover was then slightly opened to allow slow evaporation of the water. The sample was air-dried in about 48 hr (stage A). This procedure gave a thin, highly oriented film. Once the XRD and IR absorption measurements of this sample were carried out, 2 ml of water was carefully added and rapidly evaporated at 60°C. The XRD and IR measurements were repeated to verify that this treatment did not affect the orientation of the sample. Then, 2 ml of a 0.1% sonicated clay suspension was carefully placed on the oriented film, and the added suspension was rapidly evaporated at 60°C (stage B). This formed a much thicker film than in stage A, in which a high

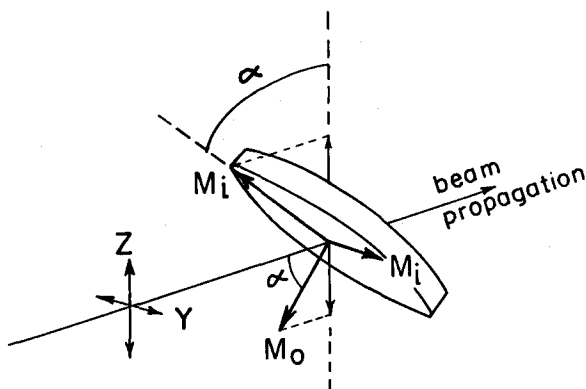


Figure 1. Schematic representation of the spatial orientations of in-plane and out-of-plane transition moments (M_i and M_o , respectively), and of y - and z -polarized light beams propagating inside a tilted sample of oriented montmorillonite.

fraction of the clay particles were not oriented. XRD and IR absorption measurements of the combined film were also obtained. A completely non-oriented sample of the montmorillonite was prepared for IR measurements by pressing the powder in a KBr pellet.

Infrared and X-ray powder diffraction measurements

Fourier-transform infrared linear dichroism (FT-IRLD) spectra of the clay samples, oriented on ZnS windows or randomly distributed in a KBr pellet, were measured in a Nicolet MX-S FTIR spectrophotometer interfaced to an Elite Star 16-bit PC and to a Goertz SE 284 digital plotter. The spectra were recorded at oblique incidence. The angle between the direction of the incident beam and the normal to the plane of the sample was about 55° . The light was polarized by means of a grid polarizer placed in front of the sample. Two consecutive spectra were recorded: one with light polarized parallel to the plane of the sample (y), and another one with light polarized in the orthogonal direction (z). XRD measurements were carried out on a Philips 1030 diffractometer using the $\text{CoK}\alpha$ radiation, at a scanning rate of $1^\circ 2\theta/\text{min}$ and full-scale intensity of 400 c/s.

The dichroic ratio

The intensity of absorption of IR light is a function of the square of the scalar product of the vibrational transition moment and the electric vector of the light. For a clay sample in which the silicate layers are perfectly oriented parallel to the surface of an infrared-transparent support, such as a ZnS plate, and having isotropic distribution within that plane, the absorption of polarized light in a geometrical arrangement as that shown in Figure 1 is given by

$$A_y = E^2 M_i^2 \quad (1)$$

and

$$A_z = E^2 (M_i^2 \cos^2 \alpha + M_o^2 \sin^2 \alpha), \quad (2)$$

where A_y and A_z are the absorbances for y and z polarized light, respectively, E is the magnitude of the electric vector of the light (assumed to be the same for the z and y directions), M_i and M_o are the magnitudes of the transition moment vectors associated with the in-plane and out-of-plane vibrations, respectively, and α is the angle between the normal to the plane of the silicate layers and the direction of propagation of the beam through the sample. Due to refraction, this angle might be smaller than the angle of incidence (Zbinden, 1964). The dichroic ratio d , defined as the ratio of the absorption intensities for the two orthogonal polarizations ($d = A_y/A_z$), for pure in-plane and out-of-plane transitions is therefore equal to $1/\cos^2 \alpha$ and zero, respectively.

If the clay particles are not oriented, the intensities of absorption of light of the two polarizations are each given by

$$A = \frac{1}{2} E^2 (2M_i^2 + M_o^2), \quad (3)$$

and the dichroic ratio $d = 1.00$. Therefore, measurement of the dichroic ratio at oblique incidence ($\alpha \neq 0$) yields information concerning the degree of orientation of the sample.

For partly oriented samples the degree of orientation cannot be accurately calculated because the actual distribution of the clay particles in the sample is unknown and bands corresponding to transitions of different polarizations usually overlap. Still, the dichroic ratios measured at selected wavelengths can be used, even if they do not correspond to well-resolved bands, for distinguishing between "highly oriented," "poorly oriented," and "unoriented" samples.

RESULTS AND DISCUSSION

The FT-IRLD spectra in the $900\text{--}1300\text{-cm}^{-1}$ region of the sample of montmorillonite in the two orientation stages are shown in Figures 2a (stage A) and 2b (stage B), and the dichroic spectrum of montmorillonite dispersed in the KBr pellet is presented in Figure 2c. Measurements of the oriented samples carried out at normal incidence ($\alpha = 0$) revealed no differences in the absorption intensities for y and z polarized light. These results indicate that the clay particles were symmetrically distributed around the axis normal to the plane of the film and that a model similar to that shown in Figure 1 and Eqs. (1) to (3) could be used. It should be noted that this symmetry axis was also the optical axis of the sample. Because this axis was neither parallel nor perpendicular to the z direction, the state of polarization of the light might have been changed during propagation through the sample. Using the known weights of the clay, its approximate density, and the

Table 1. Dichroic ratios (d)¹ calculated from linear dichroism spectra of oriented, partially oriented, and completely randomized montmorillonite samples.

	1088 cm ⁻¹	1042 cm ⁻¹
Highly oriented film (stage A)	0.46	1.25
Low overall orientation in film (stage B)	0.66	1.03
Random distribution (in KBr pellet)	1.00	1.00

¹ $d = A_y/A_z$, where A_y and A_z are the measured absorption intensities for y - and z -polarized light, respectively, at the specified wavenumbers; they do not necessarily correspond to single vibrational transitions.

area of the samples, the thicknesses of the clay films in stages A and B were calculated to be about 0.1 and 1 μm , respectively. These values are much smaller than the wavelength of the light in the IR region and, therefore, the possibility of a depolarization effect in the anisotropic sample was ignored.

The intense and broad absorption band observed in the IR absorption spectrum of montmorillonite in the 1000–1200-cm⁻¹ region has been assigned to the superposition of four different Si–O stretching vibrations (Farmer, 1974). These vibrational transitions can be recognized in Figure 2a as discrete maxima at 1113, 1088, and 1042 cm⁻¹, and as a shoulder at 1022 cm⁻¹. It is evident from this Figure, even without resolving the spectra into their individual components, that the vibration corresponding to the absorption of 1088 cm⁻¹ is polarized out-of-plane, whereas the other three are polarized in the silicate plane, in agreement with previous reports (Farmer, 1974).

The dichroic ratios measured at 1088 and 1042 cm⁻¹ are given in Table 1 for the three orientation stages. Clearly, from Figure 2a and Table 1, stage A shows a strong dichroic behavior, suggesting that in this thin sample the clay particles were highly oriented, the silicate layers being parallel to the surface of the film. Addition of a relatively large amount of clay, kept at minimal orientation, on top of this oriented film resulted in a corresponding increase of absorption of light of both polarizations as well as in a pronounced decrease of the dichroism over the entire spectrum (stage B, Figure 2b). This result indicates that the added material was indeed minimally oriented. In Figure 2c no dichroism can be detected (the two absorption curves coincide, the dichroic ratio equals 1), indicating that, as expected, the clay particles were completely unoriented in the KBr pellet.

The XRD patterns from 4° to 27°2 θ of the films at stages A and B are presented in Figures 3a and 3b, respectively (the large number of strong diffractions from the crystalline ZnS support precluded extending the measurements beyond 27°2 θ). Strong bands of about the same intensity are present above the curved baseline of the ZnS support (Figure 3c) at 7.6°2 θ in Figure 3a and at 7.0°2 θ in Figure 3b, and correspond to basal

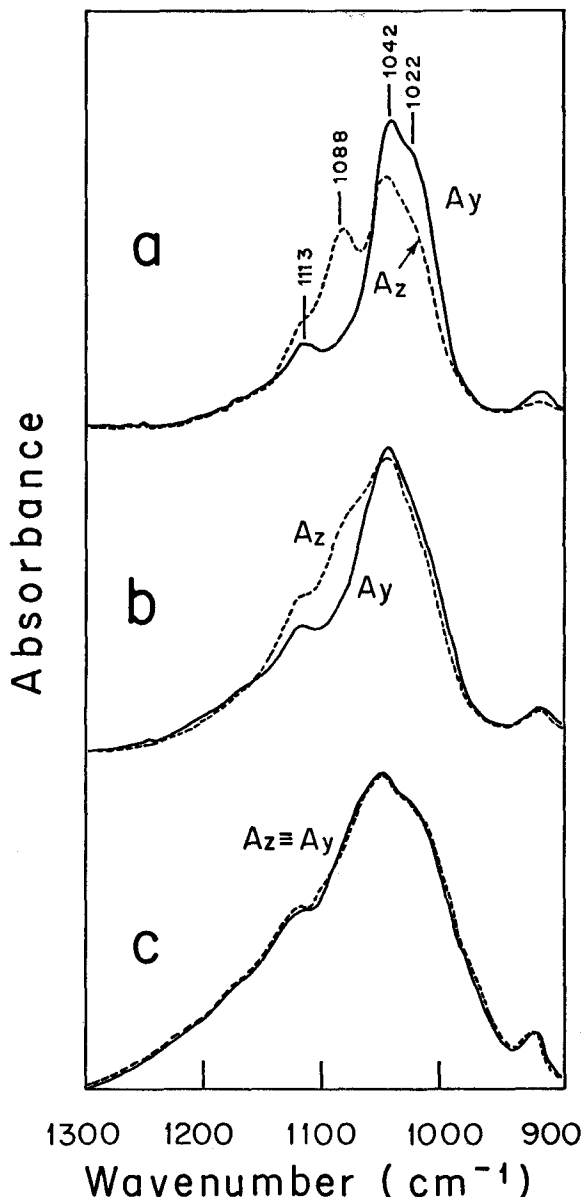


Figure 2. Fourier-transform infrared linear dichroism spectra of montmorillonite: (a) Highly oriented film (stage A); (b) low overall orientation in film (stage B); (c) random distribution (in KBr pellet). A_y and A_z are the absorbances for light polarized in the y and z directions, respectively (see Figure 1). Spectra were recorded at oblique incidence.

spacings of the air-dried montmorillonite of 13.5 Å (stage A) and 14.6 Å (stage B), respectively. Clearly, from the evidence presented above, the latter value does not represent the basal spacing of all the montmorillonite present in the sample at stage B.

The XRD pattern of a totally randomized powder sample of montmorillonite is presented in Figure 3d. The strongest band in this diffractogram appears at 23.0°2 θ (4.48Å) and corresponds to the 110 and 020

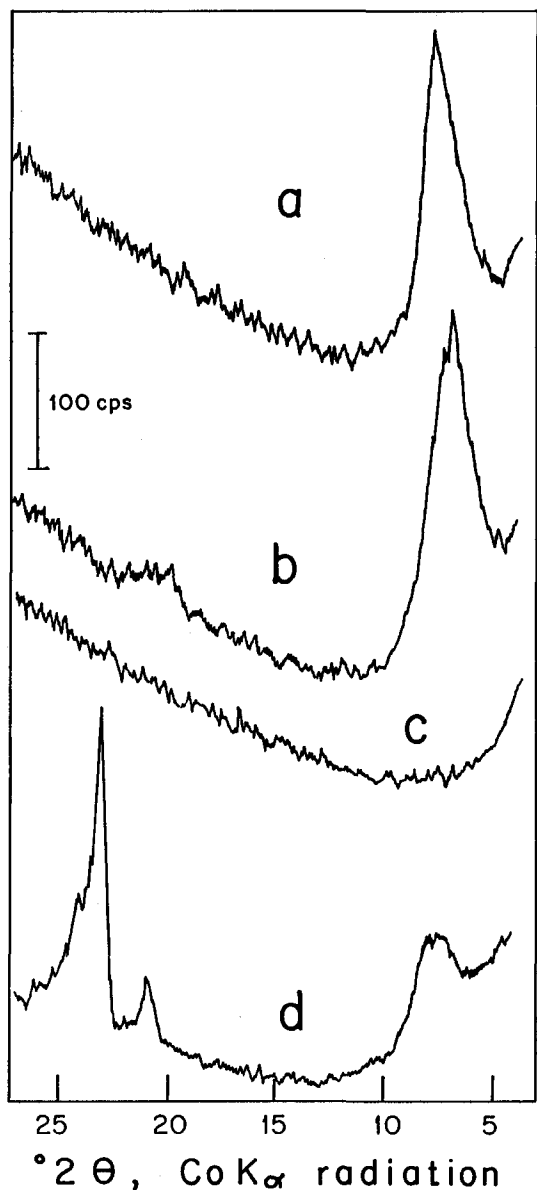


Figure 3. X-ray powder diffraction patterns of montmorillonite: (a) highly oriented film (stage A); (b) low overall orientation in film (stage B); (c) ZnS support; (d) randomized powder of air-dried montmorillonite on aluminum support.

reflections (Brindley and Brown, 1980). In principle, the relative intensity of this band in a partially oriented sample could have been used for monitoring the amount of randomly distributed clay particles. Our results with the montmorillonite films A and B show, however, that this method is not sensitive enough. From the linear dichroism measurements discussed above, most of the

clay in stage B clearly was not oriented. Nevertheless, no distinct reflections were observed at $23^\circ 2\theta$, neither for the highly oriented (stage A) nor for the poorly oriented (stage B) samples (Figures 3a and 3b, respectively). The only observable difference between the XRD patterns of stages A and B is a low-intensity peak at $20.6^\circ 2\theta$ (5.0 Å), which probably corresponds to a 003 reflection.

We conclude that the XRD technique is very sensitive to small amounts of oriented aggregates present in a clay sample, but that the technique may be misleading in estimating the overall orientation in non-homogeneous samples. In such materials, an additional orientation-dependent technique, such as IRLD, should be used to obtain a better estimate of the degree of orientation.

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(Received 24 July 1987; accepted 22 March 1988; Ms. 1701)