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Effect of Ca-Montmorillonite Expansion on X-ray Diffraction Intensities[1]

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Abstract: The most abundant clay mineral group in Iowa soils is montmorillonite, most commonly calcium-saturated (Hanway *et al.* 1960). The calcium montmorillonite-water system was therefore selected for detailed X-ray study.

Montmorillonite is unusual among minerals in that it has an expansible lattice in the *c* direction. That is, upon wetting with water, the individual silicate layers separate to allow entry of water, and the mineral expands. Characteristics of expansion are readily studied by means of X-ray diffraction: the X-ray diffraction angle gives the average layer-to-layer "d_{001}" spacing for any given moisture condition; the sharpness of the diffraction peak is a measure of uniformity of the d_{001} spacing; and the intensity of the peak relates to uniformity of the d_{001} spacing and in addition to the electron density distribution within the repeating elements. The latter is embodied in the "structure factor".

The variation of d_{001} structure factor caused by montmorillonite expansion is the subject of this paper.

DIFFRACTION INTENSITY

The structure factor is a complex quantity whose magnitude is the amplitude of the scattred wave, and whose direction is determined by the phase of the scattered wave. No matter how complicated a crystal, one may picture it as a series of simple interpenetrating simple lattices, one for each different atom in the crystal. The problem of evaluating the structure factor can be considered to be that of compounding several wave motions, all of the same period, but different in phase and amplitude.

Other factors also affect diffraction intensity:

$$I = \theta \mid Fl \mid^2 \Psi \qquad (1)$$

where θ is the combined Lorentz-polarization factor, F_l, is the layer structure factor, and ψ is the mixing function. The Lorentz-polarization factor depends in part on experimental technique, and may be estimated from the International Tables for X-ray Crystallography (1959). Importance of the Lorentz-polarization factor at low diffraction angles is illustrated by the fact that it will cause a 17 Å peak to be three times as intense as a 10 Å peak, other factors being the same.

The mixing function ψ depends on the spacings of the constituent phases and the frequency of the occurrence of these spacings. When a montmorillonite system becomes ordered (the system is made up of nearly all one primary spacing), the inten-

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sity will increase, whereas if there were many spacings present, the intensity of reflections will decrease (MacEwan *et al.* 1961).

By taking the center of the silicate layer as the plane of the origin and limiting the analysis to basal (00*l*) spacings, the structure factor reduces to

$$F^{00l} = 2 \sum_{j=1}^{J/2} f_j \cos 2\pi \, (l \, z_j) \qquad (2)$$

(Buerger 1960, p. 264), where f_j is the structure factor of the jth atomic layer, *l* is the Miller index, and z_j is fractional position of each reflecting layer in the unit cell.

MATERIALS

The clay selected was a commercially available Wyoming bentonite (Volclay-SPV), a product of the American Colloid Company. The sample was purified from coarse-grained impurities by sedimentation, and homoionic calcium montmorillonite prepared by leaching the fines with a calcium chloride solution. The clay was then washed free of electroyte as indicated by a silver nitrate test.

X-RAY APPARATUS

The relative vapor pressure of water made available to the clay sample was continuously controlled by conducting all X-ray tests inside a sealed and evacuated adsorption chamber.

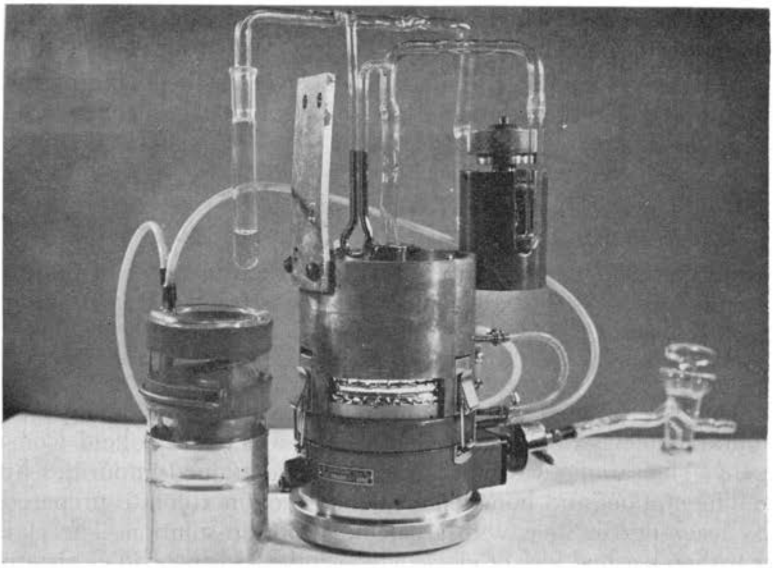
The adsorption chamber consisted of a Rigaku-Denki controlled atmosphere high-temperature X-ray diffractometer furnace modified for use at room temperature (figs. 1 and 2). Heating elements were removed, and the chamber was equipped with a sealed water reservoir separated from the chamber by a mercury-sealed ground glass stopcock and a dual limb mercury manometer. The temperature of the chamber and water reservoir was maintained at 25.0°C.

Water was introduced into the adsorption chamber by means of the mercury-sealed stopcock connecting the water reservoir to the chamber. A cathetometer capable of reading to 0.02 mm was used in measuring vapor pressure differences with the manometer.

X-ray windows on the adsorption chamber were 0.02 mm thick aluminum foil backed with ½ mil "Mylar" polyester film to prevent pin hole corrosion of the aluminum foil by water. A general Electric XRD-5 diffractometer with copper Kα radiation was utilized throughout the investigation.

PROCEDURE

Approximately 1 gm of prepared clay sample was dispersed in 250 ml of distilled water and deposited in a thin layer on a 30 mm diameter medium-porosity fritted glass disc, by draining the sus-



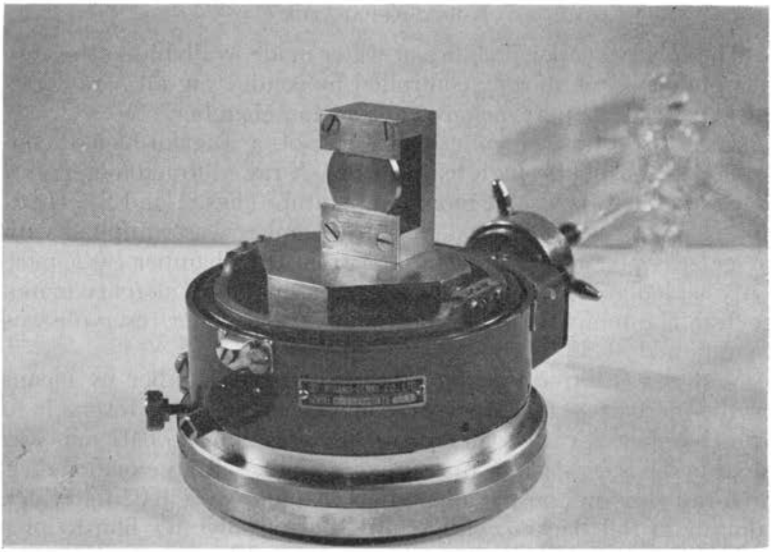


Figure 1. (a) X-ray adsorption apparatus, assembled.
(b) Base of the X-ray adsorption apparatus showing the sample holder.

pension through the disc using a water aspirator. After one day of air drying and 5 days drying over phosphorous pentoxide, the sample was placed in the adsorption chamber and the top of the

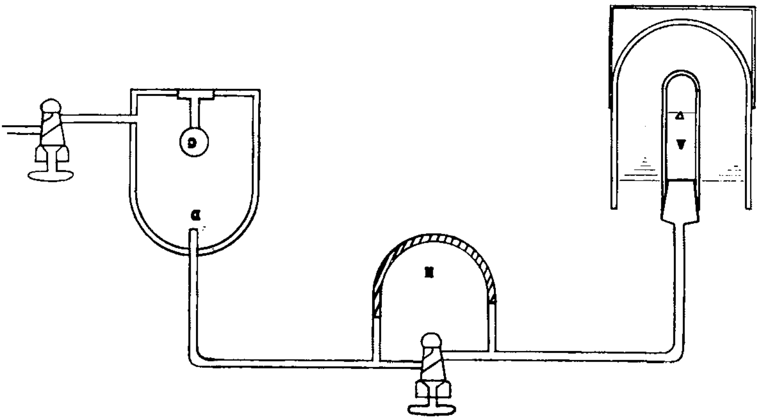


Figure 2. Schematic drawing of X-ray adsorption apparatus.
A: water reservoir
M: mercury manometer
D: adsorption chamber
C: sample

chamber was clamped tightly in place. All joints were lubricated with high-vacuum grease to eliminate leaks. Triple distilled water was placed in the water reservoir and the system was evacuated using a mechanical fore pump and an oil diffusion pump. The system was pumped for 26 days; vacuum was maintained at 5×10^{-5} mm Hg, indicated by an ionization gauge, for the last eight days.

The chamber was then removed from the pump and aligned on the X-ray diffractometer. As soon as thermal equilibrium was attained the collapsed $00l$ basal spacings were measured by X-ray diffraction. Immediately thereafter, a small increment of water vapor was distilled into the adsorption chamber and X-ray tests were made periodically up to 24 hours, which was the minimum allowed for the system to reach equilibrium after a transfer of water vapor. This procedure was repeated until saturation was reached.

A gradual desorption was then accomplished by redistilling water back into the water reservoir by employing a cold bath around the reservoir, with equilibration and test procedures performed as before.

X-ray diffraction intensities were obtained from measurements of diffraction peak areas with a planimeter. A minimum of three peaks was averaged.

RESULTS

The minimum d_{001} spacing of 10.1 Å was observed at zero relative pressure. This distance corresponds to the 9.2 Å thickness of the pyrophyllite silicate structure, with layers separated by calcium ions fitting with a coordination of six between opposing silica tetrahedra bases (Senich, 1966). The maximum basal spacing observed was 19.2 Å, occurring at saturation.

Intensities of the first through sixth order basal spacings corrected for the Lorentz-polarization factor are shown by the solid lines in figure 3.

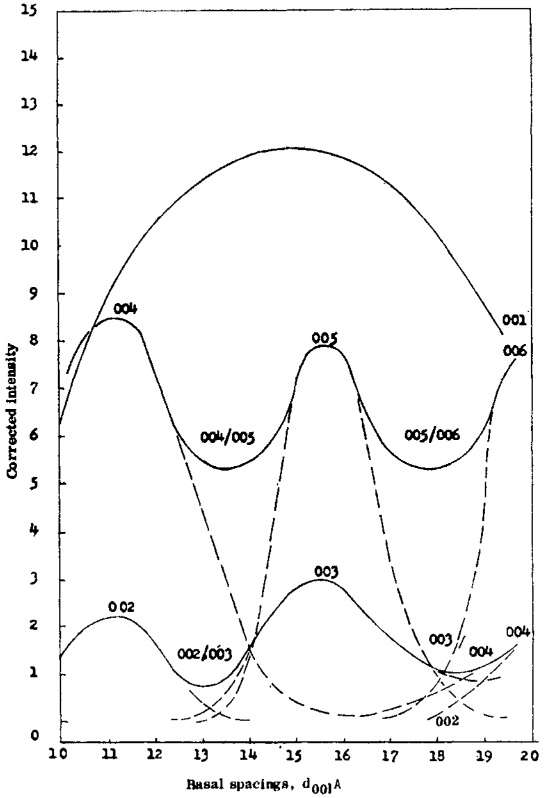


Figure 3. Intensity of higher order basal spacing reflections versus first order basal spacing.

Nearly always the first order reflection, d_{001}, was the most intense, its intensity reaching a maximum at intermediate d-spacings. On the other hand, d_{002} reflections were observed only at high and low d-spacings. This same observation applies to other higher order spacings: odd-numbered indices gave strongest reflections in the intermediate range of d-spacings, and even-numbered indices gave strongest reflections at high and low d-spacings.

For d spacings between those which give maximum intensities, for example in the range between 004 and 005 maxima, line breadths and d spacings suggest that the observed reflections are composites of two indices, in this case 004/005. Based on this interpretation, individual intensity maxima may be resolved into the contributing components, indicated by dashed lines in figure 3.

DISCUSSION

The absence of diffraction peaks qualitatively indicates the presence of repeating electron density planes at the d/2 spacing. That is, if d gives a diffraction due to waves being one wavelength out of phase, a plane of atoms occurring at d/2 will produce waves one-half wavelength out of phase, and the result will be annulment. This may be seen by equation (2), where z_j indicates the vertical positions of atoms in the unit cell. In this case the structure factor equals $2\ [f_1 \cos 2\pi\ (1) + f_2 \cos 2\pi\ (\frac{1}{2})]$, or if f_1 and f_2 are equal, $2\ [f - f] = 0$.

Referring to figure 3 extinction of the 002 when d_{001} is between 13 and 18 Å indicates a layer of atoms in the region 3.2 to 4.5 Å outward from the center of the clay layer (table 1). In the pyrophyllite structure this approximately corresponds to the outer layers of oxygen atoms.

Table 1. Inferred positions of atomic layers relative to the central Al layer.

00	d^{00l} for annulment	$Z = \frac{d^{00l}}{2}$	Probable layer identifications
001	10.1 (weak)	5	Interlayer Ca
	19.2 (weak)	9.6	Interlayer Ca and water
002	13-18	3.2 - 4.5	Outermost O layer
003	10-13	1.7 - 2.2	?
	18-20 (weak)	3 - 3.3	Silicon
004	14-18	1.7 - 2.3	?
005	10-14	1 - 1.4	O - OH layer
	18-20	1.8 - 2.0	?
006	10-18	0.9 - 1.5	O - OH layer

Similarly the lack of 003 for d_{001} of 18 to 20 Å may relate to position of the silicon layers, and extinctions of the 005 and 006 appear to relate to position of the 0 + 0H layers. The 003, 004, and 005 extinctions also indicate a layer of atoms at about 2Å from the aluminum layer; this is unexplained, and may be due to other factors.

This study was undertaken mainly to determine structure, if any, of the interlayer water and position of the cations. In this connection the d_{001} intensities were lowest when diffraction lines were sharpest and spacings were presumably most uniform. This occurred at zero relative pressure and near saturation, when d_{001} was 10.1 and 19.2 Å, respectively. As shown in table 1, in these particular cases the structure factor suggests planes of atoms occurring approximately midway in the interlayer region. Presumably these are the exchangeable calciums.

CONCLUSIONS

1. Odd 00*l* indices, i.e., 001, 003, 005 gave strongest diffraction peaks when d_{001} was in the intermediate range of observed spacings, about 14 to 18 Å to 19.2 Å.

2. Extinctions of the 002, 003, 005, and 006 reflections at certain d_{001} spacings correspond to inferred positions of the oxygen, silicon and oxygen-hydroxyl layers in the pyrophyllite structure. Extinctions also indicated presence of a layer at about 2 Å, which was not explained.

3. Loss of intensity of the d_{001} diffraction at low and at high d-spacings corresponding to zero relative pressure and to saturation suggest a plane of atoms centrally located in the interlayer region, probably the exchangeable calcium.

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