X-ray Diffraction Studies on the Arrangement of Water Molecules in a Smectite. 
I. Homogeneous Two-Water-Layer Na-Beidellite

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Abstract

A method of indirect analysis of X-ray diffraction patterns of homogeneous hydrated microcrystalline silicates is introduced. This method is applied to a sodium beidellite of Rupsroth, Bavaria, Germany, hydrated with two water layers to determine all its structural characteristics: namely, the average dimension and size distribution of coherent domains, stacking mode of the layers along the *c* direction, levels and number per unit cell of water molecules. A critical analysis on the ‘concept of homogeneity’ of hydrates and a discussion on the conditions of its application to lamellar microcrystalline silicates with a few numbers of layers are made.

Introduction

The adsorption capacity of water or some organic compounds by certain lamellar silicates (vermiculites, smectites) makes them interesting to study. The investigation of the organization of the water molecules in interlayer space has been made by various authors (Bradley & Serratosa, 1960; Shirozu & Bailey, 1966; De la Calle, Pézerat & Gasperin, 1977; Farmer & Russel, 1971; Conard, 1975; Alcover & Gatineau, 1980) using different techniques: X-ray diffraction (XRD), differential thermal analysis (DTA), thermal gravimetric analysis (TGA), IR, NMR.

These researches have generally been carried out on the thermodynamically stable states containing such an amount of water that is expressable in terms of one or two molecular diameters of water. Their interest was particularly focused on the spatial configuration of the water molecules regarding its relation with the cations saturating the exchange capacity and with the amount and localization of the isomorphic substitutions.

The most satisfactory qualitative and quantitative results appear to be those obtained with the single crystals of vermiculite (De la Calle et al., 1977; Alcover & Gatineau, 1980). This is to be expected in view of the great number of recordable reflections of this mineral. In the case of smectites, however, both microcrystallization and abundance of structural defects yield very few modulated diffraction patterns, which restricts the extension of our knowledge of them.

In this work we have undertaken to investigate the distribution of water molecules along the normal to the (a,b) plane of the layer for a sodium smectite hydrated with two water layers (that is, a Na-smectite which has been in equilibrium at the atmosphere of 90% relative humidity: Glaeser & Méring, 1968). This kind of study can be performed by using one of the following two methods.

(1) One method is direct and based on a one-dimensional Fourier transform. Unfortunately, in the case of smectites theoretical and technical difficulties arise for such a method which requires that:

(a) the mineral has to be very well dispersed to give good quality oriented films, which is not always the case;

(b) the thickness of the films is to be very small (about 100 to 200 μm); such specimens exposed to relative humidity of 90% generally buckle and lead to the deformation of experimental profiles;

(c) from the theoretical point of view, the effect of residual misorientation remaining in the films on the *p(z)* electron density function must be quantitatively considered.

(2) The other method is indirect and based on the comparison of the experimental 00l reflections obtained from a powder pattern with those calculated from models. This method adopted by us appears to be more interesting since the average structure has already been established by previous work (Pézerat & Méring, 1954).

The method which we have established can easily be applied to the investigation of all the hydrates. This method, applied to a sodium smectite [beidellite of Rupsroth, Bavaria, Germany, with structural formula (Si7.73Al0.27)(Al3.36Mg0.64)O20(OH)4Na0.91], enabled us to find the amount of water per unit cell and to determine the atomic levels of the water molecules with an accuracy better than 5%.
1. The principle of the method

The recordable 001 reflections which do not superimpose with hk bands in powder diffraction pattern of the Na-beidellite with two water layers are: 001, 003 and 005. This hydrate with a basal spacing of 15.25 Å* constitutes a stable state in which the thickness of the interlayer is about 5.65 Å, which corresponds approximately to two diameters of water molecules. In considering the orientation of particles in a powder specimen (Plançon & Tchoubar, 1977; Ben Brahim, 1979; Plançon, 1980; Tchoubar, Plançon, Ben Brahim, Clinard & Sow, 1982), the diffracted intensity for a unit cell along the 00 rod of reciprocal space is given by the relation

\[ I_{00}(s) = \frac{N(\pi/2)}{2\pi \Omega s^2} |F_{00}(s)|^2 G_{00}(s), \]  

where \( s = 2 \sin \theta/\lambda; \) \( \Omega \) is the area of the (a,b) planar unit cell; \( N(\pi/2) \) is the density of particles contributing to the diffraction at the 20 angle. \( N(\pi/2) \) was derived from the experimental orientation function (Fig. 1), which was determined by using the technique established by De Courville, Tchoubar & Tchoubar (1979). \( F_{00}(s) \) is the structure factor of the layer and takes into account both the structural formula of the mineral and the number of water molecules per unit cell as well as their atomic levels. \( G_{00}(s) \) is the modulation function which depends on the stacking mode along the normal to the (a,b) plane and the size of the average coherent domain.

In this work, it is for the first time shown how it would be possible to determine the physical parameters describing the hydration of the mineral from three observable 001, 003 and 005 reflections, namely, the number and levels of the water molecules for a unit cell.

The atomic levels of the micaceous part of a layer are those of a Wyoming Na-montmorillonite determined by Pézerat & Mérign (1954) (Table 1). They were checked by Besson (1980) for the studied beidelite. It is also assumed† that the interlayer Na cation is located exactly at the middle of the interlayer space. This is particularly the case for the bivalent cations in the natural vermiculites (Bradley & Serratosa, 1960; De la Calle et al., 1977; Alcover & Gatineau, 1980). Having made this assumption, the effect of the variation of the number of water molecules per unit cell on the relative intensities and on the profiles was determined.

The modulation function was calculated in assuming that the average diffracting volume is the same for all the 001 reflections. Inside the average coherent volume the layers are equidistant, \( d_{001} = 15.25 \) Å. In this case, the function \( G \) takes the form

\[ G_{00}(s) = \sum_{M} \frac{2(M)}{M} \frac{\sin^2(M\pi s d_{001})}{\sin^2(\pi s d_{001})}, \]  

where \( \alpha(M) \) is the statistical weight distribution of the stackings with \( M \) layers.

In Table 2, the \( I_{003}/I_{001} \) and \( I_{005}/I_{001} \) ratios are given in terms of the number of water molecules crystallographically bound to the layer at the level of \( z = \pm 6 \) Å. Since the tangential plane to the surface oxygens of the layer is located at a level of about 4.60 Å, this level implies that the water molecules are distributed in the interlayer space at two levels without having any restriction imposed on their \( x, y \) coordinates.

It can be seen from Table 2 that the ratio \( I_{005}/I_{001} \) is appreciably susceptible to the water content of the unit cell whereas \( I_{003}/I_{001} \) remains practically insensitive.‡ By having \( 8H_2O \) for a unit cell, a similar calculation has revealed the influence of their levels on these intensity ratios (Table 3). As can be seen from Table 3, the interlayer positions of the water molecules

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* The value of 15.25 Å for the basal spacing is consistent with the positions of the observable 001 reflections to a good precision.

† Other possibilities are discussed later on.

‡ In fact, as the number of water molecules per unit cell increases, the maximum intensities of \( I_{001} \) and \( I_{003} \) both decrease at the same rate so that the ratio remains almost the same. On the contrary, \( I_{005} \) increases with the increasing number of water molecules, consequently the ratio \( I_{005}/I_{001} \) also increases.

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Table 1. Atomic levels with respect to an octahedral sheet of the layer

<table>
<thead>
<tr>
<th>(Al,Mg)\textsuperscript{V\textsc{i}}</th>
<th>(O,OH)\textsubscript{aper}</th>
<th>(Si,Al)\textsuperscript{V\textsc{i}}</th>
<th>O\textsubscript{surface}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levels (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>±1.09</td>
<td>±2.71</td>
<td>±3.24</td>
</tr>
</tbody>
</table>

Table 2. Variation of the \( I_{003}/I_{001} \), \( I_{005}/I_{001} \) ratios with number of \( H_2O \) per unit cell

<table>
<thead>
<tr>
<th>( I_{003}/I_{001} )</th>
<th>( I_{005}/I_{001} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_{003}/I_{001} )</td>
<td>( I_{005}/I_{001} )</td>
</tr>
<tr>
<td>( 6H_2O )</td>
<td>( 8H_2O )</td>
</tr>
<tr>
<td>( \sim 1/47 )</td>
<td>( 1/47 )</td>
</tr>
<tr>
<td>( \sim 1/13 )</td>
<td>( \sim 1/19 )</td>
</tr>
</tbody>
</table>

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Fig. 1. Experimental orientation function.
Table 3. Variation of the $I_{003}/I_{001}$, $I_{005}/I_{001}$ ratios with $H_2O$ levels

<table>
<thead>
<tr>
<th>$z$(Å)</th>
<th>± 5.75</th>
<th>± 6.0</th>
<th>± 6.25</th>
<th>± 6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{003}/I_{001}$</td>
<td>≈ 1/97</td>
<td>≈ 1/47</td>
<td>≈ 1/26</td>
<td>≈ 1/16</td>
</tr>
<tr>
<td>$I_{005}/I_{001}$</td>
<td>≈ 1/24</td>
<td>≈ 1/19</td>
<td>≈ 1/18</td>
<td>≈ 1/21</td>
</tr>
</tbody>
</table>

affect noticeably the $I_{003}/I_{001}$ ratio, though they hardly influence the $I_{005}/I_{001}$ ratio. The theoretical range extending from ± 5.75 to ± 6.50 Å almost covers all the results given in the literature for the $z$ level of the water molecules (De la Calle et al., 1977; Alcover & Gatineau, 1980; Pons, Tchoubar & Tchoubar, 1980).

It therefore appears that the use of the relative intensities of the recordable 00l reflections of beidellite with two water layers is sufficient to determine its hydration parameters without any ambiguity. The use of $I_{003}/I_{001}$ and $I_{005}/I_{001}$ ratios permits the interlayer levels of the water molecules to be fixed as well as their number corresponding to a unit cell. In the following section the concept of homogeneous hydration, usually adopted but inaccurate, is discussed. Then, the sample preparation and the experimental set-up developed by us to study the thermodynamically stable states of hydration are briefly described. Finally, the experimental results are presented and the structural parameters are discussed. Before reaching a conclusion the results are compared with those of the thermogravimetric analysis.

II. Criterion of homogeneity of a hydrate of two water layers

What is a homogeneous hydrate?

Up to the present time, in the general case, homogeneity of a hydrate is verified on the rationality of its 00l reflections. Unfortunately, in the case of the smectites, the number of 00l reflections which can be studied is very limited. Moreover, the average diffracting domain of natural smectites is generally reduced to a few layers. In this case, the calculation shows that even in homogeneous states there exist more or less important shifts of the maximum intensities depending on the slope of the square of the structure factor at the vicinity of the reflections (Reynolds, 1968; Ross, 1968; Tettenhorst & Robertson, 1973; Ben Brahim, 1979; Tchoubar et al., 1982). The variation of $|F_{00l}(s)|^2$ versus $s$ for Na-beidellite is shown in Fig. 2 where the values of $l = 15-25$ ($l$ integer) are indicated by the vertical lines.

The existence of such shifts casts some doubts on the rationality criterion characterizing the homogeneous state of a hydrate. In the case of accurate recordings one can always detect a weak irrationality due to the sharp variation of the square of the structure factor. Thus the question which arises is to know how one can distinguish an irrationality of the 00l reflections coming from the existence of a weak interstratification of basal spacing from that caused by the sharp variation of the square of the structure factor. In order to answer this question the profiles of the 00l reflections were calculated for the case of interstratification. The modulation function then becomes (Méring, 1949)

$$
G_{00l}(s) = \frac{1 - U^2}{1 + U^2 - 2U \cos \beta} + \frac{2U}{M} \frac{[2U - (1 + U^2) \cos \beta][1 - U^M \cos M \beta]}{[(1 + U^2 - 2U \cos \beta)^2]^{1/2}}
$$

where $M$ is the number of layers in the average stacking; $U$ and $\beta$ are related to the $d_r$ basal spacings and their corresponding $P_j$ frequencies by

$$
Ue^{i\beta} = \sum_j P_j \exp(2\pi i S d_j).
$$

We have considered at most a ternary stratification with the $d_1, d_2, d_3$ basal spacings which respectively correspond to one, two, three layers of water. Several trials have shown that even a stratification with small proportions (the probability of having $d_1$ and $d_3$ is of the order of 1%) not only affects the positions of the 00l reflections, but also both the full widths at half maximum intensities (FWHM) and the relative intensities. The striking features were:

(a) while the 003 reflection considerably widens the 005 becomes narrower;

(b) the ratio of relative intensities $I_{005}/I_{001}$ increases.

These features cannot be accounted for by an irrationality produced only by the variation of the square of the structure factor. It does become evident that it is not possible to make a final judgment on the homogeneity of a hydrate only by examining the apparent basal spacings of the 00l reflections. It is also

Fig. 2. Variation of $FF_{00l}(s)$ versus $s$. 

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necessary to be very attentive that the FWHM and relative intensities of the 00l reflections do not manifest any anomalies.

### III. Experimental conditions and determination of the hydration parameters

#### III.1. Preparation of the sample

500 mg of beidellite from Rupsroth were left in contact with 100 cm$^3$ 1 mol dm$^{-3}$ sodium chloride solution for several hours and then centrifuged. This process was repeated seven times. The silicate obtained was washed with distilled water and then centrifuged. Following the washing process, which was maintained until the removal of chlorine ions was complete, the silicate was air dried before introducing it into a chamber with controlled relative humidity.

#### III.2. Experimental set-up for an investigation, in situ, of the sample with controlled relative humidity

The common procedure in hydrating the silicates consists of placing the sample inside a desiccator which has a constant relative humidity and then waiting for several days to attain an equilibrium. Having obtained an equilibrium, the sample is investigated by X-rays. In this work the sample was placed inside a chamber with controlled humidity constructed on the basis of our design (Ben Brahim, Armağan & Besson, 1983) adapted to the GS 2000 spectrogoniometer of CGR. The apparatus additionally contains various slits allowing all the undesired diffusions to be limited (Fig. 3).

The recordings of the X-ray diffraction patterns were made using transmission geometry with Cu Kα radiation and employing a linear detector of LETI type having an angular range of about 10° in 2θ with a resolution of 0.01° in θ. The 001, 003, 005 reflections were successively recorded at such constant time intervals that the counting statistics were good enough. Then, by a new recording of the 001 reflection, it was possible to check whether the sample remained in its initial state of equilibrium or had undergone any change during the experiment. As soon as the recordings of the 00l reflections were completed, a series of background recordings were performed without the sample under the same conditions. The final spectra corrected for the effects of background, absorption and polarization factors can be seen in Fig. 4 (filled circles).

#### III.3. Quantitative investigation of the FWHM and the positions of the observable 00l reflections

No relative anomalies concerning widths and intensities as described in § II have been observed in the recorded 003 and 005 reflections.

In examining the profiles, a single basal spacing of 15.25 Å was found, accounting very well for the positions of all the three 00l reflections, despite the slight disagreement existing among the apparent experimental $\ell d_{00l}$ periods varying from 0.02 to 0.03 Å. But it was observed that the FWHM enlarged with increasing $l$ index. This variation must be related to the apparent diminution of the coherent domain with increasing $s$ (Table 4). Similar variations have been observed on the graphitable carbons (Maire & Méring, 1970) and on microcrystallized muscovites (Kodama, Gatineau & Méring, 1971). The interpretations made by these authors have been based on a distortion of layers along the normal to the (a,b) plane. This implies that the distance of 15.25 Å found in this work is in fact an average period about which small fluctuations occur. Thus the true distance is $d_0 = d_0 + \delta$, where $d_0$ is the true distance, $d = 15.25$ Å, $\delta$ is the distortion parameter whose average value over all the stackings is zero. The expression of the modulation function therefore becomes (Maire & Méring, 1970)

$$G_{00l}(s) = 1 + \text{Re} \left\{ \sum_{M} \mathcal{Z}(M) \sum_{n=1}^{M-1} \frac{M-n}{M} \times (1 - 2\pi^2 s^2 \delta^2 \exp(2\pi n s d_{00l})) \right\},$$

where $\delta^2$ is the mean square deviation of the distortion parameter.

#### III.4. Agreement between the experimental and theoretical patterns

The best agreement simultaneously obtained for all three reflections is given in Fig. 4. This agreement

<table>
<thead>
<tr>
<th></th>
<th>001</th>
<th>003</th>
<th>005</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta s$ ($\text{Å}^{-1}$)</td>
<td>$3.2 \times 10^{-3}$</td>
<td>$3.4 \times 10^{-3}$</td>
<td>$5.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>$M_{\text{app}}$ (apparent number of layers)</td>
<td>19 to 20</td>
<td>19</td>
<td>12 to 13</td>
</tr>
<tr>
<td>$(\ell d_{00l})_{\text{app}}$ (Å)</td>
<td>15.27</td>
<td>15.23</td>
<td>15.24</td>
</tr>
</tbody>
</table>

Table 4. Parameters of apparent coherent domain and basal spacings for 00l reflections

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Fig. 3. Experimental set-up: s X-ray source, m monochromator, e sample, d detector, c$_1$ atmosphere-controlled chamber, c$_2$ vacuum chamber, f$_1$, f$_2$, f$_3$, f$_4$, f$_5$ slits having apertures adjustable in height and width.
comprises three aspects of the reflections, namely, positions, profiles and relative intensities. The resulting structural parameters are as follows:

(a) $\delta^2 = (0.06 \pm 0.01) \text{Å}^2$ is close to the $0.0358 \text{Å}^2$ found by Kodama et al. (1971) for a microcrystallized muscovite from Japan. The most probable explanation of the existence of such a distortion may be the inhomogeneity of the distribution of the negative surface charge density of the layers (Lagaly & Weiss, 1975).

(b) $\bar{M} = (16 \pm 1)$ layers corresponds to an average diffracting domain of $L = (244 \pm 15) \text{Å}$. The $\alpha(M)$ used is symmetric about 16 and extends from 2 to 30 layers. The statistical weight given to the stackings having 2 and 30 layers is roughly six times smaller than that corresponding to 16 layers.

(c) The $z_{H_2O}$ level of the water molecules is equal to $\pm(6.20 \pm 0.04) \text{Å}$, which is near to $z = \pm 6.40 \text{Å}$ (Shirozu & Bailey, 1966) and $z = \pm 6.13 \text{Å}$ (De la Calle et al., 1977) obtained from single vermiculite crystals.

(d) The water content of the unit cell which yields the best agreement is $(10.0 \pm 0.5)$ water molecules. This number is close to that determined from the gravimetric analysis curve of the mineral studied.

III.5. Remarks on the position of the interlayer cation

In the smectites the polyvalent interlayer cations have a tendency to leave the hexagonal cavities which they occupy in the anhydrous state, and move towards the middle of the interlayer space when the system undergoes a change from the anhydrous state to the hydrated state with two water layers (Mering & Glaeser, 1954). This position in fact corresponds to a minimum electrostatic energy and therefore to a position of stable equilibrium. This reasoning may not necessarily apply to the case of a monovalent cation. Since it was not possible to carry out one-dimensional Fourier analysis, which allows one to determine the precise positions of the interlayer monovalent cation, an indirect approach was made by examining the case in which the Na cation slightly enters the hexagonal cavity ($z_{Na} = \pm 4.30 \text{Å}$). However, it was noticed that one can then find appreciably the same agreement previously obtained, with a slight change of the level ($z_{H_2O} = \pm 6.30 \text{Å}$) and the number of water molecules $(9.6 \text{H}_2\text{O/unit cell})$. It becomes evident that it is therefore not possible to localize the sodium precisely, merely by means of the agreements of profiles and relative intensities of three 00l reflections.

IV. Conclusion

The impression that the investigation of swelling microcrystalline silicates, which are rich in structural defects producing in consequence weakly modulated X-ray diffraction powder patterns, may only yield qualitative results has restricted crystallographic studies for a long time to the phyllosilicates existing in the form of large single crystals such as vermiculite. In this paper a simple method is proposed which is applicable to all homogeneous hydrates of microcrystalline silicates. This method, based on the simultaneous investigation of the profiles and the relative intensities of the observable 00l reflections, allows one to determine with a reasonable accuracy the following features:
(a) the size distribution and the dimension of the average coherent domain of the 00l reflections.
(b) the number of water molecules per unit cell as well as their levels.
(c) the stacking mode of layers normal to their (a, b) plane, which, in the case of dioctahedral smectites, revealed a distortion characterized by a $\delta^2$ fluctuation of the basal distances. This distortion may be attributed to the heterogeneity of the charge distribution of the layer which may also vary from layer to layer in the stacking.

This work is a part of a general project which aims to determine the exact configuration of the water molecules. The next stage of the investigation will consist of the treatment of $hk$ diffraction bands, where $h$ and/or $k \neq 0$, in order to determine the $x, y$ coordinates of the water molecules. This will subsequently lead to an extension of the knowledge of the water–silicate systems and an explanation for the physical process responsible for their stability.

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References