

## X-RAY STUDY OF THE INTERLAYER REGION OF A BARIUM-VERMICULITE

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**Abstract**—An X-ray diffraction analysis of a barium-vermiculite shows it to have a triclinic unit cell with the following dimensions  $a = 5.33$ ,  $b = 9.26$ ,  $c = 12.47$  Å,  $\alpha = 100.75^\circ$ ,  $\beta = 93.5^\circ$  and  $\gamma = 90^\circ$ . The proposed structure, adjusted in space group C1, has the exchangeable cations approximately over the ditrigonal holes of the silicate surface and on either side of a hexagonal network of water molecules extending over the middle of the interlamellar region. The interlayer material imposes a relative displacement of  $\pm b/4$  on adjacent silicate sheets. The importance of these displacements, not previously found in layer silicates, is emphasized.

### INTRODUCTION

Structure analyses of magnesium-vermiculite (Gruner, 1934, 1939; Hendricks and Jefferson, 1938) were in general agreement regarding the structure of the silicate layers and their relative disposition when viewed along the  $y$ -axis. Mathieson and Walker (1954), Mathieson (1958), Bradley and Serratos (1960) and Shirozu and Bailey (1966) have also studied the general problem of the configuration of water molecules and exchangeable cations in the vicinity of layer silicate surfaces and also the relationships between adjacent silicate layers. Recently, studies have been made of the influence some exchangeable cations have on the relative position of one silicate layer with respect to an adjacent one (De la Calle *et al.*, 1975a; De la Calle *et al.*, 1975b) and also of the arrangement of cations and water molecules in the interlayer space of vermiculite in different hydration stages (Fernandez *et al.*, 1975). On the basis of anomalous diffuse reflections observed in electron diffraction patterns of barium-illite, barium-vermiculite and barium-beidellite, Besson *et al.* (1974a, b) deduced that the exchangeable cations in these minerals are partially ordered over the ditrigonal holes of the silicate surface. By assuming that the barium ions are localized in the immediate neighbourhood of a charge imbalance in the silicate layer, these authors deduced that the isomorphous substitutions responsible for the charge defects are also partially ordered.

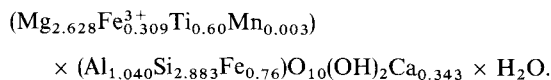
The present paper, on the basis of an analysis of the  $00l$  and  $h0l$  X-ray reflections, further elaborates upon a model for the interlamellar cation-water system in barium-vermiculite. An unusual set of systematic absences in the  $06l$  series also is described and used as evidence for  $b/4$  shifts between adjacent silicate sheets in the direction of the  $y$ -axis.

### EXPERIMENTAL

#### Sample preparation

The barium-vermiculite used for single crystal

studies was produced by cation-exchange of natural vermiculite from Kapirikamodzi. The latter was obtained from Dr. K. Norrish who previously analysed a calcium-saturated sample and calculated its formula as:



Its cation exchange capacity is 1.74 mequiv./g on an ignited basis.

The natural vermiculite was cut into flakes about  $0.5 \times 0.3 \times 0.1$  mm and treated with 1 N solution of barium chloride for 24 hr at  $70^\circ\text{C}$ . Flakes were then washed with distilled water and dried at room temperature. The basal spacings of all samples used for subsequent work were checked by diffractometry.

Additional vermiculites used for powder diffraction experiments were Llano, Stop 10; Llano, Stop 11 and Phalaborwa; these are numbered 7, 3 and 6 by Norrish (1973). Each of these vermiculites was treated with barium chloride as above.

#### Powder diffraction

X-ray powder diffraction photographs were taken in the back reflection mode with a 19 cm camera fitted with a modified Straumanis mounting and knife-edges. Several lines, repeated on both sides of the direct beam aperture, were measured relative to an arbitrary zero and the centre of each film accurately calculated. After the camera diameter had been established from a pattern for transistor-grade silicon the knife-edge shadows on films enabled corrections to be made for shrinkage and absorption.

#### Single crystal diffraction measurements

To obtain the  $00l$  spectra at different temperatures, single crystals were mounted on Pyrex plates clamped to a Nichrome-wound heating stage, powered by a Variac. Filtered cobalt radiation was used in a Nor-elco powder diffractometer with the following slits:

divergence  $0.25^\circ$ , receiving 0.146 mm in front of a  $1^\circ$  slit. The scan rate was  $1^\circ/\text{min}$ .

Flakes of vermiculite were mounted upon glass fibres and oscillation photographs taken with filtered  $\text{CoK}\alpha$  radiation; flakes which gave the nearest approximation to sharp crystal patterns were chosen for structural work. As the water content of the sample changed with small changes in room temperature, all Weissenberg photographs were taken with the crystal maintained at  $35^\circ\text{C}$  by passing warm air over it. To resolve the problem of choosing the unique  $x$  or  $y$ -axis, Weissenberg photographs were taken about each of the three  $x$ -axes. Only one such photograph showed  $0kl$  and  $0k\bar{l}$  reflections equal in intensity and symmetrically arranged about  $b^*$ . This unique direction was taken as the true  $b^*$  for the crystal.

By using  $\text{CoK}\alpha$  radiation and multiple-film-pack Weissenberg photographs intensity data were initially recorded for the  $00l$  and  $h0l$  reflections. All intensity measurements were made by comparison with a set of standards obtained from time exposures of a selected  $00l$  reflection oscillated over a small angular range. Corrections were applied for Lorentz and polarization factors and for the absorption factor by the integration method of Busing and Levy (1957); the absorption coefficient ( $\mu$ ) at the  $\text{CoK}\alpha$  wavelength was calculated as approximately  $95\text{ cm}^{-1}$ .

#### Determination of the unit cell constants

The angle  $\beta$  ( $93.5^\circ$ ) was measured from a precession film of the  $a^*c^*$  plane. The basal spacing ( $12.23\text{ \AA}$ ) was obtained from six  $00l$  peaks recorded on the Nor-elco diffractometer. The  $b$ -cell parameter for barium-vermiculite was deduced from the strong line usually indexed as  $060$ ; from careful measurements on a 19 cm film this line corresponds to a spacing of  $1.5405\text{ \AA}$ . On the basis of a two-layer monoclinic cell

the only  $0kl$  reflections observed in barium-vermiculite all satisfy the following criteria:—

$$\begin{aligned} &\text{for } 02l \text{ and } 06l \text{ reflections } l = 2n + 1; \\ &\text{for } 04l \text{ and } 08l \text{ reflections } l = 2n. \end{aligned}$$

Several unsuccessful attempts were made to reconcile these extinction conditions with the standard monoclinic space groups. The reflections were finally indexed on the basis of a non-primitive triclinic cell with  $\alpha = 100.75^\circ$ . The rationale for such a cell can be seen from Figure 1, which shows a reciprocal net for the  $b^*c^*$  planes of the alternative monoclinic and triclinic cells. The observed reflections are plotted on this net and their two alternative indices are shown in italics for a monoclinic cell and bold type for a triclinic cell. Figure 1 illustrates how the reflection with the monoclinic index of  $061$  becomes  $06\bar{1}$  in the single-layer triclinic cell. After calculating  $c$  as  $14.472\text{ \AA}$  from  $c = (d_{001}/\sin\beta \sin\alpha^*)$  the  $b$ -parameter for the triclinic cell was computed as  $9.262\text{ \AA}$  by using the general equation relating  $\sin\theta$  and the reciprocal lattice constants for a triclinic cell. Therefore a set of cell dimensions which describe the one-layer triclinic cell are  $a = 5.33\text{ \AA}$ ,  $b = 9.26\text{ \AA}$ ,  $c = 12.47\text{ \AA}$ ,  $\alpha = 100.75^\circ$ ,  $\beta = 93.5^\circ$ , and  $\gamma = 90^\circ$ . An alternative set would require  $\alpha$  to be  $79.25^\circ$ ; we have referred our atomic parameters to the cell with  $\alpha = 100.75^\circ$ . As will subsequently be seen, these alternative descriptions correspond to positive or negative shifts between adjacent silicate sheets.

The argument set out above demonstrates that the indexing of  $0kl$  reflections for barium-vermiculite is simpler on a triclinic than on a monoclinic basis, and furthermore allows the apparent extinction conditions to be satisfied. In addition, it also implies a reduction of the spacing for the strong line (at  $\approx 1.542\text{ \AA}$ ) of magnesium-vermiculite after its conversion to barium-vermiculite. In barium-vermiculite, the two

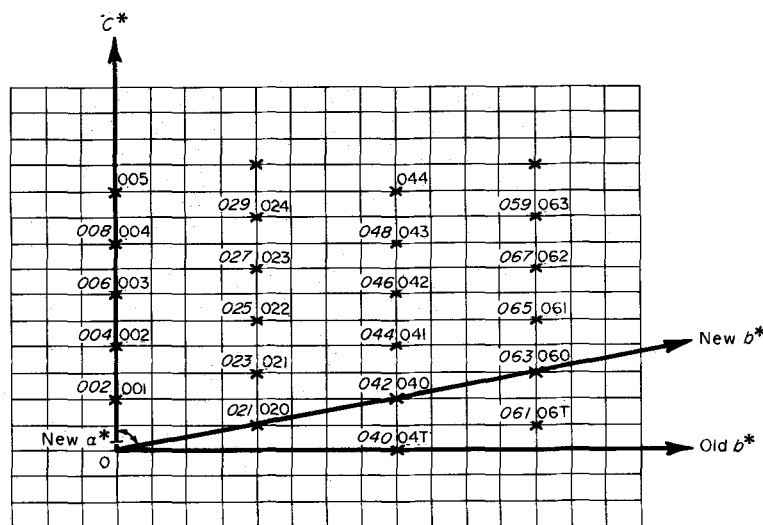


Figure 1.  $b^*c^*$  plane of barium-vermiculite with populated reciprocal lattice points marked with X. Monoclinic indices in italics and triclinic indices in bold type.

Table 1.  $d$ -spacings for the 060 line in some natural vermiculites compared with the 06 $\bar{1}$  line of their barium saturated equivalents

	Natural ( $d_{060}$ )	Ba Sat. ( $d_{06\bar{1}}$ )	Decrease $\Delta d$
Llano (Stop 11)	1.5424 Å	1.5364 Å	0.0060 Å
Llano (Stop 10)	1.5426	1.5377	0.0049
Phalaborwa	1.5449	1.5405	0.0044
Kapirikamodzi	1.5424	1.5405	0.0019
	Average $\Delta d =$		0.0037 Å

centres of maximum intensity near that region indexed as 060 for a natural two-layer magnesium-vermiculite are such that they would be indexed as 061 and 06 $\bar{1}$  (monoclinic, two-layered) or 06 $\bar{1}$  and 06 $\bar{2}$  (triclinic, one-layer cell). Back reflection films of the 060 reflections for a number of natural magnesium-vermiculites, and the related reflections in their barium-saturated equivalents, do show a small change in  $d$ -spacing following the exchange of magnesium by barium. The results for some measurements are set out in Table 1. The average measured difference (0.0037 Å) is of the order of the calculated difference in  $d$ -spacing (0.0031 Å) between the 060 and the 061 monoclinic reflections.

#### STRUCTURE ANALYSIS

Phases for the 00 $l$  and  $h0l$  reflections were computed from the known configuration of the silicate part of the structure and assigned to the structure amplitudes. This assumes that the contribution to the total scattering from the interlayer material is comparatively small. The positional parameters for the atoms of the silicate structure were taken from Mathieson and Walker (1954) and modified for the unit

cell of our material. Space group C1 was chosen for all structure factor calculations.

#### Electron density distribution projected on to the $c$ -cell edge

One dimensional Fourier projections were computed from the 13 orders of 00 $l$  structure amplitudes measured at several different temperatures. Figure 2 shows the electron density projections of barium-vermiculite under the specified conditions. Apart from the electron distribution corresponding to the silicate layer, two additional peaks can be seen in each projection, one at  $z = 0.5$  and another one at  $z = 0.408$ . The fact that the height of the latter remains constant whilst that of the former varies with temperature is good evidence that the water molecules are located midway between the silicate sheets. This implies that the cations are arranged on either side of the central plane of water molecules, at  $z = 0.408$ ; this parameter was subsequently adjusted by least squares analysis to  $z = 0.416$ .

#### Projection along the $y$ -axis

The  $h0l$  structure factors were used to compute both Fourier and difference ( $F_0 - F_c$ ) Fourier projections of electron density on to the (010) plane (Figure 3). In the interlayer region two sets of peaks of similar height occur; those representing the barium cations are closest to the silicate surfaces, with the water peaks midway between. This model was chosen as a basis for the calculation of a set of structure factors which were compared with their experimental equivalents.

Adjustment of the model was carried out with the least squares program of Busing *et al.* (1962). After least squares scaling of the  $|F_c|$  values to the  $|F_0|$

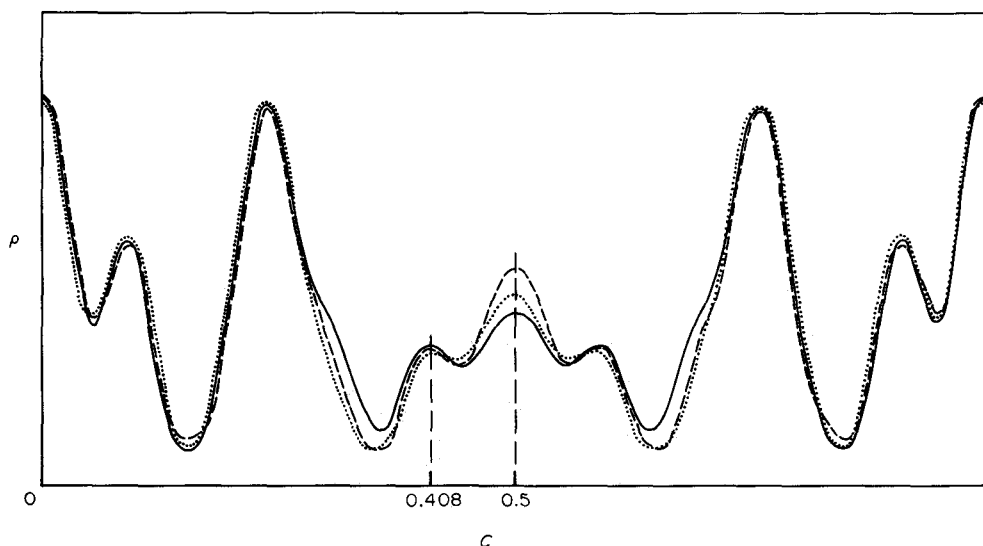


Figure 2. Projection of barium-vermiculite structure on to the  $c$ -cell edge. Sample heated at 150°C and left at room temperature for 1 hr shown thus: —; sample heated at 150°C and left 2 hr at room temperature shown thus: - - -; the same sample heated again at 65°C shown thus: ····.

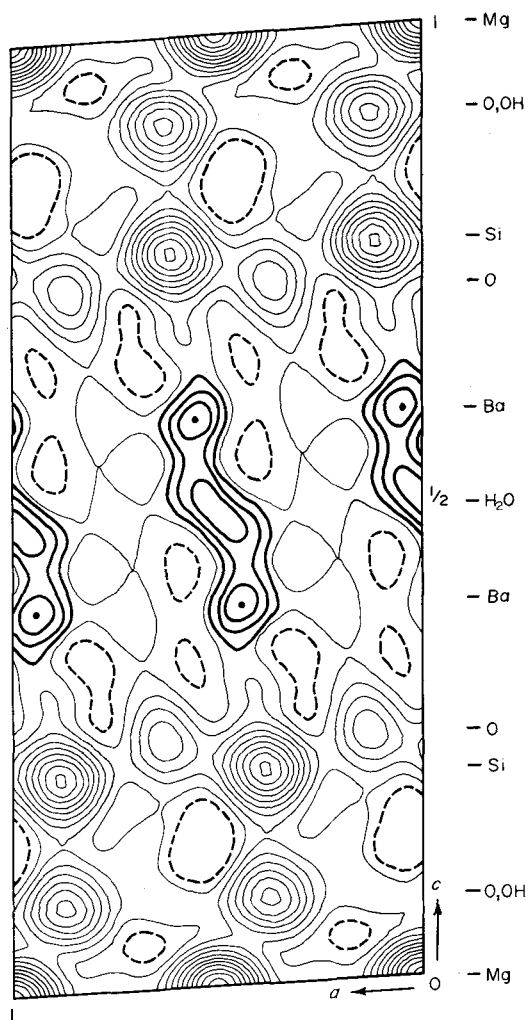


Figure 3. Projection of barium-vermiculite structure on to (010), i.e. along the  $y$ -axis. Contour interval  $1e \times \text{\AA}^{-2}$ , interlayer atom contours shown boldly and zero level contour dashed.

values the scale factor  $b$  was held constant and the independent  $x$  and  $y$  parameters for the silicate atoms were adjusted. A minor adjustment was then made to the scale factor and the overall temperature factor, which had initially been set at 1.8. A difference Fourier map after this stage enabled the positional parameters for the interlayer atoms to be more accurately defined. These interlayer positional parameters were further adjusted along with the occupancy and temperature factors for the interlayer atoms. The final values for the atomic parameters are given in Table 2.

Forty-six reflections were used in these calculations, after eight had been deleted by applying Cruikshank's weighting scheme (Cruikshank *et al.*, 1961). A review of these eight reflections showed five to be close to the film-edge with the other three at the limits of intensity; hence all were difficult to measure and could be justifiably omitted as unreliable data.

Table 3 shows the calculated and observed structure factors for the set of reflections. The final  $R$  value was 0.21;

$$R = \frac{\sum [|F_o| - |F_c|]}{\sum |F_o|}$$

#### Description of the model

These data allow us to postulate a configuration for the interlayer region in which a hexagonal network of water molecules encloses barium ions which are themselves positioned approximately over the ditrigonal holes formed by the oxygens of the silicate structure (Figure 4). Alternative positions for the barium cations over the Si/Al tetrahedra were considered, but the  $z$  coordinates required to allow the cations to fit did not agree with the Fourier projections, and therefore the alternative model was rejected. The X-ray work upon barium-vermiculite therefore accords well with the electron diffraction work upon barium-illite and barium-beidellite by Besson *et al.* (1974b) who also deduced that the barium ions were over the hexagonal holes of the oxygen sheets.

In barium-vermiculite cations are not positioned directly over the centres of the ditrigonal holes; this can be deduced from the inter-atomic distances between the barium ions and their surrounding oxygens (Table 4). On the other hand, each barium cation is surrounded fairly symmetrically by six water

Table 2. Final atomic coordinates and temperature factors for barium-vermiculite (S.G. C1)

Atom	$x$	$y$	$z$
(Mg, Fe, Ti, Mn) oct (1)	0.000	0.000	0.000
(Mg, Fe, Ti, Mn) oct (2)	0.000	0.333	0.000
(Mg, Fe, Ti, Mn) oct (3)	0.000	0.667	0.000
(Si, Al, Fe) tet (1)	0.327	0.042	0.207
(Si, Al, Fe) tet (2)	-0.365	-0.042	-0.225
(Si, Al, Fe) tet (3)	0.365	0.375	0.226
(Si, Al, Fe) tet (4)	-0.365	-0.375	-0.225
O oct (1)	0.346	0.016	0.087
O oct (2)	-0.346	-0.016	-0.087
O oct (3)	0.346	0.349	0.087
Oct (4)	-0.346	0.349	-0.087
Oct (5)	0.346	0.683	0.087
Oct (6)	-0.346	0.651	-0.087
O tet (1)	0.144	0.397	0.255
O tet (2)	-0.144	0.397	-0.255
O tet (3)	0.143	0.943	0.262
O tet (4)	-0.143	0.943	-0.262
O tet (5)	0.429	0.187	0.254
O tet (6)	-0.429	0.187	-0.254
Ba (1)	0.420	0.667*	0.416
Ba (2)	-0.420	0.667*	-0.416
H <sub>2</sub> O (5)	0.450	0.348*	0.500
H <sub>2</sub> O (2)	0.450	0.000*	0.500
Temperature factors (B)			
Atoms of the silicate structure	$2 \times 10^{-15} \text{ cm}^2$		
Ba	$3.5 \times 10^{-15} \text{ cm}^2$		
H <sub>2</sub> O	$4.1 \times 10^{-15} \text{ cm}^2$		

\* Infrared values.

Table 3. Structure factors

<i>hkl</i>	$F_{\text{calc.}}$	$F_{\text{obs}}$	<i>hkl</i>	$F_{\text{calc.}}$	$F_{\text{obs}}$
0 0-1	126	90	4 0 2	43	60
0 0-2	20	24	4 0-2	106	110
0 0-3	37	46	4 0 3	39	55
0 0-4	166	200			
0 0-6	85	100	4 0 4	8	15
0 0-7	21	22	4 0-4	13	16
0 0-8	66	60	4 0 5	26	18
0 0-9	62	61	4 0-5	18	47
0 0-10	42	58	4 0 6	66	66
0 0-11	12	6	4 0-6	104	102
0 0-12	53	40	4 0-8	10	6
0 0-13	31	28	4 0-9	12	11
2 0 0	65	72			
2 0 1	105	130			
2 0-1	68	102			
2 0 2	146	148			
2 0-2	29	32			
2 0 3	107	100			
2 0-3	18	33			
2 0 4	58	61			
2 0-4	84	99			
2 0-5	15	7			
2 0 6	113	66			
2 0-6	11	15			
2 0 7	34	23			
2 0 8	14	24			
2 0-8	107	102			
2 0-9	64	50			
2 0 10	52	49			
2 0-10	13	7			
2 0 11	20	21			
2 0-12	55	41			
4 0 0	52	60			
4 0 1	20	38			
4 0-1	24	62			

molecules; see the barium-water distances given in Table 4. The extension of this arrangement will produce a hexagonal network of water molecules fixed about those barium cations required to neutralize the charges of the silicate structure. The water-surface oxygen distances (Table 4) suggest that a system of hydrogen-bonds is present to link the interlayer water molecules to the surface oxygens. The calculation of the two nearest distances between one water molecule and the adjacent surface oxygens shows at least one of the distances to correspond to a hydrogen-bond. No attempt was made to calculate the errors associated with the interatomic distances, but they may be as large as  $\pm 0.2 \text{ \AA}$ .

#### DISCUSSION

The length ( $\approx 3 \text{ \AA}$ ) of the proposed hydrogen-bonds between interlamellar water molecules and the silicate oxygens of barium-vermiculite indicates that these bonds are rather weak, as has been previously suggested for hydrogen-bonds between water molecules in clay minerals (Russell and Farmer, 1964; Farmer and Russell, 1967; Fripiat *et al.*, 1960). By contrast the interactions between the cations and water dipoles seem to be fairly strong. This can be deduced from

the constancy of the basal spacing shown by crystals heated to at least  $65^\circ\text{C}$ , although at this temperature an appreciable amount of water is lost.

The water molecules are situated essentially in the mid-plane of the structure, in agreement with the system proposed for montmorillonites by Pezerat and Mering (1969), and also by Mamy (1968). In contrast to the results obtained by these authors for montmorillonite, neither our one-dimensional nor our two-dimensional projection resolved into two peaks those electron density peaks assigned to water molecules. However, the large temperature factor for water ( $4.1 \times 10^{-16}$ ), and the shape of the midway point in the (010) projection (Figure 3), can be interpreted as an indication that the water molecules vibrate about the point at  $z = 0.5$ ; but mainly along the  $z$  direction.

Hendricks and Jefferson (1938) proposed that natural magnesium-vermiculites have their water molecules in two hexagonal networks. Shirozu and Bailey (1966) in a full refinement of the structure of magnesium-vermiculite were not able to determine the exact distribution of water molecules in the interlayer region. They suggested that each  $\text{Mg}^{2+}$  would be surrounded by a hydration shell of six water molecules, because the high polarizing power of the cation tends to force the coordinated water molecules into regular octahedra. Barium, with its smaller polarizing power, does not impress this type of coordination upon water molecules and a single hexagonal net is possible.

Because of their size, barium cations must simultaneously occupy holes in the water molecule network and ditrigonal holes in the silicate surface. To achieve this condition, the barium cations, which are positioned both above and below the water network, impose a relative displacement upon adjacent silicate sheets.

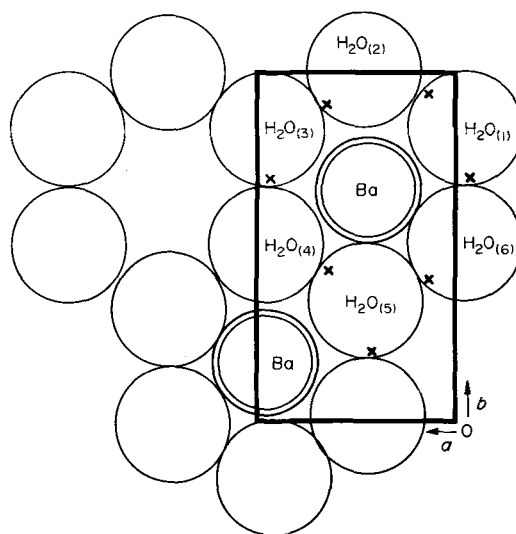


Figure 4. Drawing of the interlayer region for barium-vermiculite as viewed along the  $z$ -axis. Centres of oxygens comprising a silicate surface marked thus:  $\times$ .



Table 4

Water-water distances (Å)		Ba-water distances (Å)		Ba-surface oxygens distances (Å)		Water-surface oxygens distances (Å)	
H <sub>2</sub> O <sub>(1)</sub> -H <sub>2</sub> O <sub>(2)</sub>	3.00	Ba-H <sub>2</sub> O <sub>(1)</sub>	3.15	Ba-O <sub>y</sub>	3.74	H <sub>2</sub> O <sub>(1)</sub> -O <sub>x</sub>	3.48
H <sub>2</sub> O <sub>(2)</sub> -H <sub>2</sub> O <sub>(3)</sub>	3.19	Ba-H <sub>2</sub> O <sub>(2)</sub>	3.08	Ba-O <sub>x</sub>	3.47	H <sub>2</sub> O <sub>(1)</sub> -O <sub>y'</sub>	3.15
H <sub>2</sub> O <sub>(3)</sub> -H <sub>2</sub> O <sub>(4)</sub>	3.19	Ba-H <sub>2</sub> O <sub>(3)</sub>	3.30	Ba-O <sub>y'</sub>	3.52	H <sub>2</sub> O <sub>(2)</sub> -O <sub>y</sub>	3.25
H <sub>2</sub> O <sub>(4)</sub> -H <sub>2</sub> O <sub>(5)</sub>	3.00	Ba-H <sub>2</sub> O <sub>(4)</sub>	3.39	Ba-O <sub>x'</sub>	2.83	H <sub>2</sub> O <sub>(2)</sub> -O <sub>x</sub>	3.26
H <sub>2</sub> O <sub>(5)</sub> -H <sub>2</sub> O <sub>(6)</sub>	3.00	Ba-H <sub>2</sub> O <sub>(5)</sub>	3.24	Ba-O <sub>y'</sub>	3.16		
H <sub>2</sub> O <sub>(5)</sub> -H <sub>2</sub> O <sub>(1)</sub>	3.19	Ba-H <sub>2</sub> O <sub>(6)</sub>	3.23	Ba-O <sub>x'</sub>	3.24 (*)		

The other four pairs are identical to these as required by the symmetry conditions.

\* The surface oxygens nomenclature has been made taking the symbols used by Mathieson and Walker (1954).

The magnitude of this displacement can be deduced by viewing the triclinic cell of barium-vermiculite perpendicular to its base plane. Figure 5 shows that portion of the unit cell containing the interlayer material. The rectangle outlined with a dotted line represents the boundary in the plane of the lower oxygen sheet, and the rectangle outlined with a continuous line the boundary of the cell in the plane of the upper oxygen sheet. H and H' represent the ditrigonal holes in the lower and upper oxygen sheets. Figure 5 shows a relative displacement between the adjacent sheets of  $\pm b/4$  and  $\approx a/5$ . Calculations of geometric structure factors based upon a monoclinic unit cell show that the 06*l* ( $l = 2n$ ) will be suppressed when translations of  $b/4$  occur between adjacent sheets and therefore support the conclusions drawn from the alternative triclinic cell. The  $y$  coordinates of the atoms of the silicate layer are approximately in multiples of  $b/6$ , and therefore relative displacements of  $b/4$  cause out-of-phase scattering from adjacent sheets; this will markedly affect the intensities of those 06*l* reflections for which

$k = 3n$ . An example of this is seen in the suppression of 06*l* reflections with  $l = 2n$  in barium-vermiculite. We have observed an identical sequence of 0*kl* reflections for lysine-vermiculite, thus demonstrating that both inorganic and organic cations can influence stacking of silicate sheets.

Along with De la Calle *et al.* (1975a) we believe that the shape and polarizing power of the interlayer units are responsible for the shift between sheets, but a detailed understanding of the stacking mechanism requires a study of the energetics involved.

The present work indicates that caution must be used in studies seeking to establish a connection between the chemical composition (or other properties) and the  $b$ -cell parameters of layer silicates when these are determined from measurements of the strong line traditionally indexed as 060.

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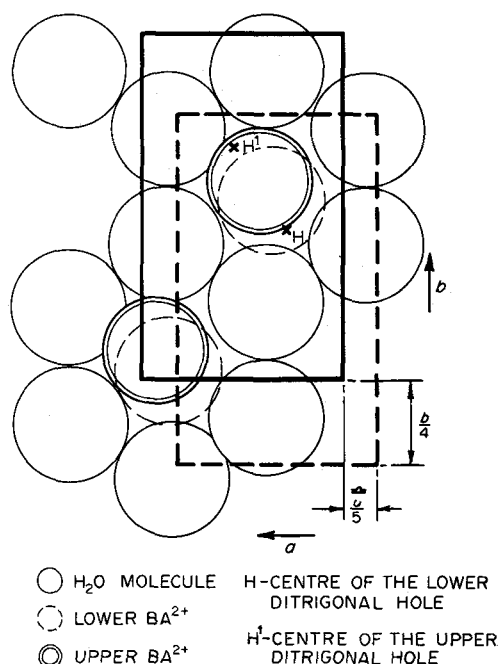


Figure 5. Drawing of the interlayer region for barium-vermiculite viewed perpendicular to the base.

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