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THE INTERLAYER STRUCTURE OF La-VERMICULITE

PHILLIP G. SLADE,[1] PETER G. SELF[2] AND JAMES P. QUIRK[3]

[1] CSIRO Land and Water, Glen Osmond, South Australia 5064

[2] Ian Wark Research Institute, University of South Australia, The Levels, South Australia 5095

[3] Department of Soil Science and Plant Nutrition, University of Western Australia, Nedlands, Western Australia 6009

Abstract—The structure of the interlayer cation-water system in La-vermiculite with a unit cell of a = 5.33(5), b = 9.18(6), c = 15.13(9) Å and β = 96.82(7)° has been determined in space group $C2/m$. Under ambient conditions, the interlayer La cations are distributed on a $3a \times b$ superlattice which disappears on dehydration but returns on rehydration. The basal spacing does not change during the dehydration/rehydration process. The character of the superlattice spots indicate that the cation-water system, at ambient conditions, is ordered over relatively large domains. The La cations are surrounded by 8 neighboring water molecules in a distorted cubic arrangement. The spaces between the La-water clusters are occupied by triads of water molecules that are relatively mobile.

Key Words—8-Coordinated La, La-vermiculite, Ordered, Structure.

INTRODUCTION

Detailed descriptions of water-cation networks between the silicate layers in the frequently fine-grained and imperfectly crystalline expansive layer silicates are difficult to obtain by crystallographic methods. Even vermiculites, which are available as large, relatively well-crystallized flakes, exhibit layer stacking disorder that causes their diffraction patterns to show streaks parallel to Z^* for $0kl$ reflections where $k \neq 3n$. Such stacking disorder, involving semi-random layer displacements of $\pm b/3$, is always found in Mg-vermiculite. There it seems to be part of a mechanism enabling layer charges, resulting from disordered substitutions in tetrahedral sites (Shirozu and Bailey 1966), to be balanced by interlayer cations adjacent to those sites (Slade et al. 1985).

However, for the 2-layer hydrates developed by Na- and Ca-vermiculites at humidities with $P/P_0 > 0.5$, sharp diffraction patterns indicative of a high degree of stacking order can be obtained. It has been shown by de la Calle (1977) and Slade et al. (1985) that, in the ordered structures of these vermiculites, the ditrigonal cavities in adjacent silicate layers face each other across the interlayers as they commonly do in micas.

This relative disposition of adjacent silicate layers contrasts with that found in natural semi-ordered Mg-vermiculite (Mathieson and Walker 1954; Shirozu and Bailey 1966; Alcover and Gatineau 1980), where the tetrahedral bases in any given silicate layer can be opposite to the ditrigonal cavities in the adjacent silicate layer. This arrangement of adjacent silicate layers leads to a structure in which the interlayer Mg ions can occur between the bases of aluminous tetrahedra. In the 2-layer hydrates of Na- and Ca-vermiculites, however, Na and Ca ions have a high probability of occurring between the bases of silicon tetrahedra but Ca ions also occur between ditrigonal cavities (Slade et al. 1985).

The positions and properties of the interlayer cations and the structure of the adjacent silicate layers influence the organization of the interlayer water molecules which generally have an ordered arrangement, although they are somewhat mobile. The positions of water molecules associated with exchangeable cations with high hydration energies should be the most readily characterized because such cations can be expected to "lock" the positions of the water molecules. The results of a study by Slade and Quirk (1991) indicate that La^{3+} would be such a cation.

The exchange reactions between trivalent lanthanide ions and clay minerals have been examined in studies of the uptake of radioactive wastes (Miller et al. 1982) and of the distribution of rare earths in soil clays (Bonot-Courtois and Jaffrezic-Renault 1982). Work by Bruque et al. (1980), Laufer et al. (1984) and Olivera-Pastor et al. (1988) showed that lanthanide ions can be taken up in excess of a clay's exchange capacity. This effect was reported to be pH-dependent, with the excess increasing with increasing pH.

Slade and Quirk (1991) reported that the interlayer expansion that occurs when smectites take up La^{3+} ions from $LaCl_3$ solutions is less than if solutions of chlorides of lower-charged ions such as Mg^{2+}, Ca^{2+} or Na^+ were used. The intense electrostatic field about interlayer trivalent La ions produces relatively strong attractive forces between the hydrated La ions and the adjacent silicate layers; such forces not only restrict swelling, but also contribute to the structural order. The present study of La-exchanged vermiculite has taken advantage of its high degree of stacking order and examined its interlayer structure at ambient conditions by X-ray methods.

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Table 1. EDX analysis of Llano vermiculite after La exchange. The data of Norrish (1973) for the original material is given for comparison.

	After La exchange		Original material	
SiO_2	39.96		45.56	
Al_2O_3	15.05		15.82	
Fe_2O_3	0.74		1.40	
MnO	—		0.13	
TiO_2	—		0.38	
MgO	25.95		29.66	
K_2O	—		0.17	
CaO	—		6.86	
NaO_2	—		—	
La_2O_3	12.50		—	
	Cations per 22 oxygen equivalents		Cations per 22 oxygen equivalents	
Si	5.735	8.00	5.79	8.00
Al^{IV}	2.265		2.21	
Al^{VI}	0.251	5.89	0.16	5.97
Fe^{3+}	0.077		0.13	
Mg	5.565		5.62	
Ti	—		0.04	
Mn	—		0.01	
La^{3+}	0.650	charge 1.95	—	charge 1.89
K	—		0.03	
Ca	—		0.93	

MATERIALS AND METHODS

After being Na-saturated as described by Slade et al. (1985), the highly charged vermiculite from Carl Moss Ranch, Llano County, Texas, was used as the starting material for the current work. La-exchange was carried out by refluxing the Na-saturated flakes in 0.5 *M* $LaCl_3$ (pH = 4.5) at 50 °C for 3 d; the solution was changed daily. The flakes were finally washed with warm distilled water until they were chloride free. Table 1 shows the results of analyzing the product with a Cambridge SEM fitted with an energy-dispersive X-ray (EDX) analysis system. The X-ray fluorescence (XRF) analysis and the structural formula obtained by Norrish (1973) for the original vermiculite are also given in Table 1. A comparison of the 2 sets of results shows that the composition of the silicate layers did not change significantly during treatment.

Preliminary Study

By using an evacuable 57.3-mm-diameter Gandolfi X-ray diffraction (XRD) camera, in the rotation mode, and with a La-vermiculite flake set either perpendicular (and stationary) to the X-ray beam or rotated about the axis perpendicular to the beam, the following were observed:

1) Under ambient conditions, a well-developed set of superlattice reflections was present (Figure 1a). These indicated that the La ions are ordered within domains and occupy positions in a *C* face-centered supercell, having dimensions $3a \times b$, where a and b are the dimensions of the standard vermiculite cell.

2) Under a vacuum, $\sim 9 \times 10^{-2}$ mbar, the superlattice reflections disappeared (Figure 1b). The superlattice reflections were found to reappear when ambient conditions were restored.

3) The basal spacing of the crystal was unaffected by the vacuum and remained at ~15 Å throughout the experiment.

X-ray Weissenberg photographs, taken under ambient conditions, were used to examine the Y^*Z^* lattice planes in the diffraction patterns of orientated flakes. The subcell $0kl$ reflections, including those with $k \neq 3n$, were found to be discrete and so, for the silicate layers, a high degree of stacking order exists parallel to the *Y*-axis. The superlattice reflections were streaked parallel to Z^* and, hence, the ordering of the La ions is 2-dimensional with no coupling between adjacent interlayers. The distribution of the reflections showed the structure to have a repeat distance along the *Z* axis corresponding to a single silicate layer and with the ditrigonal cavities in adjacent layers opposite each other, as in Na- and Ca-vermiculite.

Zero and non-zero layer Weissenberg photographs taken about the *X* and *Y* axes were used to determine the unit cell dimensions and probable space group for La-vermiculite. The dimensions obtained for the subcell are: $a = 5.33(5)$, $b = 9.18(6)$, $c = 15.13(9)$ Å, and $\beta = 96.82(7)°$. In the absence of any direct evidence to the contrary, and without regarding the superlattice reflections, the space group usually associated with 1*M* mica polytypes (*C2/m*) was used in calculations to establish the structure.

Data Collection and Determination of Silicate Layer Structure

Single-crystal diffraction data were collected on a SUPPER 2-circle X-ray diffractometer, whose method of use for data collection on intercalated vermiculites has been discussed by Slade and Stone (1983) and also by Slade et al. (1987). For the present work, the control algorithm was rewritten to operate on a Toshiba laptop T1200 PC. Accumulated counts were displayed for each 0.05° step along scans through reflections so that their profiles could be monitored during measurements. An $\omega/2\theta$ step scan and filtered Mo$K\alpha$ radiation were used. The La-vermiculite crystal employed for data collection had the dimensions $405 \times 596 \times 28$ μm. Data from 7 reciprocal lattice layers perpendicular to the *X* rotation axis were measured and the index ranges were $0 \leq h \leq 6$, $-12 \leq k \leq 12$, $-20 \leq l \leq 20$. Of the 3420 reflections measured, 2024 were above zero intensity. The experimental intensities were corrected for Lp factors and for absorption (linear absorption coefficient = 8.76 cm^{-1}). Conjugate reflec-

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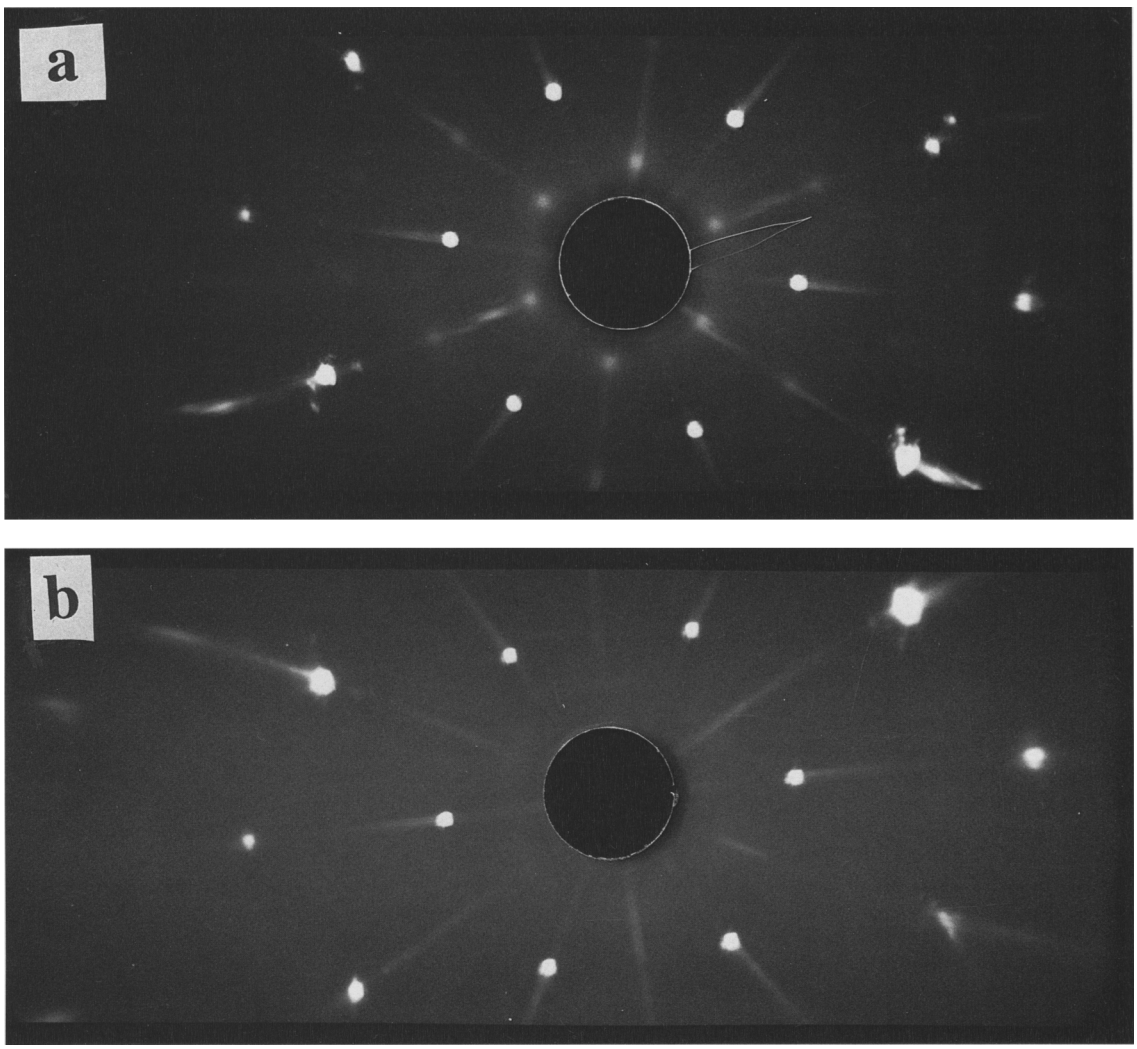


Figure 1. XRD photographs of a La-vermiculite crystal with basal cleavage perpendicular to the X-ray beam. a) Ambient conditions; b) under vacuum. Camera cylindrical, d = 57.3 mm. Radiation Co$K\alpha$.

tions were averaged and duplicate reflections were also merged. To phase the structure amplitudes, a trial model incorporating only the atoms in the silicate layers was set up in the program ORFLS (Busing et al. 1962). This program was also used for all least-squares structural refinements. The scaling factors for the reciprocal lattice layers were adjusted first, followed by the positional parameters and then the isotropic temperature factors. As the intensities of relatively few unique superlattice reflections were measurable, and then only in the X^*Y^* plane, they were not included in the data set. The structure amplitudes were each weighted according to the scheme of Cruickshank et al. (1961). After adjusting the atom parameters for the silicate layer atoms only, the R factor on the set of 1108 unique reflections (omitting zeros) was 21%.

RESULTS

Following the least-squares adjustments, a series of 3-dimensional Fourier electron density maps based upon F_{obs} and F_{obs}-F_{calc} were computed.

Since superlattice reflections could not be included in the calculations, the Fourier maps necessarily showed the C face-centering associated with the subcells. However, the true interlayer structure is based upon a C face-centered supercell, whose origin, within a given domain, may be at 0, 0, ½ or ½, ½, ½ with reference to the subcell. The computed Fourier maps for the subcell therefore necessarily represent an average of the contents of subcells within different domains comprising the whole crystal.

The section at z/c = 0.5 showed a strong peak at 0, 0, ½ and also at the related position ½, ½, ½, while

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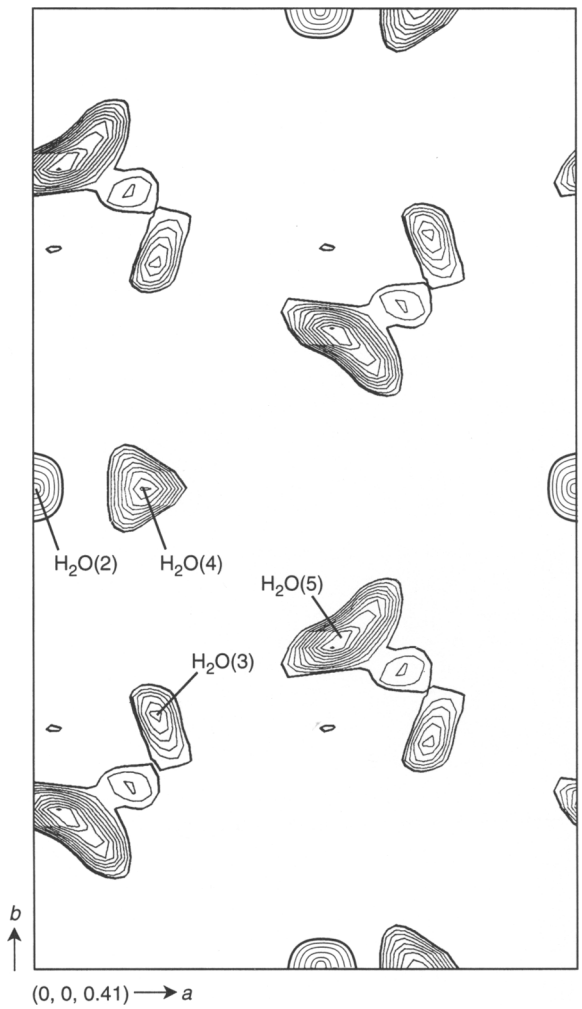


Figure 2. Section through a 3-dimensional (Fo-Fc) synthesis at z/c = 0.41. Contour interval regular but uncalibrated.

the sections at z/c = 0.41, 0.39 and 0.34 showed well-developed peaks of approximately equal height, but only about a sixth of the height of the peak at 0, 0, ½.

At this stage, the computer program DLS-76 for the simulation of crystal structures by geometric refinement (Baerlocher et al. 1977) was used to generate the possible coordinates for a set of water molecules about La at (0, 0, ½) or (½, ½, ½). The La-H_2O distance was specified as 2.52 Å in order to conform with the result obtained with X-ray absorption fine structure (EXAFS) spectroscopy by Jones et al. (1991). The distances between the water molecules and the nearest related surface oxygens were constrained at 2.84 Å to accord with the results published by Mathieson and Walker (1954).

After 10 cycles of least-squares adjustment, DLS-76 generated a set of positional coordinates for 8 water molecules. These coordinates accorded well with those of the 8 closest neighboring peaks about the La peaks in the electron density maps. The positions of the remaining peaks had triangular distributions on the symmetry related planes of z/c = 0.41 and z = 0.59. These remaining peaks can be attributed to uncoordinated water molecules between the La/water polyhedra. Figure 2 shows the electron density section at z/c = 0.4 on which peaks associated with both the coordinated and the uncoordinated water molecules appear together.

Table 2. Positional and thermal parameters for La-vermiculite.

	x/a	*y/b*	*z/c*	B (Å²)
M(1)	0.000	0.500	0.000	0.49
M(2)	0.000	0.167	0.000	0.38
O(1)	0.358(1)	0.167	0.0716(5)	0.64
OH(1)	0.859(1)	0.000	0.0698(5)	0.64
T(1)	0.394(1)	0.167	0.1818(5)	0.67
O(2)	0.143(2)	0.236(1)	0.2222(6)	1.39
O(3)	0.438(2)	0.000	0.2209(6)	1.56
La	0.500	0.500	0.500	11.25
$H_2O(1)$	0.479(9)	0.500	0.336(7)	10.62
$H_2O(2)$	0.000(9)	0.500	0.431(7)	6.82
$H_2O(3)$	0.265(9)	0.261(6)	0.435(7)	20.48
$H_2O(4)$	0.167	0.500	0.396(7)	3.83
$H_2O(5)$	0.579(9)	0.351(6)	0.394(7)	5.46

Key: Errors in parentheses are for last decimal place listed. $H_2O(1)$, $H_2O(2)$ and $H_2O(3)$ are directly coordinated to La; $H_2O(4)$ and $H_2O(5)$ are uncoordinated.

The coordinates for the crystallographically distinct water molecules, along with the coordinates for La, were then included in the structure model. Three further least-squares cycles were used to simultaneously adjust all of the atom parameters and the scale factors. These adjustments resulted in the thermal parameters for the water molecules becoming large but still positive, the R factor on the non-zero reflections was 17.5% for 50 variables. Table 2 gives the resulting positional and thermal parameters of both the silicate layer atoms and the interlayer atoms within a single ordered domain. In Table 2, the positional parameters for all atoms are referred to the standard unit cell. However, because of the superstructure, space group *C2/m* can only be applied to the interlayer atoms by referring them to the supercell that requires their x/a values given in Table 2 to be divided by 3. The bond lengths, calculated from positional coordinates for the interlayer atoms, are shown in Table 3, and Figure 3 shows the structural relationship of a single sheet of water molecules to the interlayer cations and the oxygens in the adjacent silicate layer. Observed and calculated structure factors may be obtained from the authors upon request.

DISCUSSION

The 8 water molecules ($H_2O(1)$, $H_2O(2)$ and $H_2O(3)$; Table 2) directly coordinated to the La cations are at the corners of distorted cubes that have one of

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Table 3. Bond lengths involving interlayer atoms in La-vermiculite.

Atoms	Distances (Å)
La-$H_2O(1)$	2.5 (1)
La-$H_2O(2)$	2.7 (1)
La-$H_2O(3)$	2.7 (1)
La-$H_2O'(3)$	2.7 (1)
$H_2O(1)$-O(2)	3.0 (1)
$H_2O(1)$-O(3)	3.2 (1)
$H_2O(4)$-O(3)	2.8 (1)
$H_2O(5)$-O(2)	2.8 (1)
$H_2O(4)$-$H_2O(5)$	3.3 (1)
$H_2(4)$-$H_2O'(4)$	3.3 (1)
$H_2O(2)$-$H_2O(3)$	4.5 (1)
$H_2O(3)$-$H_2O'(3)$	4.4 (1)
$H_2O(2)$-O(3)	3.2 (1)
$H_2O(3)$-O(2)	3.2 (1)

their body diagonals passing through the centers of water molecules ($H_2O(1)$; Table 2) buried in opposite ditrigonal cavities. The La cations, including their hydration shells, are distributed through the interlayers on a face-centered lattice with dimensions ~16 × 9 Å ($3a \times b$). The intervals between the La/water polyhedra are occupied by uncoordinated water molecules ($H_2O(4)$ and $H_2O(5)$; Table 2) which are in ordered, trigonally arranged sites.

From an extended EXAFS study of local environments about lanthanide ions in vermiculites, Jones et al. (1991) found that the coordination numbers of interlayer lanthanide ions appeared to depend on whether the lanthanide-exchanged vermiculite was examined in the form of a powder or as a film. Disparities were also noted between these results and the coordination numbers obtained for the corresponding lanthanides in solution as nitrates. For La, the EXAFS study showed coordination numbers of 6.1, 8.5 or 9, depending on whether the La was in a vermiculite powder, a vermiculite-film or in solution. The coordination number of 8, obtained here from XRD, compares well with the value of 8.5 obtained by EXAFS on a vermiculite-film.

Earlier X-ray studies of Ca-vermiculite by de la Calle (1977) and Slade et al. (1985) revealed that interlayer Ca ions can be present in both 6- and 8-fold coordination. This contrasts with the result for La ions, which are present only in the larger 8-fold coordination sites; the available, but smaller, 6-fold coordination sites remain unfilled. The univalent radii of ions (Pauling 1960) can be used to calculate the radius ratios relative to oxygen as 0.67 for Ca^{2+} and 0.79 for La^{3+}. These values show that the radius ratio for Ca^{2+} is slightly below, and for La^{3+} slightly above, the value of 0.732 at which the transition from cubic to octahedral coordination takes place. La is therefore more ideally surrounded by a cubic disposition of water molecules than is the case for Ca.

The present study shows that the interlayer La ions occupy sites on centers between large triads of water molecules adjacent to the larger of the triangular groups of surface oxygens. To accommodate the La ions, the normally larger triads of water molecules, which are hydrogen-bonded to the nearest surface oxygens, are further expanded so that H_2O-H_2O distances increase from ~3.4 to ~4.4 Å. The data from Table 3 show that this expansion is accompanied by an increase in the H_2O-surface oxygen distances to 3.2 Å, which exceeds the lengths of effective hydrogen

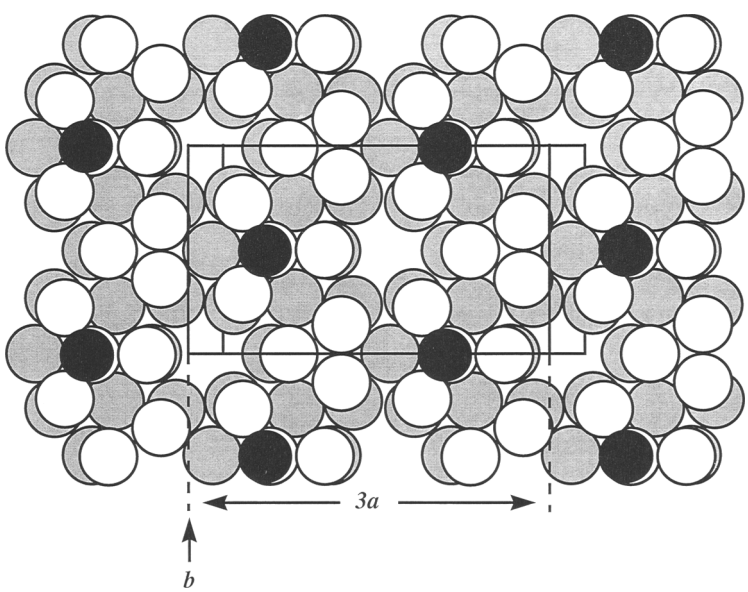


Figure 3. Single lower sheet of water molecules in La-vermiculite. Water molecules are unshaded; adjacent surface oxygens are shaded gray; La cations are black. View perpendicular to the *ab* plane.

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bonds. In addition, the cubic clusters of water molecules about the La ions necessitate that ditrigonal cavities in adjacent silicate layers should face each other across the interlayers and so produce a structure with only minimal stacking disorder.

Except for those water molecules embedded in the ditrigonal cavities, only minor displacements of water molecules from positions in the usually distorted hexagonal arrays are needed to create cubic environments about interlayer cation sites.

The average La-water distance (2.65 ± 0.1 Å) obtained in the present study is within the range of 2.52 ± 0.11 Å determined by Jones et al. (1991) from the EXAFS work. However, the X-ray results must be viewed in the context of there being considerable positional disorder associated with the interlayer atomic positions. In particular, a Fourier section, at $y/b = ½$, shows that the *La* peaks are spread out along a line parallel to the *X* axis. The large temperature factors associated with the water sites provide further evidence of the high degree of positional disorder that characterizes the structure of the water network. In the present study, the difficulties of specifying exact positional coordinates for the water sites are further compounded by the low electron densities associated with them.

Diffraction photographs showed that the basal spacing of La-vermiculite is the same under vacuum as under ambient conditions. Apparently the hydration energy of La is sufficiently high, 768 K cal g^{-1} ion (Bernal and Fowler 1933), to retain directly bonded water molecules. Hence, the size and shape of the cation/water polyhedra remain constant. This situation contrasts with that for Na- and Ca-vermiculites which have basal spacings that vary with changes in relative humidity (the hydration energies of Na^+ and Ca^{2+} are 114 and 205 Kcal g^{-1} ion, respectively). Under vacuum, however, the uncoordinated interstitial water molecules in La-vermiculite are removed and, as shown by the disappearance of the superlattice reflections, the spatial distribution of the polyhedra changes. These phenomena demonstrate that the interstitial water molecules play a crucial role in producing the ordered distribution of hydrated interlayer cations. Slade et al. (1989) showed that the well-ordered stacking of the silicate layers in 1,4-diazabicyclo[2,2,2]octane (DABCO)-intercalated vermiculite also displayed considerable disorder when heated. This disorder was attributed to the removal of water from between the organic cations. On rehydration, sharp diffraction patterns reappeared and, hence, ordered cation/water structures were reestablished.

The structural formula computed from the analytical results (Table 1) shows that if the *effective* charge for the La ions is assumed to be 3 then, within the limits of experimental error, the uptake of La by the Llano vermiculite used in this work does not exceed the amount needed to balance the layer charge. Under these conditions, a form of hydrolysis within the interlayers is still possible. The protons created in the process of reducing the charges on the La-water groups can also contribute to the neutralization of the layer charge.

The superlattice reflections given by La-vermiculite are sharp and occur at reciprocal lattice points well out from the direct beam. This is consistent with the interlayer cations and water molecules being ordered within extensive domains. Alcover et al. (1973) reported that the diffraction pattern of Kenya vermiculite also included additional reflections, between the normal Bragg reflections. The additional reflections, although more diffuse than those given by La-vermiculite, also showed that the interlayer Mg^{2+} cations and water molecules in Kenya vermiculite are distributed on a centered $3a \times b$ lattice. The diffuseness of the extra reflections produced by Mg-vermiculite demonstrates that the ordered domains in its interlayers are smaller, and perhaps less highly ordered within themselves, than are the ordered domains in La-vermiculite.

The R factors obtained during the refinements of the La-vermiculite structure are higher than given for example by refinements of mica structures. Apparently, even if the stacking disorder of vermiculite is reduced, by specific interlayer species, other structural imperfections remain. These degrade the overall diffraction patterns in ways that are not readily allowed for in structure refinements and so the derived structural parameters are of relatively low accuracy. Despite these limitations, the present study demonstrates that valuable structural information is obtainable from Fourier images.

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