

INTERLAYER STRUCTURES OF THE TWO-LAYER HYDRATES OF Na- AND Ca-VERMICULITES

P. G. SLADE, P. A. STONE, AND E. W. RADOSLOVICH

CSIRO Division of Soils, Glen Osmond, South Australia 5064, Australia

Abstract—The three-dimensional order shown by the two-layer hydrates of Na- and Ca-vermiculite, prepared from Mg-vermiculite from Llano, Texas, has enabled clear, two-dimensional Fourier projections of their interlayer structures to be obtained. Structure factor calculations were made in space group $C2$ and with unit-cell dimensions of $a = 5.358 \text{ \AA}$, $b = 9.232 \text{ \AA}$, and $\beta = 96.82^\circ$; for Na-vermiculite $c = 14.96 \text{ \AA}$ and for Ca-vermiculite $c = 15.00 \text{ \AA}$. In Na-vermiculite the interlayer cations are octahedrally coordinated to water molecules with the sodium-water polyhedra only located between the triads of oxygen atoms forming bases to tetrahedra in adjacent silicate layers. In Ca-vermiculite the interlayer cations are in both octahedral and 8-fold (distorted cubic) coordination with water molecules. The octahedrally coordinated Ca ions are between the bases of tetrahedra in adjacent silicate layers, but the 8-fold coordinated Ca ions are between the ditrigonal cavities. In both Na- and Ca-vermiculite some water molecules are drawn from planar networks appreciably towards the ditrigonal cavities. The three-dimensional order observed for these vermiculites contrasts with the stacking disorder reported for Mg-vermiculite from Llano. The distinct crystallographic behavior of Na^+ , Ca^{2+} , and Mg^{2+} in the hydration layers of Llano vermiculite probably depends on cation sizes and field strengths, together with the need to achieve local charge balance near the sites of tetrahedral Al-for-Si substitution.

Key Words—Crystal structure, Fourier projection, Hydrates, Interlayer cation, Vermiculite.

INTRODUCTION

Structural studies on Mg-vermiculites by Hendricks and Jefferson (1938a, 1938b), Mathieson and Walker (1954), and Shirozu and Bailey (1966) have all drawn attention to the partial stacking disorder within the double silicate layer structure. This disorder arises from random relative displacements of the two silicate layers by $\pm b/3$. The ensuing diffuseness of X-ray diffraction reflections with indices where $k \neq 3n$ has made studies of the interlayer region difficult. By contrast, the $0kl$ reflections with $k \neq 3n$ for the two-layer hydrates of Ca- and Na-vermiculites were found by de la Calle (1977) to be sharp and discrete; therefore these materials have ordered structures. The *pattern* of the $0kl$ reflections for the two-layer hydrates of Ca- and Na-vermiculites shows that their unit cells include only one silicate layer.

Suquet *et al.* (1975) and many others recognized that the positions of adjacent silicate layers are controlled by cation-dipole interactions and hydrogen bonding between interlayer water molecules and charged oxygens within the silicate surfaces. For the Mg-vermiculite from Llano, Texas, Shirozu and Bailey (1966) proposed that the exchangeable cations are located on symmetry centers between those triangular groups of surface oxygens forming the bases of tetrahedra for which there is a higher probability of aluminum having substituted for silicon (the T_1 tetrahedra). The relative positions of adjacent silicate layers are therefore largely controlled by local charge balance. The water mole-

cules are distributed randomly over the anion positions about the exchangeable cations so forming an octahedral interlayer network.

Diffuse reflections, present between the normal Bragg reflections in X-ray diffraction patterns from single crystals of Kenya vermiculite, enabled Alcover *et al.* (1973) and Alcover and Gatineau (1980) to demonstrate that interlayer Mg ions and water molecules are two-dimensionally ordered within domains. Similar local ordering patterns were predicted for the interlayer structure of Mg-vermiculite by Mathieson and Walker (1954) and by Bradley and Serratosa (1960).

In their Y -axis projection of the structure of a Mg-vermiculite from Kenya, Mathieson and Walker (1954) noted that the electron-density contours for the interlayer water molecules were extended in the negative X direction. This extension was interpreted as a distortion of the water sheet caused by interactions between each water molecule and the nearest oxygen atom in the adjacent silicate layer surface. de la Calle *et al.* (1977) proposed a model for the structure of the two-layer hydrate of "Ca-vermiculite" prepared by alteration of a phlogopite. In their model, the exchangeable calcium ions are located not only between the bases of tetrahedra in adjacent silicate layers but also between opposed ditrigonal cavities in those layers. The latter calcium ions have 8 water molecules as nearest neighbors, rather than 6. From a nuclear magnetic resonance study of the water in the two-layer hydrate of Na-vermiculite from Llano, Texas, Hougardy *et al.* (1976,

1977) concluded that the water molecules are strongly coordinated to the Na^+ cations which they surround octahedrally.

The present paper reports new electron-density projections for the interlayer structures of Na-saturated and Ca-saturated vermiculite from Llano, Texas. The results are compared with a projection derived from the data on "Ca-vermiculite" by de la Calle *et al.* (1977) and also with the conclusions drawn for the Llano Mg-vermiculite by Shirozu and Bailey (1966).

EXPERIMENTAL

Material

The vermiculite used came from the Carl Moss Ranch, Llano County, Texas. When Ca-saturated this material has been reported (Norrish, 1973, Table II) as having the following composition: $(\text{Mg}_{2.810}\text{Al}_{0.080}\text{Fe}^{3+}_{0.065}\text{Ti}_{0.020}\text{Mn}_{0.005})(\text{Si}_{2.895}\text{Al}_{1.105})\text{O}_{10}(\text{OH})_2\text{Ca}_{0.465}\text{K}_{0.015}$ for one half layer. Flakes, ~ 1 mm across, were cut from larger sheets and saturated with sodium by refluxing with 2 M NaCl for a week; the solution was changed daily. A washed subsample was refluxed in a 2 M CaCl_2 solution for a week and again washed. Because an X-ray fluorescence analysis indicated that some sodium remained, the refluxing was continued for a further two weeks, then an atomic absorption analysis confirmed that the product was free from sodium.

X-ray diffraction

Under ambient conditions, the degree of three-dimensional order shown by Na- and Ca-vermiculites can vary. Therefore, to maintain two sheets of water between the silicate layers of the flakes used for intensity measurements, they were bathed in a stream of air which had previously passed through warm water. The humid atmosphere during data collection caused several flakes to split, it also affected the Araldite used for mounting and occasionally caused condensation on the crystal surfaces. Although these problems were closely monitored and corrected as well as possible, they limited the accuracy of the data.

A single crystal diffractometer (with Weissenberg geometry) operating in a slow $\omega/2\theta$ step-scan mode was used to measure intensities with either $\text{CoK}\alpha$ or $\text{MoK}\alpha$ radiation; the circular apertures were replaced by suitable slits. A reference reflection was monitored regularly to minimize errors arising from the humidification of the crystal. Experimental intensities were adjusted for L_p factors, and absorption corrections were made by using linear absorption coefficients of 7.01 for the Na- and 8.39 cm^{-1} for the Ca-vermiculite ($\text{MoK}\alpha$) or 91.35 and 109.19 cm^{-1} , respectively, when $\text{CoK}\alpha$ radiation was used.

The unit-cell dimensions (obtained from the diffractometer data) are as follows: $a = 5.258 \pm 0.005$, $b = 9.232 \pm 0.009$ Å, and $\beta = 96.82^\circ$. For Na-ver-

miculite $c = 14.97 \pm 0.02$ Å and for Ca-vermiculite $c = 15.00 \pm 0.02$ Å. The 1M mica or vermiculite polytype is usually described in space group $C2/m$ which requires all 8 tetrahedral sites in the unit cell to be equivalent. For Llano vermiculite, as shown by Shirozu and Bailey (1966), Slade and Stone (1983), and J. G. Thompson (Geology Department, James Cook University, Townsville, Queensland 4811, Australia, personal communication, 1983), Si/Al ordering occurs in the tetrahedral sites, and hence a mirror plane is unlikely in the Na- or Ca-forms. Of the remaining possible space groups ($C2$ or $C\bar{1}$) for a 1M polytype $C2$ has $|F0k\bar{l}| = |F0k\bar{l}|$, whereas for $C\bar{1}$ $|F0k\bar{l}| \neq |F0k\bar{l}|$. For the latter, however, the differences between $|F0k\bar{l}|$ and $|F0k\bar{l}|$ can be shown by calculation to be fairly small and hence difficult to detect experimentally. For convenience, $C2$ was chosen as the basis for the calculations, but, in any case, the two-dimensional projections are identical for these two space groups.

Although the presence of a symmetry center between opposed ditrigonal rings on the upper and lower silicate half-layers in both the Na- and Ca-forms of Llano vermiculite remains uncertain, such centers are likely from the evidence obtained in this study and discussed below. Furthermore, Llano Mg-vermiculite is centric.

RESULTS

Electron-density projections

The experimental structure amplitudes were assigned phases calculated on the basis of scattering by the atoms of the silicate layers only, and the resulting observed structure factors (F_o values) were used, in conjunction with the calculated structure factors (F_c values), to compute (F_o - F_c) projections of the electron densities onto the (010) and the (100) faces of the unit cells for the Llano Na- and Ca-vermiculites. These projections (Figures 1 and 2) indicate that the interlayer structures of the two materials are significantly different.

Interlayer cations. The (F_o - F_c) projection onto (100) for Na-vermiculite (Figure 2a) shows that the interlayer cation sites over the ditrigonal cavities (the m_3 sites of Mathieson and Walker, 1954) are vacant, but those over the tetrahedral bases (the m_1 and m_2 sites) are occupied. For Ca-vermiculite, the corresponding projection (Figure 2b) shows that all three sites are occupied, but the peaks at the m_3 sites are higher than those at the m_1 and m_2 sites, which are equal.

The Na and Ca interlayer cations have similar x- and z-coordinates on their (010) projections (Figures 1a, 1b), but the electron-density contours about the Ca positions are drawn out along a line at about 20° to the Z axis.

Interlayer water. From the (100) projections (Figure 2) the interlayer water sites appear to have comparable

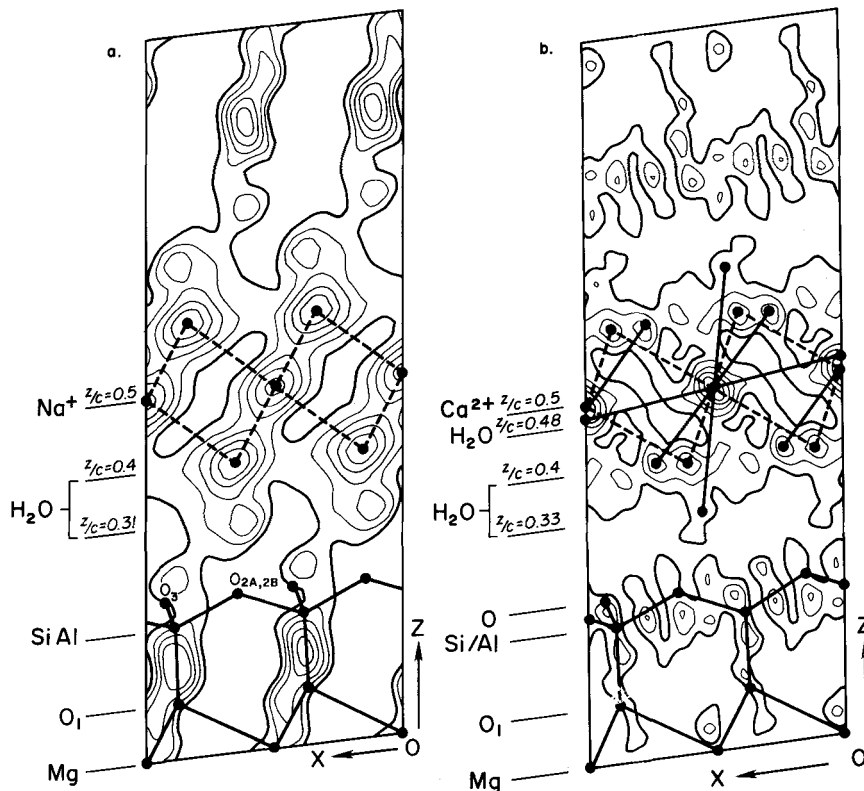


Figure 1. (Fo-Fc) projections onto the (010) cell faces of the structures for (a) Llano Na-vermiculite and (b) for Llano Ca-vermiculite. Only positive contours are given. The molecular model is outlined.

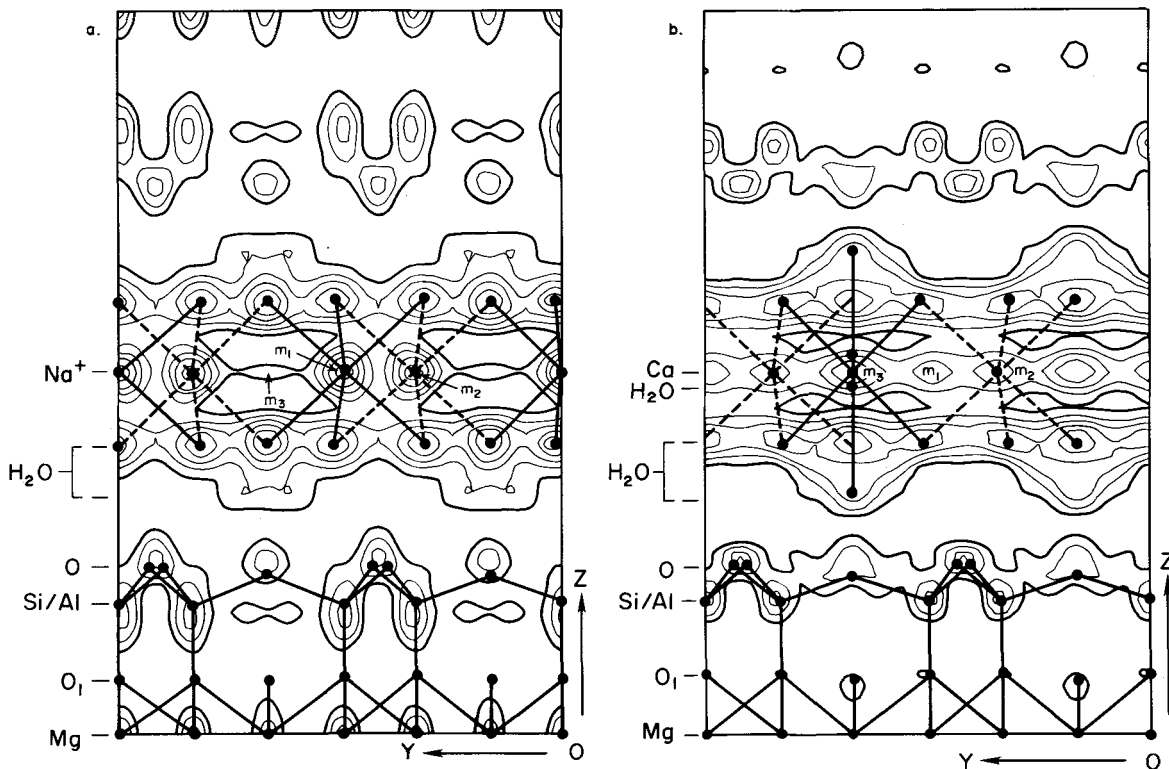


Figure 2. (Fo-Fc) projections onto the (100) cell faces of the structures for (a) Llano Na-vermiculite and (b) Llano Ca-vermiculite. Only positive contours are given. The molecular model is outlined.

distributions for the two materials, although, in relation to the other peaks, those at $y/b = 1/6$, $z/c \sim 0.33$ differ in height.

Whilst the water sites at $z/c \sim 0.4$ in the (010) projections (Figures 1a, 1b) are generally similar, they are split into two peaks for the Ca-vermiculite, suggesting that the water molecules in Ca-vermiculite are in several sites for which the x-coordinates differ slightly from the mean positions occupied in Na-vermiculite. Figure 1a shows that the main water peaks in the (010) projection of Na-vermiculite have well-resolved secondary peaks at $z/c \sim 0.31$. These peaks are weak, but present in the equivalent projection for Ca-vermiculite. They form part of the peaks at $y/b = 1/6$, $z/c \sim 0.33$ in the (100) projections.

Structures of the interlayers

Llano Na-vermiculite. That the interlayer cations and water molecules are in octahedral coordination in the Llano Na-vermiculite accords with the Fourier projections described above. The cations only occupy the m_1 and m_2 sites over the bases of tetrahedra. Apparently some of the water molecules are displaced from regular octahedral sites towards the ditrigonal cavities. This displacement is inferred from the tailed electron-density contours about the water sites shown in the (010) projection and also from those shown at $y/b = 1/6$ and $2/3$ in the (100) projection.

As there are two m_1 and two m_2 sites per unit cell and as the chemistry requires each unit-cell to contain ~ 1.9 Na^+ ions, just less than half the available sites are filled. Twelve possible water sites exist per unit cell, and, therefore, to provide the octahedral coordination about the m_1 and m_2 sites, these must largely be filled. Those water molecules not fully coordinated to Na^+ ions are the most likely to be displaced towards the ditrigonal cavities in the surfaces of the silicate layers.

On the basis of this interlayer structural model, separate least squares refinements of atomic coordinates, temperature factors, and multiplicities yielded the values set out in Table 1 wherein the calculated cation-water distances are also listed.

The final R-factor for the $h0l$ reflections was 10.7% and for the $0kl$ reflections 13.1%.

The coordinates for the atoms of the silicate layers in both the Llano Na- and Ca-vermiculite were based upon those reported by Shirozu and Bailey (1966) for the Mg-vermiculite; z-coordinates, however, were modified for single-layer unit cells, and the origins were shifted to the centers of the octahedral sheets of the silicate layers. Although the coordinates for the atoms of the silicate layers were not adjusted during refinement they are reported in Tables 1 and 3 for the sake of completeness.

Because temperature factors and multiplicities are closely correlated, the atom multipliers were initially fixed at chemically realistic values during temperature-

Table 1. Atomic parameters for Na-vermiculite.

Atom	x/a	y/b	z/c	B (\AA^2)	m
Octahedral cations					
1	0	0.9971	0	1.86	0.5
2	0	0.3330	0	1.86	0.5
3	0	0.6665	0	1.86	0.5
Tetrahedral cations					
1	0.3974	0.9980	0.1838	1.12	1.0
2	0.3958	0.3303	0.1838	2.64	1.0
Oxygen					
O ₁₁	0.3590	0.0016	0.0753	1.85	1.0
O ₁₂	0.3570	0.3372	0.0715	3.46	1.0
O ₁₃	0.3580	0.6713	0.0721	2.31	1.0
Oxygen					
O _{2A}	0.1421	0.4030	0.2259	1.90	1.0
O _{2B}	0.1471	0.9297	0.2244	1.90	1.0
O ₃	0.4407	0.1649	0.2257	1.96	1.0
Water					
Site 1	0.1546	0.0169	0.4045	3.90	0.38
Site 2	0.1546	0.6667	0.4045	3.90	0.38
Site 3	0.1546	0.3121	0.4045	3.90	0.38
Site 4	0.1176	0.1200	0.3158	3.90	0.10
Site 5	0.1176	0.2100	0.3158	3.90	0.10
Na^+					
Site m_1	0.5000	0	0.5000	1.84	0.12
Site m_2	0.5000	0.3450	0.5000	1.84	0.12
Distances about sodium (\AA)					
In the m_1 site	Na-(H ₂ O)1			2.21	
	Na-(H ₂ O)2			2.32	
	Na-(H ₂ O)3			2.46	
In the m_2 site	Na-(H ₂ O)1			2.36	
	Na-(H ₂ O)2			2.40	
	Na-(H ₂ O)3			2.22	

Water sites 4 and 5 are produced by distortions of the water sheet and are not occupied simultaneously with sites 1 and 3.

factor adjustment. The temperature factors were then held constant while the multiplicities were relaxed. The net result of these adjustments allowed the ratio of the number of water molecules to the number of Na ions to be obtained; it is 5.83:1, a reasonable value, within experimental error of the theoretical ratio of 6:1. Table 2 gives the observed structure amplitudes and the calculated structure factors for the $h0l$ and $0kl$ reflections of Llano Na-vermiculite.

Llano Ca-vermiculite. de la Calle *et al.* (1977) published three-dimensional X-ray diffraction data for a "Ca-vermiculite" produced from phlogopite. The direct projection of its structure on (100), as computed in the present investigation from the published values of the observed structure amplitudes is shown in Figure 3. Although the projection shown in Figure 3 and that shown in Figure 2b for Llano Ca-vermiculite are similar, Figure 2b does not show a peak at $y/b = 0.25$, $z/c \sim 0.4$, which is the position equivalent to the (H₂O)E

Table 2. Comparison of the observed and calculated structure amplitudes for Na-vermiculite and Ca-vermiculite.

h0l	Fobs	Fcalc	h0l	Fobs	Fcalc	h0l	Fobs	Fcalc
Na-vermiculite								
001	140.8	158.5	206	102.5	101.4	403	40.6	32.3
002	18.2	-9.1	206	41.6	42.2	403	107.7	96.1
003	46.5	-32.2	207	97.7	93.8	404	10.5	-12.1
004	57.9	84.8	207	31.7	-34.1	404	87.9	84.8
005	158.4	135.9	208	30.7	26.9	405	10.4	-11.5
006	15.7	-3.2	208	39.7	46.3	405	3.2	-3.8
007	68.4	-71.3	209	85.7	97.5	406	37.5	54.9
008	34.6	-35.1	209	85.7	97.5	406	9.0	11.6
009	16.9	19.4	2010	38.5	32.4	407	70.8	63.6
0010	82.3	79.9	2010	119.1	125.1	407	50.3	56.0
0011	30.5	43.2	2011	14.3	18.3	408	65.1	60.2
0012	61.7	54.7	2011	56.3	53.5	408	80.3	80.2
0013	25.9	30.9	2012	54.1	59.2	409	32.2	20.8
0014	22.2	23.2	2012	7.8	-11.8	409	43.4	47.0
0015	31.4	27.5	2013	21.0	20.6	4010	12.3	9.2
200	54.4	61.9	2013	7.1	-1.0	4010	4.1	0.9
201	91.5	92.3	2014	1.3	-4.0	4011	6.9	9.7
201	15.4	1.5	2014	27.7	34.9	4011	14.8	-12.4
202	133.6	137.4	2015	18.8	-11.3	4012	13.1	13.5
202	73.5	-83.6	2015	38.2	40.4	4012	6.1	2.3
203	58.1	56.4	400	58.5	-53.4	4013	20.1	18.3
203	23.0	-21.9	401	34.7	31.6	4014	20.0	15.6
204	70.4	73.4	401	50.4	-47.5	4014	21.3	25.0
204	42.3	52.7	402	83.9	70.5	4015	5.1	2.6
205	40.1	48.5	402	54.7	54.8	4015	15.1	12.6
205	51.6	64.6						
Ca-vermiculite								
001	148.4	137.8	0012	61.8	65.8	201	22.3	-18.4
002	14.8	10.0	0013	29.2	34.4	202	124.9	142.9
003	59.3	-44.9	0014	19.8	26.7	202	65.4	-71.8
004	87.3	87.3	0015	29.6	32.9	203	78.2	63.8
005	175.6	133.8	0016	38.0	42.0	203	41.6	-32.5
006	14.8	13.8	0017	40.4	49.2	204	59.7	73.8
007	97.4	-81.5	0018	11.7	20.8	204	50.1	57.4
008	31.0	-36.8	0019	24.4	-21.3	205	46.2	47.4
009	3.4	12.0	0020	11.3	-18.3	205	67.9	58.9
0010	90.6	86.4	200	81.4	82.6	206	102.9	110.5
0011	40.1	45.3	201	84.9	83.4	206	53.2	57.9
207	86.1	96.1	409	22.5	29.0	6011	20.5	-15.4
207	35.9	-41.9	409	64.2	51.0	6012	10.7	-8.6
208	33.5	42.1	4010	11.9	13.4	6012	38.3	32.0
208	43.4	42.9	4010	10.0	10.0	6013	19.8	14.0
209	25.4	-32.1	4011	11.1	6.7	6013	55.4	50.0
209	104.6	99.6	4011	19.5	-21.0	6014	33.2	39.3
101 2010	32.8	-38.6	4012	14.5	20.4	6014	29.1	25.1
2010	135.0	142.9	4012	6.7	1.0	6015	26.9	21.9
2011	9.4	13.1	4013	11.8	18.7	6015	10.7	-8.8
2011	58.0	63.3	4013	10.9	11.0	6016	6.6	-6.7
2012	55.7	66.7	4014	12.4	20.5	6016	8.7	4.1
2012	9.2	-5.2	4014	24.1	24.9	6017	15.1	-17.8
2013	20.5	32.1	4015	9.7	2.5	6017	14.8	21.8
2013	7.5	-7.9	4015	13.7	19.4	6018	6.9	-0.8
2014	4.7	5.1	4016	17.4	-15.4	6018	35.7	32.0
2014	24.3	33.6	4016	17.8	14.4	6019	12.1	16.2
2015	11.1	-15.0	4017	12.0	-8.5	6019	11.3	13.0
2015	43.5	51.9	4017	6.2	-2.0	6020	6.7	3.5
2016	24.7	28.1	4018	12.3	16.6	800	33.8	24.7
2016	22.0	26.8	4018	12.8	9.8	801	4.9	0.2
2017	58.7	59.5	4019	24.7	33.0	801	45.2	35.6
2017	16.1	-24.4	4020	17.6	20.8	802	6.2	-4.1
2018	28.9	47.6	4020	29.0	40.7	802	24.7	16.5
2018	9.2	14.9	600	14.3	9.1	803	18.9	18.1
2019	14.1	9.9	601	6.2	5.9	803	20.1	19.2

Table 2. Continued.

h0l	Fobs	Fcalc	h0l	Fobs	Fcalc	h0l	Fobs	Fcalc
2019	9.5	4.4	601	45.5	35.0	804	29.2	31.2
2020	10.3	8.4	602	15.5	17.9	804	24.6	16.6
2020	25.5	32.3	602	71.6	57.6	805	21.3	20.2
400	50.2	-46.3	603	21.7	18.1	805	7.4	2.9
401	20.6	15.9	603	69.0	58.0	806	6.5	-1.6
401	57.9	-57.9	604	25.4	27.6	806	26.7	22.1
402	88.0	90.9	604	39.4	27.5	807	11.4	-12.9
402	54.4	52.6	605	4.9	3.1	807	27.9	14.3
403	37.3	33.5	605	21.6	-20.1	808	6.7	-1.4
403	116.8	115.7	606	12.3	-10.9	808	17.8	-5.1
404	12.5	-15.4	606	10.3	3.2	809	9.6	7.3
404	108.9	89.2	607	11.9	-14.3	809	11.0	-4.7
405	14.0	-10.0	607	21.7	30.8	8010	16.9	10.3
405	4.7	-0.7	608	13.1	18.0	8010	20.3	11.4
406	34.0	51.8	608	59.8	46.8	8011	9.9	6.5
406	10.2	12.5	609	28.4	47.7	8011	25.1	23.9
407	71.2	81.4	609	5.7	1.2	8012	4.9	0.9
407	70.5	56.4	6010	20.6	33.6	8012	34.6	26.6
408	58.1	67.7	6010	40.5	-31.5			
408	92.5	96.4	6011	6.0	2.5			

Ok/	Fobs	Fcalc	Acalc	Bcalc	Ok/	Fobs	Fcalc	Acalc	Bcalc
Na-vermiculite									
002	20.2	9.1	-9.1		043	9.2	11.5	-8.5	-7.8
003	50.8	32.1	-32.1		044	42.2	42.8	-24.4	-35.2
004	62.2	84.4	84.4		045	8.0	3.9	0.5	-3.8
005	155.8	134.9	134.9		046	43.5	43.9	23.4	37.1
006	16.4	3.2	-3.2		047	23.9	23.4	10.0	21.2
007	69.9	70.3	-70.3		048	22.3	32.8	-21.9	-24.5
008	34.7	34.4	-34.4		049	37.9	42.0	-23.6	-34.8
009	16.7	19.0	19.0		0410	13.7	17.5	12.8	11.9
0010	79.8	77.7	77.7		0411	35.4	39.8	27.0	29.3
0012	57.6	52.5	52.5		0412	13.4	10.5	8.2	6.5
0013	23.8	29.5	29.5		0413	23.4	31.2	-17.7	-25.7
0014	20.0	21.9	21.9		060	146.4	127.7	127.7	-2.0
0015	27.6	25.7	25.7		061	87.9	73.4	73.4	-0.5
020	62.4	63.3	31.2	-55.1	062	41.8	38.4	38.0	5.7
021	18.2	21.2	9.7	-18.9	063	7.2	5.2	-4.3	2.9
022	44.7	44.7	-23.3	38.2	064	12.6	15.4	15.4	-1.2
023	61.8	55.1	-29.7	46.4	065	54.1	52.8	53.0	-9.3
024	29.3	24.1	10.3	-21.8	066	45.3	42.6	42.1	-6.2
025	36.0	40.1	18.3	-35.7	067	2.6	4.1	-2.2	-3.5
026	22.0	17.9	8.6	-15.6	068	28.4	28.6	-28.6	1.0
027	21.2	28.3	-15.7	23.5	069	18.8	15.6	-15.5	-1.7
028	20.4	18.0	-10.9	14.4	0610	39.1	47.6	47.5	-3.0
029	3.4	2.2	-1.7	1.4	0611	49.8	54.4	54.4	-3.3
0210	17.1	17.0	11.4	-12.6	080	4.8	4.4	3.6	2.7
0211	13.9	14.2	11.3	-8.5	081	8.1	5.8	3.2	-4.8
0212	7.0	3.9	3.9	-0.3	082	6.3	7.4	1.9	-7.2
0213	10.2	11.3	-7.0	8.9	083	14.7	11.1	-8.8	6.8
0214	7.5	7.7	-5.8	5.0	084	15.7	10.4	-5.6	8.7
0215	4.8	3.1	-1.0	3.0	085	2.5	1.9	-0.5	1.9
040	21.4	21.1	-4.9	-20.5	086	28.9	27.5	14.0	-23.7
041	4.4	5.2	1.6	-5.0	087	7.9	7.3	0.4	-7.3
042	32.2	33.0	16.1	28.8	088	18.4	17.4	-11.3	13.2
Ca-vermiculite									
001	115.4	137.8	137.8		049	49.0	52.6	-27.8	-44.6
002	22.6	10.0	10.0		0410	10.5	13.9	9.3	10.3
003	57.8	44.9	-44.9		0411	51.1	48.9	27.4	40.4
004	73.6	87.3	87.3		0412	17.6	15.9	11.4	11.1
005	166.5	133.8	133.8		0413	28.6	32.2	-13.6	-29.1
006	10.0	13.9	13.9		0414	32.0	32.3	-14.6	-28.3
007	91.3	-81.5	-81.5		0415	5.6	11.3	7.3	8.6
008	36.9	-36.8	-36.8		060	133.6	152.1	152.0	-5.6

Table 2. Continued.

0k/	Fobs	Fcalc	Acalc	Bcalc	0k/	Fobs	Fcalc	Acalc	Bcalc
009	6.0	12.0	12.0		061	93.7	72.1	72.1	2.5
0010	93.3	86.4	86.4		062	38.6	47.1	46.9	4.0
0011	44.7	45.3	45.3		063	5.3	6.3	-4.9	3.9
0012	69.5	65.8	65.8		064	16.6	14.9	14.9	-0.2
0013	32.2	34.4	34.4		065	54.8	56.6	55.5	-11.1
0014	27.7	26.7	26.7		066	53.4	53.9	53.5	-7.0
0015	35.3	32.9	32.9		067	4.0	4.6	-1.2	-4.4
020	38.9	56.7	26.1	-50.4	068	41.3	33.2	-33.2	0.3
021	25.7	30.0	14.8	-26.1	069	22.1	25.0	-25.0	0.5
022	48.0	52.7	-27.1	45.2	0610	44.4	54.4	54.2	-5.5
023	65.6	47.3	-24.6	40.4	0611	73.2	65.8	65.7	-3.2
024	23.0	9.0	2.9	-8.4	0612	55.8	56.3	56.3	-0.8
025	48.2	58.7	25.6	-52.8	0613	7.7	4.7	2.8	3.7
026	10.2	4.6	0.0	-4.6	0614	2.4	4.3	1.3	4.1
027	16.5	17.9	-9.6	15.1	0615	34.6	35.4	35.4	-0.6
028	32.4	25.7	-1.2	5.7	080	1.9	5.2	-4.1	3.2
029	1.7	5.8	-1.2	5.7	081	6.7	10.4	4.6	-9.3
0210	19.0	19.0	9.7	-16.2	082	6.5	7.8	4.7	-6.3
0211	18.9	16.7	9.3	-13.9	083	13.5	8.5	-2.4	8.2
0212	5.4	2.5	2.3	1.0	084	15.8	18.8	-9.4	16.2
0213	8.1	7.6	0.3	7.6	085	7.3	5.8	-2.6	-5.2
0214	14.7	11.7	-2.9	11.4	086	29.1	24.3	6.7	-23.4
0215	4.5	4.0	-2.0	3.4	087	13.5	14.7	5.4	-13.7
040	31.9	30.0	-9.9	-28.3	088	21.0	21.4	-8.3	19.7
041	7.2	4.4	3.2	3.0	089	25.9	27.0	-11.3	24.6
042	27.7	29.9	17.0	24.6	0810	8.0	7.2	1.7	-7.0
043	6.8	5.9	-3.5	-4.7	0811	31.9	32.4	13.5	-29.4
044	46.3	53.5	29.8	-43.2	0812	12.6	9.9	5.8	-8.0
045	9.1	3.4	1.7	3.0	0813	18.5	19.8	-4.7	19.2
046	43.1	35.5	16.5	31.5	0814	18.5	19.0	-5.4	18.2
047	31.5	35.2	17.5	30.6	0815	4.2	7.2	2.8	-6.6
048	32.8	35.2	-19.2	-29.5					

site of de la Calle *et al.* (1977). Figure 3 also shows that the peaks corresponding to the Ca sites over the ditrigonal cavities are elongated in the *Y* direction. The ratio of the height of these peaks to those over the tetrahedral bases is greater than for the equivalent peaks seen in Figure 2b.

For Llano Ca-vermiculite the 0.95 Ca²⁺ ions available were distributed equally over the *m*₁, *m*₂, and *m*₃ sites, and an (Fo-Fc) projection on (100) of this model was almost flat at the *m*₁ and *m*₂ sites, whereas the substantial peak remained at the *m*₃ site. This result accords with the proposed model of de la Calle *et al.* (1977) in which a water site, (H₂O)D, would also project close to the *m*₂ site. In an (Fo-Fc) projection on (010) using a model which only included Ca²⁺ ions in the interlayer region, well-resolved peaks appeared closely to and on either side of the Ca sites. Taken together, these (Fo-Fc) projections provide clear evidence for water sites close to the mid-plane of the interlayer region in Llano Ca-vermiculite. The positional parameters for the water molecules in these, the 3B sites (Table 3), were measured from the projections and subsequently refined by least-squares adjustment. The location of the other water molecules was carried

out as follows: The (Fo-Fc) projections on (100) show that the water sites in Llano Na- and Ca-vermiculite have essentially non-equivalent sites at *y/b* ~ 0, 1/3, and 2/3 plus a fourth site at *y/b* = 2/3, *z/c* ~ 0.33. The *x*-coordinate of the latter was obtained from the (010) projection on which the three principal non-equivalent sites are superimposed. The two strong and approximately equal peaks at *z/c* ~ 0.4 suggest that water molecules exist at *x/a* ~ 0.08 and *x/a* ~ 0.20 with very similar *y*-coordinates.

Using a three-dimensional scale model of steel wires in a cork base, possible relationships between cation sites and their adjacent water molecules at each of the two possible *x*-coordinates were examined. For any specified polyhedron, the model showed that the most realistic cation-water distance was ~2.45 Å; this choice was confirmed by refining the trial parameters and computing interatomic distances (Table 3).

The final R-factor for the *h0l* reflections was 18.5%, and for the *0kl* reflections, 15.4%. Table 2 reports the observed structure amplitudes and calculated structure factors for Llano Ca-vermiculite. Figure 4 shows the proposed structural relationship in Ca-vermiculite.

Six cation sites exist per unit cell for 1*M* vermiculite,

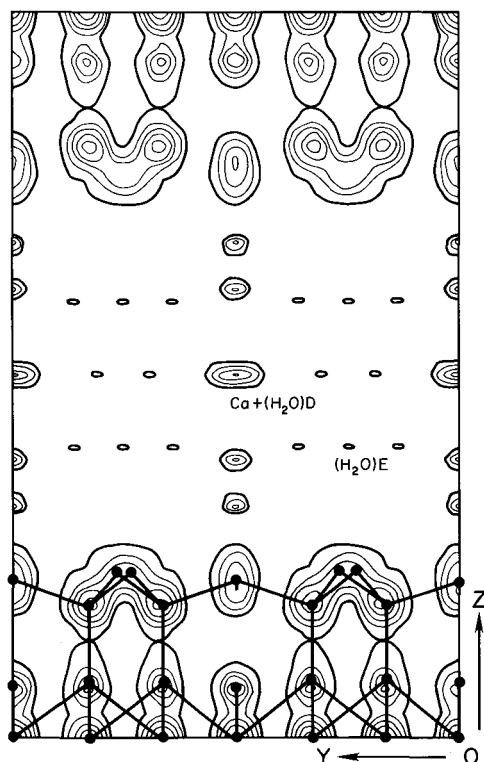


Figure 3. (Fo) projection onto the (100) cell faces of the structure for "Ca-vermiculite." Data from de la Calle (1977).

but only 0.95 Ca^{2+} ions per cell are present chemically; therefore, on average, less than one sixth of the cation sites are occupied. The number of water molecules per cell is difficult to determine from chemical data, but the number found by least-squares refinement in this study is 7.4 per single-layer cell, close to the 7.44 reported for Llano Mg-vermiculite by Shirozu and Bailey (1966).

DISCUSSION

The present study supports the conclusions drawn by Hougardy *et al.* (1976, 1977), that Na^+ exists in octahedral coordination in the two-layer hydrate of Llano vermiculite. Additionally, the study shows that the Na ions must be located (in relation to the silicate surfaces) in the m_1 and m_2 sites between the bases of opposite tetrahedra. By contrast, the interlayer Ca^{2+} ions in the two-layer hydrate of Llano Ca-vermiculite can occupy not only the m_1 and m_2 sites but also the m_3 sites between opposed ditrigonal rings of surface oxygens, where Ca^{2+} is in 8-fold coordination. This work confirms that the conclusions drawn by de la Calle *et al.* (1977) also apply to the Llano vermiculite and shows that the distorted two-water-layer arrangement, described by Mathieson and Walker (1954) for Mg-

Table 3. Atomic parameters for Ca-vermiculite.

Atom	x/a	y/b	z/c	B	m	
Octahedral cation						
1	0	0.9971	0	0.98	0.5	
2	0	0.3330	0	1.05	0.5	
3	0	0.6665	0	0.94	0.5	
Tetrahedral cation						
1	0.3974	0.9980	0.1835	0.72	1.0	
2	0.3958	0.3303	0.1839	1.00	1.0	
Oxygen						
O_{11}	0.3590	0.0016	0.0745	0.68	1.0	
O_{12}	0.3576	0.3372	0.0709	2.17	1.0	
O_{13}	0.3580	0.6713	0.0715	1.69	1.0	
Oxygen						
O_{2A}	0.1421	0.4030	0.2238	0.60	1.0	
O_{2B}	0.1471	0.9297	0.2223	1.05	1.0	
O_3	0.4407	0.1649	0.2236	1.18	1.0	
Water						
Site 1	A	0.2253	0.0013	0.4083	2.5	0.18
	B	0.0791	0.0013	0.4004	2.5	0.38
Site 2	A	0.2253	0.3183	0.4083	2.5	0.18
	B	0.0791	0.3183	0.4004	2.5	0.33
Site 3	A	0.2253	0.6667	0.4083	2.5	0.24
	B	0.9629	0.6667	0.4827	2.5	0.28
Site 4		0.5441	0.6667	0.3325	2.5	0.31
Calcium						
Site m_1		0.5000	0	0.500	3.8	0.079
Site m_2		0.5000	0.333	0.500	3.8	0.079
Site m_3		0.5000	0.6667	0.500	3.8	0.079

Distances about calcium (Å)

In the m_1 site	Ca-(H ₂ O)1B	2.55
	Ca-(H ₂ O)3A	2.48
	Ca-(H ₂ O)2A	2.57
In the m_2 site	Ca-(H ₂ O)3A	2.48
	Ca-(H ₂ O)1A	2.48
	Ca-(H ₂ O)2B	2.56
In the m_3 site	Ca-(H ₂ O)1A	2.47
	Ca-(H ₂ O)2A	2.39
	Ca-(H ₂ O)3B	2.52
	Ca-(H ₂ O)4	2.55

vermiculite, is further distorted in Ca-vermiculite to accommodate Ca^{2+} ions in 8-fold coordination.

Shirozu and Bailey's (1966) work on Llano Mg-vermiculite indicates that the interlayer Mg ions only occupy one set of the non-equivalent cation sites. These sites are between the triangular bases of opposed T_1 tetrahedra in which the lattice charge mostly originates by Al-for-Si substitution.

Contrasting interlayer structures of Na-, Ca-, and Mg-vermiculites

The contrasting arrangements of interlayer cations and water molecules in Na-, Ca-, and Mg-vermiculites can be explained as follows. In vermiculites, strong

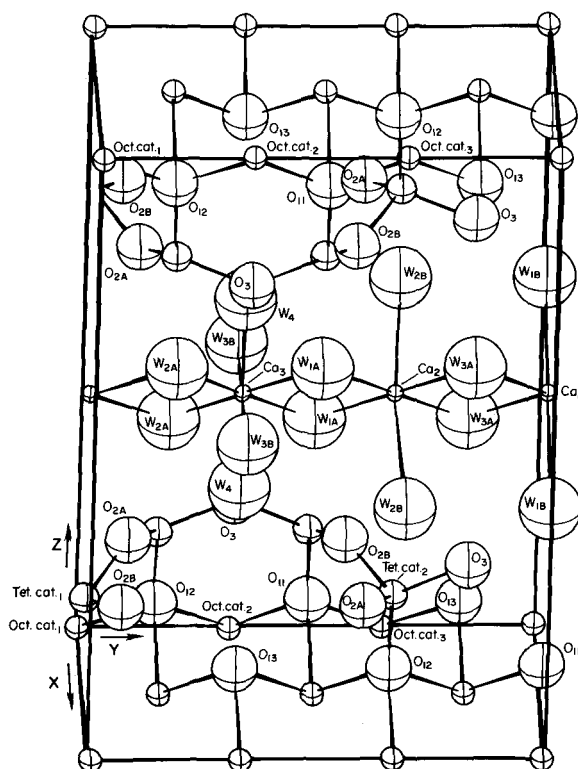


Figure 4. The structure of the two-layer hydrate of Ca-vermiculite. For clarity, only 3 of the possible 6 exchangeable cation sites per unit-cell are shown. In reality, an average unit-cell of Llano Ca-vermiculite will only have ~ 0.95 exchangeable cation sites occupied. Similar layer-interlayer relations exist in Na-vermiculite in which only the sites providing 6-fold coordination are occupied.

hydrogen bonds between the water molecules and surface oxygens (Farmer and Russell, 1971) combine with packing considerations to establish a basic structure for the interlayer water system. Ideally the spaces between the water molecules provide interstitial sites for which octahedral coordination will be normal for ions with ratios of univalent radii, with respect to oxygen, of 0.414–0.732. The present work shows that considerable distortions of the planar water network occur, even around the unoccupied m_3 sites in Na-vermiculite. Mathieson and Walker (1954) noted rotations of triads of water molecules adjacent to the m_3 site, but the (100) projections reported here show that water molecules are also drawn from their plane towards the ditrigonal cavities. In an ideal planar water network all three sets of m sites would be available for occupancy by Na ions, but in reality, the distorted environment about the m_3 site and the maintenance of local charge balance near the silicate tetrahedra results in Na^+ only entering the m_1 and m_2 sites. The relatively weak electric fields about univalent Na ions are probably unable to modify the distorted water cages suffi-

ciently about the m_3 sites to produce energetically favorable environments for occupancy.

For Ca ions the situation is different because Ca^{2+} has a radius ratio with O^{2-} high enough (Pauling, 1960) to make 8-fold coordination possible. The interlayer sites occupied by Ca ions will therefore be governed both by local charge balance (satisfied with Ca ions entering the m_1 and m_2 sites) and by the tendency of Ca^{2+} to enter 8-fold coordination, as in the m_3 sites. These sites are not only sufficiently large for 8-fold coordinated ions but they also have water molecules in the ditrigonal cavities to assist such coordination. The high electric field about Ca ions in such m_3 sites enables them to move surrounding water molecules, including those in the ditrigonal cavities and those moved out of the normal water sheets to positions at $z/c \sim 0.48$ (3B, Table 3), into a stable configuration—a distorted cube.

Mg ions normally have a coordination number of 6 in relation to water, and their small size enables them to produce highly polarized water molecules in the first hydration shells to form positively charged polyatomic ions. These ions will be positioned at places of the most intense negative layer charge, i.e., between the bases of aluminous tetrahedra (the T_1 tetrahedra) in two adjacent sheets.

The number of water molecules per unit cell in Llano Ca-vermiculite (7.4), although close to the result found by Shirozu and Bailey (1966) for the Mg form, is lower than would be expected if much water existed outside of the first hydration shells as it apparently does in the two-layer hydrate of Ca-montmorillonite (Ormerod and Newman, 1983). The water at the position E in the study of de la Calle *et al.* (1977) is not one of the octahedral anion sites but can be derived from such a site by a displacement of $+0.083$ (y/b) along Y . Neither the (100) nor the (010) projection of our Llano Ca-vermiculite shows the position E to be significantly occupied. Here, the equivalent water molecules, those in the 2A sites, apparently are derived from the octahedral anion sites by displacements along $+x$ (hence the multiple peaks in the (010) projection). de la Calle *et al.* (1977) did not publish a full set of $h0l$ data, hence an (010) projection for the altered phlogopite is not available for comparison.

The differences between the results of this study and those of de la Calle *et al.* (1977) may possibly be explained by some differences in relative humidity during data collection or by considerable disorder in the position of the relevant water molecules. These differences do not alter our main conclusion, that Ca can exist in both 6- and 8-fold coordination in the Llano vermiculite.

Three-dimensional order

It is noteworthy that the Na- and Ca-vermiculites exhibit three-dimensional order whereas Mg-vermic-

ulite does not. This difference depends on a number of complex interactions, but the most important is the means by which *local* charge balance is maintained in response to any ordering of Si and Al in the tetrahedral sites. In the two-layer hydrates of Na- and Ca-vermiculite the ditrigonal cavities in adjacent silicate layers face each other. By contrast in Mg-vermiculite the cavities in one layer face tetrahedra in the opposite layer (Shirozu and Bailey, 1966). Given that at least partial Si/Al ordering occurs around the ditrigonal rings the following possibilities exist: (1) that aluminous tetrahedra are opposite silicon-rich tetrahedra; (2) that aluminous tetrahedra are opposite aluminous tetrahedra; and (3) that silicon-rich tetrahedra are opposed.

If the adjacent silicate layers described by Shirozu and Bailey (1966) in Llano Mg-vermiculite are translated by $\pm b/3$ to bring ditrigonal cavities face to face, the Si/Al ordering results in there being a high probability (~ 0.8) that aluminous tetrahedra will be opposite silicon-rich tetrahedra (possibility 1). Symmetry centers will therefore occur midway between the opposed ditrigonal cavities, but in possibilities 2 and 3, which have low probabilities of occurrence, a diad axis must exist parallel to *Y*. The electric fields between tetrahedra arranged as in possibility 1 will be moderate and equal at the m_1 and m_2 sites so that on average Na^+ or Ca^{2+} ions can achieve local charge balance equally in either site; indeed, the (100) projections have peaks of equal height at the m_1 and m_2 sites.

In Na-vermiculite the sodium-water polyhedra have specific linkages to adjacent basal oxygens. These polyhedra, arranged in zig-zag rows parallel to [100], help fix the relative positions of the silicate layers, and translations between layers are unlikely. If such translations do occur, they must leave aluminous tetrahedra opposite silicon-rich tetrahedra. The only possible translations are $\pm(b/2 + a/2)$ which are indistinguishable from the C-face centering of the layers. In Ca-vermiculite the relative positions of adjacent silicate layers must be dominated by the 8-fold calcium-water polyhedra between opposed ditrigonal cavities. Stacking disorder is therefore not readily possible here either. To balance the intense electric fields about the smaller Mg ions the ions must be between the bases of opposite aluminous tetrahedra (possibility 2). Given that ditrigonal rings when *opposite* are related by a symmetry center, possibility 2 requires adjacent silicate layers to be translated by $\pm b/3$ in Mg-vermiculite; i.e., T_1 sites are opposite T_1 sites as found by Shirozu and Bailey (1966). Such translations relocate the centers of symmetry to positions midway between the T_1 sites.

The stacking disorder observed in Mg-vermiculite is puzzling if Mg ions are only located between opposed T_1 tetrahedra because such an arrangement would three-dimensionally fix the relative positions of adjacent silicate layers. Shirozu and Bailey (1966) measured the X-ray diffraction pattern for Mg-vermiculite exactly at

the Bragg angles in reciprocal space; their data (when transformed into real space) indeed shows Mg ions between T_1 tetrahedra only. The intensity diffracted into the non-Bragg angles, however, might well have provided additional Mg peaks at the alternative T_{11} sites.

We believe that Shirozu and Bailey's (1966) results indicate that Mg ions are only *probably* between T_1 tetrahedra, and furthermore that these tetrahedra are only *on average* the most aluminous. In reality, a significant proportion of T_{11} tetrahedra is likely to be aluminous and therefore may have Mg ions between them. Adjacent silicate layers will then have an opposite displacement (by $+b/3$) at this point to that when T_1 tetrahedra are opposed. This arrangement could explain the stacking faults implied by the streaking of reflections for $k \neq 3n$. Because of the weak electric fields associated with tetrahedra arranged as for in possibility 3, cations are unlikely to be found between them.

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(Received 29 December 1983; accepted 22 June 1984)

Резюме—Пространственный порядок двухслойных гидратов Na- и Ca-вермикулита, подготовленных из Mg-вермикулита из Ллано в Техасе, давал возможность получения отчетливых плановых проекций фурье для структуры этих минералов. Расчеты факторов структуры были проведены в пространственной группе C2, для размеров элементарной ячейки $a = 5,358 \text{ \AA}$, $b = 9,232 \text{ \AA}$, и $\beta = 96,82^\circ$; для Na-вермикулита $c = 14,96 \text{ \AA}$, а для Ca-вермикулита $c = 15,00 \text{ \AA}$. В случае Na-вермикулита межслойные катионы находятся в октаэдрической координации к молекулам воды, с полиэдрами натрий-вода, расположенными только между триадами атомов кислорода, образующими основы тетраэдров в соседних силикатовых слоях. В Ca-вермикулите межслойные катионы находятся в обоих, октаэдрических и 8-кратных (искаженные кубы) координациях к молекулам воды. Октаэдрически координированные ионы Ca расположены между основами тетраэдров в соседних силикатовых слоях, а 8-кратно-координированные ионы Ca расположены между дитригональными пустотами. В обоих, Na- и Ca-вермикулитах, некоторые молекулы воды вытеснены из плоских сетей в основном по направлению дитригональных пустот. Пространственный порядок, наблюдаемый для этих вермикулитов, не согласовывается с беспорядочным расположением слоев, описанным для Mg-вермикулита из Ллано. Отличающееся кристаллографическое поведение ионов Na^+ , Ca^{2+} , и Mg^{2+} в гидратированных слоях вермикулита из Ллано, зависит, вероятно, от размеров катионов и мощности поля вместе с потребностью достигнуть равновесие местного заряда близко мест тетраэдрического замещения атомов Si атомами Al. [E.G.]

Resümee—Die 3-dimensionale Ordnung, die 2-Schichthydrate von Na- und Ca-Vermiculit aufweisen, die aus dem Mg-Vermiculit von Llano, Texas, hergestellt wurden, haben eindeutige 2-dimensionale Fourierprojektionen ihrer Zwischenschichtstrukturen ermöglicht. Berechnungen der Struktur Faktoren wurden in der Raumgruppe C2 durchgeführt mit folgenden Ausmaßen der Elementarzelle: $a = 5,358 \text{ \AA}$, $b = 9,232 \text{ \AA}$, $\beta = 96,82^\circ$; für Na-Vermiculit betrug $c = 14,96 \text{ \AA}$, für Ca-Vermiculit war $c = 15,00 \text{ \AA}$. Im Na-Vermiculit waren die Zwischenschichtkationen gegenüber den Wassermolekülen oktaedrisch koordiniert, wobei die Natrium-Wasser-Polyeder nur zwischen den Dreiecken der Sauerstoffatome liegen, die die Basis der Tetraeder in der angrenzenden Silikatschicht bilden. Im Ca-Vermiculit sind die Zwischenschichtkationen sowohl in oktaedrischer als auch in 8-Koordination (verzerrter Würfel) gegenüber Wassermolekülen. Die oktaedrisch koordinierten Ca-Ionen sitzen zwischen den Basen der Tetraeder der benachbarten Silikatschichten, die 8-koordinierten Ca-Ionen sind jedoch zwischen den ditrigonalen Hohlräumen. Sowohl im Na- als auch im Ca-Vermiculit sind einige Wassermoleküle aus dem planaren Netzwerk bevorzugt in Richtung auf die ditrigonalen Hohlräume verlagert. Die dreidimensionale Ordnung, die bei diesen Vermiculiten beobachtet wurde, steht im Gegensatz mit der Stapelungsunordnung, die für den Mg-Vermiculit von Llano angegeben wird. Das jeweilige kristallographische Verhalten von Na^+ , Ca^{2+} , und Mg^{2+} in den Hydratschichten des Llano-Vermiculites hängt wahrscheinlich von der Kationengröße und den Feldstärken ab zusammen mit der Notwendigkeit einen lokalen Ladungsausgleich in der Nähe der tetraedrischen Al-für-Si-Substitution zu erreichen. [U.W.]

Résumé—L'ordre à trois dimensions démontré par des hydrates de vermiculite-Na et -Ca à 2 couches, préparé à partir de la vermiculite-Mg de Llano, Texas, a permis d'obtenir des projections Fourier claires et à 2 dimensions de leurs structures intercouche. Des calculs de facteurs de structure ont été faits dans le groupe d'espace C2 et avec des dimensions de maille de $a = 5,358 \text{ \AA}$, $b = 9,232 \text{ \AA}$, et $\beta = 96,82^\circ$; pour la vermiculite-Na, $c = 14,96 \text{ \AA}$ et pour la vermiculite-Ca, $c = 15,00 \text{ \AA}$. Dans la vermiculite-Na, les cations intercouche sont coordonnés octaédralement aux molécules d'eau avec les polyèdres sodium-eau placés seulement entre les triades d'atomes oxygène formant les bases de tétraèdres dans des couches silicates adjacentes. Dans la vermiculite-Ca les cations intercouche sont à la fois en coordination octaédrale et à 8 plis (cubique déformée) avec les molécules d'eau. Les ions Ca coordonnés octaédralement sont entre les bases des tétraèdres dans les couches silicates adjacentes, mais les ions Ca coordonnés à 8 plis sont entre les cavités ditrigonales. A la fois dans la vermiculite-Na et -Ca quelques molécules d'eau sont attirées de façon appréciable de réseaux plans vers les cavités ditrigonales. L'ordre à trois dimensions observé pour ces vermiculites contraste avec le désordre d'empilement rapporté pour la vermiculite-Mg de Llano. Le comportement cristallographique distinct de Na^+ , Ca^{2+} , et Mg^{2+} dans les couches d'hydratation de vermiculite de Llano dépend probablement des tailles des cations et des forces de champs, en même temps que du besoin d'atteindre l'équilibre de charge locale près des sites de substitution tétraédrale d'Al pour Si. [D.J.]