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CRYSTAL STRUCTURE OF A TWO-LAYER Mg-VERMICULITE

HARUO SHIROZU[1] AND S. W. BAILEY, *Department of Geology, University of Wisconsin, Madison, Wisconsin.*

ABSTRACT

The Llano, Texas, Mg-vermiculite, which is a normal 14.3 Å phase, belongs to space group $C2/c$ with $a=5.349$, $b=9.255$, $c=28.89$ Å, and $\beta=97° 07'$. The structure has been refined by three-dimensional least squares analysis, using 822 observed reflections, to an R value of 9.1%.

The two-layer structure is different than that found for vermiculite from Kenya by Mathieson and Walker (1954) and corresponds to their hypothetical stacking sequence *s*. There is an L type shift within each talc sheet of $-a/3$ parallel to the symmetry plane. Alternate layers are displaced relative to one another by $+b/3$ and $-b/3$ parallel to the Y axis. There are occasional mistakes in these regular $b/3$ displacements.

Tetrahedral ordering of Si, Al is indicated by significant differences in the mean T—O bond lengths and in the tetrahedral cation temperature factors. The talc network is distorted by 5.7° planar rotations of the tetrahedra towards the nearest interlayer water molecules.

The exchangeable cations, which lie midway between the talc sheets, are located in only one out of the three available octahedral interlayer sites. This site is positioned vertically between the ordered Al tetrahedra of the talc sheets above and below. This pattern of local charge balance should be the most stable configuration possible, so that in the ideal case the positions of the exchangeable cations will tend to be controlled directly by the sites of Al for Si substitution. The water molecules, which form hydration shells about the exchangeable cations, are distributed randomly over the three sets of anion positions in the interlayer octahedral sheet.

Llano vermiculite has formed by surface weathering of a parent 1M phlogopite, for which the accepted space group of $C2/m$ does not permit tetrahedral ordering. Either this space group is in error or surface weathering is more effective in producing cation order than heretofore realized.

INTRODUCTION

The structure of vermiculite was first studied by Gruner (1934), who chose a monoclinic unit cell with $a=5.3$, $b=9.2$, $c=28.57$–28.77 Å, $\beta=97° 09'$, and space group Cc or $C2/c$. Gruner showed from consideration of powder pattern intensities that the structure must consist of talc sheets, between which lie double planes of water molecules occupying a space nearly equal to that of the brucite sheet in the chlorite structure. Hendricks and Jefferson (1938*a*) confirmed Gruner's general conclusions by single crystal study, and suggested that vermiculites have partially random displacements of structural layers parallel to the Y axis. Henricks and Jefferson (1938*b*) further postulated a hypothetical arrangement of the interlayer water molecules in planar hexagonal rings with

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[1] Present address: Department of Geology, Kyushu University, Fukuoka, Japan.

the oxygen of each water being tetrahedrally bonded to four neighboring oxygens through hydrogen atoms. Alternate water molecules in each of the two interlayer planes bond to the adjacent talc surfaces. No provisions for exchangeable cation sites were made in any of these earliest studies.

Later studies by Mathieson and Walker (1954), Grudemo (1954), and Mathieson (1958) have demonstrated that the water molecules and exchangeable cations occupy definite sites in the interlayer space. Mathieson and Walker (1954) and Mathieson (1958), who studied a "14.36 Å phase" Mg-vermiculite from Kenya, showed that the talc tetrahedral networks are distorted from regular hexagons by planar rotations of the tetrahedra. The exchangeable Mg^{2+} cations lie in a plane midway between adjacent talc sheets and have a plane of water molecules on each side. Thus, the interlayer material takes the form of an incomplete octahedral sheet, similar to the brucite sheet in chlorite but with only 1/9 of the cation sites and 2/3 of the anion sites filled in the specimen studied. The available diffraction data do not specify which of these fixed sites are actually occupied in adjacent unit cells. Mathieson and Walker favor a dynamic system allowing cation and anion migration between the available positions. They further suggest a tendency to maintain a regular, hexagonal distribution of the occupied cation sites as a result of mutual repulsion, with the water clustering around the occupied sites as octahedral hydration shells. Every water molecule is linked by a hydrogen bond to an oxygen in the nearest talc surface, but no attraction was believed to exist between the exchangeable cations and the talc surfaces. This postulated interlamellar structure is quite different from that of Hendricks and Jefferson.

Bradley and Serratosa (1960) have suggested another modification of the interlamellar region. This model retains the tetrahedrally bonded planar water nets of Hendricks and Jefferson but disposes them differently to form an incomplete octahedral sheet in which only certain water molecules furnish hydrogen bonds to the talc surfaces. The pattern of occupancy postulated would create a base centered superstructure extending laterally over three cells for the lower observed levels of exchangeable cations and a regular array over one cell for the highest level of exchange. The orderly arrays are not believed to extend throughout the entire crystal.

Mathieson and Walker deduced that two stacking sequences, designated *q* and *r*, occur with equal probability in the Kenya vermiculite. Two other possible stacking sequences, designated *p* and *s*, were considered but were found to be excluded by the diffraction data for their specimen. In the present study vermiculites from Llano, Texas, and New

Canaan, Connecticut, have been found to have the *s* type of layer sequence. Although reflections with $k \neq 3n$ are diffuse in all vermiculites, the reflections for the Llano vermiculite are sufficiently good to permit a three-dimensional structure determination. The results of refinement show the structure within the layers of the Kenya and Llano vermiculites to be quite similar despite their different stacking arrangements. The additional detail furnished by the three-dimensional data demonstrate tetrahedral cation ordering for the Llano vermiculite with definite control of the location of the exchangeable cation by the sites of Al substitution within the adjacent tetrahedral sheets.

EXPERIMENTAL

The vermiculite used in this study comes from the Texas Mines magnesite quarry near Llano, Texas, and was obtained through the courtesy of Dr. M. L. Jackson. Haase *et al.* (1963) have studied the orientation of organic molecules in the interlayer region of Llano vermiculite, but do not give details of the silicate portion of the structure. The vermiculite forms by the surface weathering of phologopite contained in a dolomite and magnesite marble (Clabaugh and Barnes, 1959). It is unusual in that it is essentially iron-free. It is white in color with a pearly luster. Foster (1963) lists the composition of the talc portion of the Llano vermiculite as

$$\overset{+0.14}{[\mathrm{Mg}_{2.83}\mathrm{Fe}^{3+}{}_{0.01}\mathrm{Al}_{0.15})_{2.99}}\overset{-1.14}{(\mathrm{Si}_{2.86}\mathrm{Al}_{1.14})}\overset{-1.00}{\mathrm{O}_{10}(\mathrm{OH})_2]}$$

She lists the interlayer cation content as $(\mathrm{Mg}_{0.48}{}^{2+}\mathrm{K}_{0.01})$ and the cation exchange capacity as 195–200 meq/100 g. Bradley and Serratosa (1960) cite the interlayer water content for the same sample as 4.72 H_2O.

A small section $0.2 \times 0.3 \times 0.1$ mm, cut from a larger cleavage flake and carefully pressed flat, was used to obtain the experimental data. All data refer to the flake in its natural state without further hydration or cation exchange. Accurate cell dimensions obtained by the θ method of Weisz, Cochran, and Cole (1948) are $a = 5.349 \pm 6$, $b = 9.255 \pm 10$, $c = 28.89 \pm 2$ Å, $\beta = 97° \, 07' \pm 06'$, $d(001) = 28.67$ Å, and $V = 1419.2$ Å^3. The b repeat distance of 9.255 Å is longer than that of 9.18 Å given by both Hendricks and Jefferson (1938*a*) and by Mathieson and Walker (1954), but agrees with the recent data of 9.222 to 9.262 Å given by Radoslovich (1962) for vermiculite. The measured and calculated densities are $D_m = 2.19$ and $D_x = 2.22$ g/cm^3 respectively. A different section was cut from the same large cleavage flake for optical study. Refractive indices measured on a universal stage using double variation are $\alpha = 1.520 \pm 1$ and $\beta \cong \gamma = 1.5304 \pm 5$. The optic angle 2V is small but not exactly 0°, varying vetween 5° and 15° across the large cleavage flake.

Intensity data for 822 observed reflections were collected by means of multiple film pack Weissenberg photographs of the *h*0*l* through *h*6*l* and 0*kl* through 2*kl* reciprocal levels, taken with CuKα radiation. The intensities were estimated visually by comparison with a standard multiple scale and corrected for the Lorentz and polarization factors. An absorption correction, which was small, was made by a graphical means based on the transmission factors calculated by Joel, Vera, and Garaycochea's (1953) method. The reflections occur only for $h+k=2n$. There is also a systematic relation between the *k*, *l* indices and the nature of the reflection as follows:

$k=0, 3n$	$l=2n$	sharp (spot)
$k=0, 3n$	$l=2n+1$	absent
$k\neq 3n$	$l=2n$	very diffuse (streaking parallel to Z*)
$k\neq 3n$	$l=2n+1$	slightly diffuse (lenticular shape elongated parallel to Z*)

Two space groups, *C*2/*c* and *Cc*, are consistent with the observed data. The N(*z*) statistical test for a center of symmetry (Howells *et al.*, 1950)

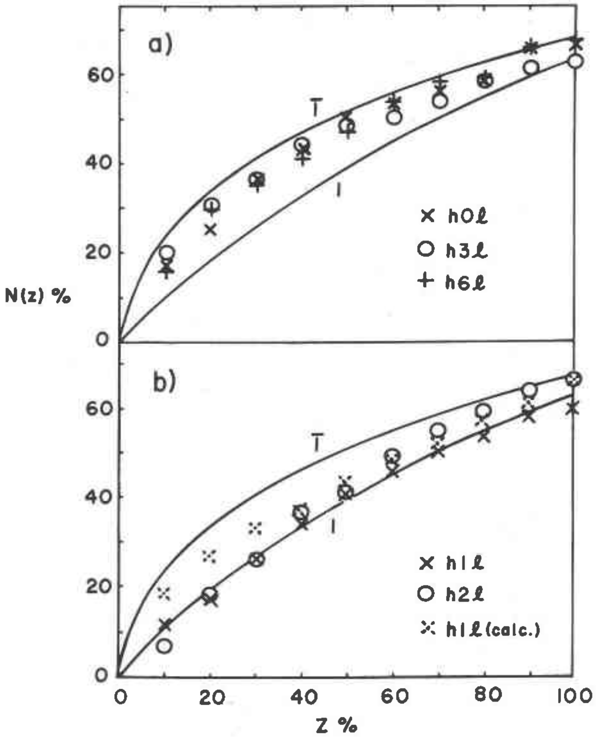

FIG. 1. N(*z*) test for center of symmetry. Numbers of reflections used are (in parentheses): *h*0*l* (98), *h*3*l* (90), *h*6*l* (67), *h*1*l* (119), *h*2*l* (137), *h*1*l* calc. (187).

was applied in an attempt to determine the exact space group. The distribution of observed intensities for the $k=3n$ reflections falls between the theoretical distributions for centrosymmetric and non-centrosymmetric structures (Fig. 1*a*), but that for the $k\neq 3n$ reflections falls closer to that for a non-centrosymmetric structure (Fig. 1*b*). These results might lead one to infer the symmetry to be non-centrosymmetric, because a hypersymmetry effect due to the many atoms that repeat at $b/3$ intervals must be taken into account for the $k=3n$ reflections.

It was believed that there might be some uncertainty in the N(z) test because $k\neq 3n$ reflections with $l=2n$ could not be measured at high θ values due to their diffuseness and weakness. To test the effect of their omission an N(z) test was made for all calculated $h1l$ intensities within the diffraction sphere for copper radiation, using a centrosymmetric vermiculite model as the basis of calculation. Surprisingly, these points also lie between the centrosymmetric and non-centrosymmetric curves (Fig. 1*b*). The P(y) test of Ramachandran and Srinivasan (1959) applied to the observed intensities likewise gave inconclusive results. The fact that the distribution of observed intensities in the N(z) test is quite close to that of the intensities calculated from a centrosymmetric model, however, suggests that the symmetry is centrosymmetric. The anomalies in the tests may be due to the imbalance of the electron densities between the two octahedral sheets. The symmetry was inferred to be centrosymmetric for purposes of the structure determination, and space group *C*2/*c* was chosen. The subsequent refinement of the structure showed that this space group is correct within experimental error.

STRUCTURE DETERMINATION AND REFINEMENT

As described in the previous section, there are systematic differences in the sharpness or diffuseness of reflections having different hkl values. Reflections with $k=3n$ and l even are sharp; those with l odd are missing. Reflections with $k\neq 3n$ and l even are drawn out into streaks parallel to the Z* axis; those with l odd are also drawn out, but the streaks are much shorter than those with l even. This situation is quite analogous to that in hexagonal cobalt (Wilson, 1949), so that the broadening of the reflections with $k\neq 3n$ is considered to be due to stacking disorder, with mistakes of $b/3$ displacement occurring parallel to the Y axis.

Considerable error may be introduced into measurement of the diffuse reflections by a visual estimate of spot density, and a correction for degree of diffuseness is desirable to place all intensities on the same scale. A direct correction is difficult in practice, so we have made a correction based on comparison with values calculated from the substructure after refinement using $k=3n$ reflections alone. Thus, the structure was refined in two stages. First the substructure was refined as far as possible using 285 $k=3n$ reflections. Then, after a diffuseness correction, all 822 reflections were used in a detailed refinement of the entire structure.

The structure analysis was carried out using the Larson-Cromer full matrix least squares and Fourier summation programs (Los Alamos Scientific Laboratory) as modified by J. J. Finney and R. A. Eggleton for use on the Wisconsin CDC 1604 computer. All the reflections were weighted arbitrarily in the least squares refinement by assigning smaller weights to the reflections with very small or very large F values, and very small weights to some potentially unreliable $k\neq 3n$ reflections. The intensity estimations for these latter reflections were difficult because they occur adjacent to strong diffuse reflections. Unobserved reflections were weighted zero.

The general agreement of the intensities of the $k=3n$ reflections of the Llano vermiculite with those of Hendricks and Jefferson (1938a) and of Mathieson and Walker (1954), allowing for different indices by Hendricks and Jefferson due to a different selection of unit cell, proves that the [010] projections of these vermiculites are very similar. Therefore the atomic arrangement within one vermiculite layer must be very similar for the three specimens involved. Least squares refinement of one vermiculite layer, which has symmetry $C2/m$, was initiated from the ideal hexagonal x and y coordinates and from the z coordinates and isotropic temperature factors obtained by Mathieson (1958). The refinement procedure was similar to that used by Shirozu and Bailey (1965) for an orthohexagonal I*b* chlorite having semirandom layer stacking. The atoms repeating at intervals of $b/3$ were grouped together and their y parameters were fixed at the ideal coordinates. The other positional and isotropic thermal parameters were allowed to vary, as were the numbers of the exchangeable cations and interlayer waters. Repeated cycles of refinement were run until the reliability factor was reduced to $R=10.5\%$.

The results of the initial refinement show that the interlayer positions are occupied a little less than originally assumed, namely $Mg^{2+}{}_{0.43}(H_2O)_{3.9}$ instead of $Mg^{2+}{}_{0.5}(H_2O)_{5.0}$. Distortion of the talc tetrahedral network is also shown. The positional and temperature parameters obtained are listed in Table 1. The positional parameters are transformed so as to correspond to those of the final two-layer structure. In order to use the standard orientation of space group $C2/c$ the origin must be placed at Mg_{IV}, which is on a center of symmetry in the interlayer region. These substructure coordinates were used to calculate structure amplitudes for the diffuseness correction and to initiate further refinement.

The diffuseness correction for the $k\neq 3n$ reflections was made in the following way. F_o/F_c values of reflections belonging to the same reciprocal rod parallel to Z* and having the same parity of l (even or odd) were plotted with respect to l. A best fit curve was drawn through the points to give the correction coefficient to be applied to F_o for a given l value. Little or no correction is needed for $l > 20$, but the F_o/F_c ratio changes progressively along each reciprocal rod by 20 to 50 per cent as l decreases. The correction thus serves to place the diffuse $k \neq 3n$ reflections on about the same scale as the sharp $k = 3n$ reflections.

Mathieson and Walker (1954) showed that there are four possible two-layer structures, namely *p*, *q*, *r*, and *s*, that contain the type of vermiculite layer observed and that belong to space groups $C2/c$ or Cc. Comparison of calculated and observed structure amplitudes for the $k \neq 3n$ reflections eliminated all of these but the *s* structure for the Llano vermiculite. In addition, careful examination of the structure amplitudes of the reflections with $k \neq 3n$ and l even indicated that the exchangeable cations are present in only one of the three possible interlayer octahedral positions. They occupy slightly less than half of site M_{IV}, which is a center of symmetry at the origin of the unit cell.

TABLE 1. LAYER PARAMETERS DETERMINED IN FIRST STAGE OF REFINEMENT

Atom	x	y	z	B
$Mg_{IV,(V)}$	.0	$0, (\frac{1}{3})$	.0	2.69
$(H_2O)_{I,II,III}$	.3581	$0, \frac{1}{3}, \frac{2}{3}$	.0407	6.12
$O_{III,IV}$	.3561	.0715, .5952	.1341	1.84
O_V	.5600	$\frac{1}{3}$	.1340	1.93
$T_{I,II}$	.1032	$0, \frac{2}{3}$	.1546	1.01
$O_{I,II}(OH)_I$	.1417	$0, \frac{2}{3}, \frac{1}{3}$	.2126	1.15
$Mg_{I,II,III}$	.0	$\frac{1}{6}, \frac{1}{2}, \frac{5}{6}$	.25	0.87

At the start of the second stage of refinement all of the parameters of the talc sheet were fixed and the configuration of the interlayer was examined by allowing the interlayer populations to vary as well as the positional and thermal parameters. The results show:

1) a slight further decrease of the interlayer population to $Mg_{0.41}(H_2O)_{3.72}$, 2) even distribution of the water molecules over the three non-equivalent sets of anion positions, 3) displacements of the water molecule sites to form a ditrigonal rather than hexagonal distribution, 4) decrease of the thermal parameters of the water molecules, and 5) concentration of the exchangeable cations in the unique site M_{IV} with the other two sites being vacant.

As a next step in the refinement all the populations were fixed and all the positional and isotropic thermal parameters in the entire structure were allowed to vary. In this step ordering of the tetrahedral cations was demonstrated. Finally, because of anistropy seen in ρ_o and ρ_o-ρ_c [010]

electron density maps, three least squares cycles were run to determine anisotropic thermal parameters for the interlayer water molecules. The final reliability factors were R = 9.8% for the $k=3n$ reflections, R = 7.9% for those with $k\neq 3n$, and R = 9.1% overall. Table 2 contains the final atomic coordinates and temperature factors with their standard deviations. Table 3 contains bond lengths and angles computed from these coordinates.[1]

TABLE 2. FINAL POSITIONAL AND TEMPERATURE PARAMETERS WITH STANDARD DEVIATIONS

		x	σ(x)	y	σ(y)	z	σ(z)	B	σ(B)
4 Mg$_{\text{I}}$		.0	.0	.1638	.0011	.25	.0	.96	.16
4 Mg$_{\text{II}}$		.0	.0	.4997	.0010	.25	.0	.82	.27
4 Mg$_{\text{III}}$		.0	.0	.8332	.0011	.25	.0	.86	.15
8 T$_{\text{I}}$		.1042	.0007	−.0003	.0007	.1545	.0002	1.23	.09
8 T$_{\text{II}}$		.1026	.0007	.6647	.0015	.1547	.0001	.83	.07
8 O$_{\text{I}}$		.1424	.0028	.0039	.0014	.2132	.0004	.83	.35
8 O$_{\text{II}}$		.1410	.0018	.6683	.0018	.2113	.0003	1.05	.21
8 (OH)$_{\text{I}}$		.1420	.0019	.3380	.0024	.2129	.0004	1.21	.23
8 O$_{\text{III}}$		.3579	.0023	.0697	.0016	.1338	.0004	2.09	.26
8 O$_{\text{IV}}$		.3529	.0018	.5964	.0016	.1346	.0004	2.01	.26
8 O$_{\text{V}}$		.5593	.0014	.3316	.0021	.1339	.0003	1.94	.14
4 Mg$_{\text{IV}}$	(Mg$_{0.41}$)	.0	.0	.0	.0	.0	.0	2.30	.29
8 $(H_2O)_{\text{I}}$	$(0.62H_2O)$	.3363	.0050	−.0264	.0032	.0397	.0006	(4.25)*	(.67)*
8 $(H_2O)_{\text{II}}$	$(0.62H_2O)$	.3515	.0045	.3274	.0045	.0412	.0005	(5.15)*	(.56)*
8 $(H_2O)_{\text{III}}$	$(0.62H_2O)$	.3832	.0040	.6520	.0040	.0414	.0005	(4.53)*	(.53)*

	B_{11} $(\sigma(B_{11}))$	B_{22} $(\sigma(B_{22}))$	B_{33} $(\sigma(B_{33}))$	B_{12} $(\sigma(B_{12}))$	B_{13} $(\sigma(B_{13}))$	B_{23} $(\sigma(B_{23}))$
$(H_2O)_{\text{I}}$	.0601	.0242	.0006	−.0024	.0036	−.0036
	(.0183)	(.0092)	(.0005)	(.0246)	(.0045)	(.0027)
$(H_2O)_{\text{II}}$	.0768	.0226	.0007	−.0187	.0011	−.0037
	(.0142)	(.0073)	(.0003)	(.0205)	(.0035)	(.0022)
$(H_2O)_{\text{III}}$	.0686	.0276	.0006	−.0181	.0067	−.0034
	(.0125)	(.0106)	(.0003)	(.0226)	(.0033)	(.0027)

* Derived from isotropic refinement.

Because there was some question as to the correct space group for vermiculite, refinement was also attempted in space group *Cc*. The coordinates of the oxygens in Table 2 were offset to make the structure acentric, and repeated least squares refinement cycles were run using all reflections. Although the refinement converged to an acentric answer, the re-

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[1] A table listing the final F_o and F_c values has been deposited as Document No. 8930 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing the document number, and remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm. Advance payment is required.

TABLE 3. INTERATOMIC DISTANCES WITH STANDARD DEVIATIONS IN Å AND BOND ANGLES IN DEGREES

Bond length		σ	Bond length around T_I		σ
T_I-O_I*	1.682	.014	O_I*-O_{III}	2.759	.018
-O_{III}	1.680	.014	O_I*-O_{IV}	2.723	.018
-O_{IV}	1.657	.013	O_I*-O_V	2.781	.018
--O_V	1.672	.013	O_{III}-O_{IV}	2.715	.018
			O_{III}-O_V	2.722	.018
Mean	1.673		O_{IV}-O_V	2.689	.017
			Mean	2.732	
			around T_{II}		
T_{II}-O_{II}*	1.624	.013	O_{II}*-O_{III}	2.702	.017
-O_{III}	1.629	.015	O_{II}*-O_{IV}	2.695	.017
-O_{IV}	1.650	.014	O_{II}*-O_V	2.689	.017
-O_V	1.663	.014	O_{III}-O_{IV}	2.657	.018
			O_{III}-O_V	2.653	.018
Mean	1.641		O_{IV}-O_V	2.683	.017
			Mean	2.680	
			around Mg_I		
Mg-O_I	2.026×2	.014	O_I-O_{II}	3.078, 3.077, $2.792\times2^{\xi}$	.018
-O_{II}	2.099×2	.012	O_I-(OH)	3.092×2	.020
(OH)	2.128×2	.015	O_{II}-(OH)	3.102, 3.102, $2.825\times2^{\xi}$	.019
			O_I-O_I	2.766^{ξ}	.019
Mean	2.084		(OH)-(OH)	2.778^{ξ}	.021
			around Mg_{II}		σ
Mg_{II}-O_I	2.071×2	.014	O_I-O_{II}	3.078, 3.077, $2.792\times2^{\xi}$	.018
-O_{II}	2.113×2	.012	O_I(OH)	3.085, 3.083, $2.764\times2^{\xi}$	.020
-(OH)	2.042×2	.015	O_{II}-(OH)	3.058×2	.019
			O_{II}-O_{II}	2.848^{ξ}	.017
Mean	2.075		(OH)-(OH)	2.778^{ξ}	.021
			around Mg_{III}		
Mg_{III}-O_I	2.100×2	.014	O_I-O_{II}	3.106×2	.018
-O_{II}	2.087×2	.012	O_I-(OH)	3.085, 3.083, $2.764\times2^{\xi}$	.020
-(OH)	2.076×2	.015	O_{II}-(OH)	3.102, 3.102, $2.825\times2^{\xi}$	.019
			O_I-O_I	2.766^{ξ}	.019
Mean	2.088		O_{II}-O_{II}	2.848^{ξ}	.017
			around M_{IV}		
Mg_{IV}-$(H_2O)_I$	2.024×2	.025	$(H_2O)_I$-$(H_2O)_{II}$	2.930×2, $3.046\times2^{\xi}$	.036
-$(H_2O)_{II}$	2.199×2	.027	$(H_2O)_I$-$(H_2O)_{III}$	2.938×2, $2.745\times2^{\xi}$	.035
-$(H_2O)_{III}$	1.997×2	.024	$(H_2O)_{II}$-$(H_2O)_{III}$	3.009×2, $2.931\times2^{\xi}$	.036
Mean	2.073				
			around vacant octahedral sites		
			$(H_2O)_I$-$(H_2O)_{II}$	3.275, 3.066, 3.046^{ξ}	.036
O_{III}-$(H_2O)_I$	2.850	.028	$(H_2O)_I$-$(H_2O)_{III}$	3.354, 2.987 2.745^{ξ}	.035
O_{IV}-$(H_2O)_{III}$	2.764	.027	$(H_2O)_{II}$-$(H_2O)_{III}$	3.274, 2.986, 2.931^{ξ}	.036
O_V-$(H_2O)_{II}$	2.769	.029	$(H_2O)_I$-$(H_2O)_I$	3.091^{ξ}	.035
			$(H_2O)_{II}$-$(H_2O)_{II}$	2.875^{ξ}	.038
Mean	2.794		$H_2O)_{III}$-$(H_2O)_{III}$	3.194^{ξ}	.034

	Angle		Angle		Angle
O_I*-T_I-O_{III}	110.28	O_{II}*-T_{II}-O_{III}	112.29	T_I-O_{III}-T_{II}	136.42
O_I*-T_I-O_{IV}	109.28	O_{II}*-T_{II}-O_{IV}	110.84	T_I-O_{IV}-T_{II}	137.98
O_I*-T_I-O_V	111.99	O_{II}*-T_{II}-O_V	109.79	T_I-O_V-T_{II}	136.76
O_{III}-T_I-O_{IV}	108.92	O_{III}-T_{II}-O_{IV}	108.25		
O_{III}-T_I-O_V	108.56	O_{III}-T_{II}-O_V	107.35	Mean	137.05
O_{IV}-T_I-O_V	107.74	O_{IV}-T_{II}-O_V	108.18		
Mean	109.46	Mean	109.45		

* = apical oxygen,

ξ = edge shared by two octahedra.

sulting structure was not reasonable. Variation in T–O bond lengths up to 0.26 Å were found within the same tetrahedron. Because a similar refinement using F_{calc} instead of F_{obs} values converged back to the centrosymmetric structure, it is concluded that the experimental F_{obs} data are not adequate to distinguish between *C*2/*c* and *Cc* due to the diffuseness of $k \neq 3n$ reflections.

STRUCTURAL DETAILS

The vermiculites that have been studied to date all have the same type of structural layer, in which the interlayer octahedral sheet is placed on the talc sheet in the same way as in the particular type of chlorite layer that has been designated I*a* by Bailey and Brown (1962). The I*a* layer type is characterized by vertical superposition of 1) the talc tetrahedral cations and the interlayer cations and 2) the talc octahedral cations and the interlayer anions. When the I*a* vermiculite layer forms a two-layer structure by means of a *c* glide operation there are four possible ways of stacking the layers, designated *p*, *q*, *r*, and *s* by Mathieson and Walker (1954).

The Llano vermiculite described here has the stacking sequence *s*. In the terminology of Bailey and Brown for chlorites the *s* structure is an alternation of I*a*-4 and I*a*-6 layers with an L type shift within each talc sheet of $-a/3$ parallel to the symmetry plane. This sequence incorporates shifts of alternate layers relative to one another by $+b/3$ and $-b/3$ along the Y axis. The layer displacements are primarily regular. Because of the nature of the broadening of the reflections with $k \neq 3n$, however, the alternations of plus and minus in the $b/3$ displacements are believed to include some random mistakes. The stacking sequences *q* and *r*, related to one another by a shift of $b/3$, were found to occur with equal probability in the Kenya vermiculite. These two structures also involve I*a*-4 and I*a*-6 layers, but with alternating M and N shifts within the talc sheets at ±60° to the symmetry plane.

The results of refinement of the Llano vermiculite indicate that the talc tetrahedral network is distorted by rotations of the tetrahedra in the (001) plane by an average angle of 5.7°, as shown in Figure 2. This angle is just slightly larger than that found by Mathieson and Walker (1954) and by Mathieson (1958) for the Kenya vermiculite. A predicted angle of tetrahedral rotation calculated from the observed *b* parameter and the tetrahedral basal oxygen—oxygen distances (Brown and Bailey, 1963) is 6.0°, which agrees closely with the observed value of 5.7°. The direction of rotation is such that each basal oxygen moves towards the position of the nearest water molecule in the adjacent interlayer space, exactly analogous to the situation in chlorite.

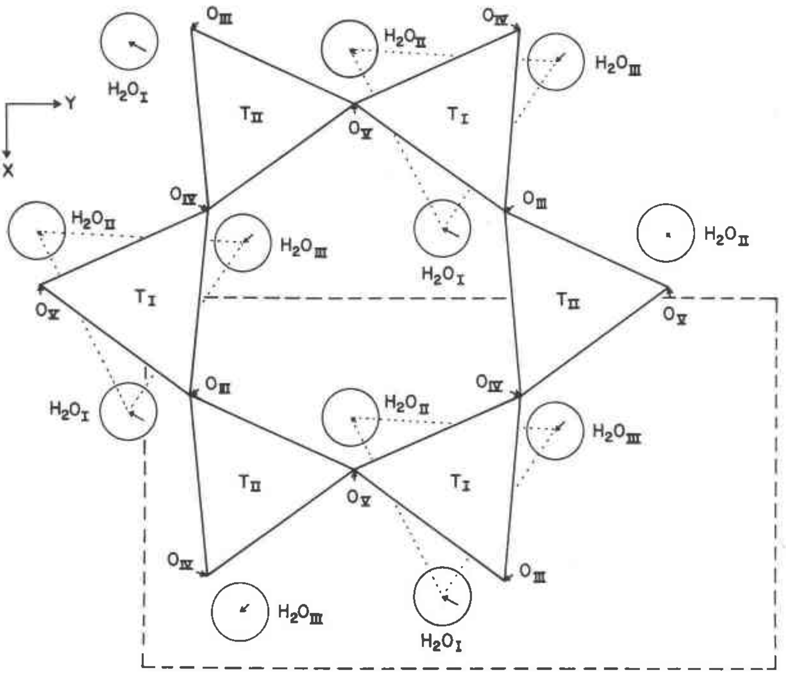

FIG. 2. Tetrahedral ring in Llano vermiculite after 5.7° rotation of tetrahedra. Adjacent talc oxygens and interlayer water molecules have shifted in the (001) plane by amounts indicated by arrows. Interlayer cations are below the T_I sites. Water molecule triads (dotted) are rotated about the exchangeable cations by an average angle of 3.3°.

Tetrahedral cation ordering is indicated by the difference in the average bond lengths of the T_I and T_{II} tetrahedra (Table 3) and also in the thermal parameters of the T_I and T_{II} cations (Table 2). The average standard deviations of the individual atoms were used to derive the standard deviation of the error of an individual T—O bond length (0.013 to 0.015 Å range) and the standard error of the mean of the four distances within each tetrahedron (0.006_7 and 0.007_0 Å). The observed difference of 0.032 Å between the mean T—O bonds is 3.3 times the standard deviation unit, and is therefore highly significant statistically. An average tetrahedral scattering factor was used for each tetrahedron during the course of refinement so that no assumption would be made as to Si,Al ordering. The resultant significantly larger B value for T_I than for T_{II} (1.23 compared to 0.83) indicates a concentration of Al in site T_I, in agreement with the larger T—O bond lengths around that site. Brown and Bailey (1965) have shown a similar, but larger, difference in the temperature factors of the ordered tetrahedral cations in maximum microcline. This difference disappears when the correct scattering factors are used for each cation.

The mean T—O distance is known to vary nearly linearly with the tetrahedral Si,Al composition. Application of the standard values of Si—O = 1.62 Å and Al—O = 1.77 Å suggested for layer silicates by Smith and Bailey (1963) indicates that

$$T_I\text{—}O = 1.673 \text{ Å is equivalent to } Si_{0.65}Al_{0.35}$$

and

$$T_{II}\text{—}O = 1.641 \text{ Å is equivalent to } Si_{0.86}Al_{0.14}.$$

The average of 1.657 Å over all tetrahedral sites gives $Si_{3.0}Al_{1.0}$ for one formula unit. This total contains slightly less Al than the $Si_{2.86}Al_{1.14}$ value resulting from chemical analysis of a different specimen from the same locality (Foster, 1963). This difference between the analyzed composition and that deduced from the mean T—O bond length is not as great as in the case of the Kenya vermiculite, discussed by Smith and Bailey (1963), and is of no statistical significance according to the errors of the present investigation.

INTERLAYER REGION

Local charge balance. By allowing the population of the interlayer region to vary during least squares refinement, is was determined that 0.41 atoms of Mg^{2+} occupy statistically one of the three available octahedral sites. A less accurate one-dimensional electron density summation indicated 0.36 Mg^{2+} atoms. These totals are less than the 0.49 interlayer atoms allocated from the chemical analysis, but are believed to be correct for our specimen. A cation exchange capacity of 156 meq/100 g. was determined for our sample by Raman (1965). This corresponds to an interlayer population of $Mg^{2+}{}_{0.38}$, very close to our *x*-ray results.

The exchangeable cation is in the M_{IV} site on a symmetry center at the origin and is located vertically between equivalent T_I sites in the talc tetrahedral sheets above and below. In this way the positive charge of the exchangeable Mg^{2+} is linked directly to and is balanced by the excess negative charge on the T_I tetrahedra due to the ordered substitution of Al for Si. It should be noted that local charge balance of this type would not be realized if either the tetrahedral Al or the interlayer Mg^{2+} were to occupy the alternative sites, T_{II} and Mg_V respectively.

The maximum Si,Al order permitted in space group *C*2/*c* amounts to $Si_{0.5}Al_{0.5}$ and $Si_{1.0}Al_{0.0}$ in the two tetrahedra. Reduced symmetry would permit complete order within a single unit cell. There is no diffraction evidence for a primitive cell, however, and attempted refinement in space group *Cc* was unconclusive for our specimen. If the true space group is *C*2/*c* the observed pattern of local charge balance must be a statistical average for the T_I and M_{IV} sites over all unit cells. The symmetry of the individual cells *must* be lower than $C2/c$ to avoid fractional tetrahedral atom types.

Although tetrahedral substitution may exceed 1.0 Al per 4.0 tetrahedral sites, the maximum net layer charge that can be satisfied by the local charge balance mechanism is limited by the structure to one electrostatic charge per formula unit, equivalent to $Mg^{2+}_{0.50}$ exchangeable cations. Most vermiculites have a net charge smaller than this, judging by observed cation exchange capacities. This smaller charge is achieved in many vermiculites by oxidation of octahedral ferrous iron and in the case of the iron-free Llano vermiculite probably by hydroxylation of O to OH, as discussed in the next section.

Mathieson and Walker (1954) deduced from consideration of the distorted octahedra of water molecules that the Mg^{2+} would probably occupy only one of the three available interlayer cation sites in the Kenya vermiculite also, but did not believe that there would be any direct electrostatic interaction between the exchangeable cations and the talc surface oxygens. It is possible, however, that the same sort of local charge balance exists in their specimen because they did not examine the possibility of Si,Al ordering. All I*a* structures have the same vertical superposition of tetrahedral and interlayer cations that will permit this type of local charge balance. Because this is the most stable configuration possible, the positions of the exchangeable cations should tend to be controlled by the sites of Al for Si substitution in the ideal case. Brown and Bailey (1963) have demonstrated a similar case of Si,Al ordering and local charge balance for a I*a* chlorite, in which all of the trivalent octahedral cations are concentrated in the brucite sheet on the unique site between ordered T_I tetrahedra above and below.

The I*a* chlorite structure is believed to be less stable than the I*b* and II*b* structures because of cation repulsion between the superposed tetrahedral and brucite cations. It has been identified in only a few specimens in the Mg-Fe system. Powder patterns indicate that most, if not all, vermiculites have a I*a* type layer. In the case of vermiculite the amount of cation repulsion is minimized by the small number of interlayer cations and by their concentration in the particular site where the best local charge balance can be obtained. Shirozu and Bailey (1965) have tabulated all of the repulsive and attractive forces within the four types of chlorite layers. It can be seen from their chart that the I*a* structure would be the most stable of the four arrangements if the tetrahedral cation-brucite cation repulsive effect were eliminated, as in vermiculite.

Water molecules. It was also found by least squares refinement in this study that 0.62 water molecules statistically occupy each of the three sets of interlayer anion sites, for a total of 3.72 H_2O per formula unit. A less accurate one-dimensional electron density summation indicated 3.74 H_2O. These totals are not consistent with the allocation of 4.72 H_2O from chemical analysis and 5.10 H_2O from thermogravimetric analysis of a different sample from the same locality by Bradley and Serratosa (1960). Three possible explanations of the discrepancy can be suggested.

1) The discrepancy can be reduced by distributing additional hydrogen either over the interlayer water sites to form mixed H_2O and H_3O^+ species or over the talc oxygens to form mixed $O^=$ and OH^- species. Experimental study of the Llano vermiculite by Raman and Jackson (1966) suggests that H_3O^+ is not present but that some hydroxylation of O to OH does occur. Although it is probable that hydroxylation has been operative in decreasing the net layer charge from that appropriate for the parent phlogopite (-1.00) to that observed for the Llano vermiculite (-0.82), the magnitude of this decrease can account for only one tenth of the discrepancy in interlayer water.

2) The difference between analyzed and observed water content, about one molecule per formula unit, may represent water displaced so far from the average H_2O sites that it forms a diffuse background of electron density that cannot be integrated by least squares analysis. This would be the case for water in the process of active diffusion between the average sites. Examination of 2-dimensional and 1-dimensional electron density difference maps does not provide any evidence to support the existence of extra water of this type.

3) Only 2.46 H_2O are required for complete hydration of 0.41 Mg atoms. The excess water is bound less tightly and is known to vary in amount according to the external humidity. The observed total of 3.72 H_2O may very well be the equilibrium water content for the humidity of the laboratory at the time of the x-ray exposures. This is the most likely explanation. The effect of heating as a result of the 48 hour x-ray exposures has been determined experimentally as negligible, but the physical effect of x-ray bombardment on the water molecules is not known.

The water that was located has a large and anisotropic temperature factor, indicating apparent larger vibration amplitudes in the (001) plane than along Z^* (Table 4). The large thermal parameters are interpreted to be due mainly to random displacements of the waters from their average positions, rather than actual vibration. The exchangeable cation has a slightly large, but isotropic, temperature factor.

This study does not provide information as to the exact distribution of the 0.41 atoms of interlayer Mg^{2+} over the M_{IV} sites from cell to cell or of the 0.62 atoms of water over each octahedral anion site. It is not possible, therefore, to confirm or to refute the several postulated interlayer configurations mentioned in the introduction of this paper. It is reasonable to

TABLE. 4. ORIENTATION OF ANISOTROPIC THERMAL ELLIPSOIDS OF WATER MOLECULES

Atom	Ellipsoid axis	r.m.s.	B	Angles to crystal axes (°)		
				X	Y	Z
$(H_2O)_I$	minor	0.129	1.31	99	75	15
	median	0.292	6.74	169	98	90
	major	0.335	8.85	84	163	75
$(H_2O)_{II}$	minor	0.144	1.64	86	71	22
	median	0.298	7.02	131	134	69
	major	0.358	10.13	42	130	86
$(H_2O)_{III}$	minor	0.124	1.21	104	81	12
	median	0.290	6.62	147	122	91
	major	0.373	10.97	60	146	78

assume that each Mg^{2+} will be surrounded by a hydration shell of six waters, and that such groups will tend to be dispersed by mutual repulsion throughout the interlayer region. This study did not detect any long-range ordering of these groups in space and time. Short-range ordering was not investigated.

Interlayer thickness. Mathieson (1958) pointed out that the *d*(002) value for vermiculite in its natural state is about 0.02 Å greater than the corresponding *d*(001) value for chlorite because of the difference in thicknesses of the interlayer materials. The chart below summarizes the perpendicular distances measured in the interlayer region for several structures determined since Mathieson's original observation. The chart shows that the difference in interlayer thickness [2×(Mg—OH,H_2O)] is even greater than Mathieson had realized, but is partly compensated by differences in the closeness of approach of the interlayer material to the talc surface.

	Vermiculite	*Vermiculite*	*Prochlorite*	*Corundophyllite*	*Cr-chlorite*	*Fe-chlorite*
	(Mathieson, 1958)	(this paper)	(Steinfink, 1961)	(Steinfink, 1958)	(Brown and Bailey, 1963)	(Shirozu and Bailey, 1965)
O–(OH,H_2O)	2.76 Å	2.67 Å	2.79 Å	2.85 Å	2.82 Å	2.75 Å
Mg–(OH,H_2O)	1.14	1.17	0.95	0.95	1.01	0.99

There are least two reasons why a vermiculite interlayer sheet should be thicker than a chlorite brucite sheet.

1) The radius of the exchangeable cation Mg^{2+} is greater than the average radius of the brucite cations, which must be at least one-third trivalent species to maintain a positive sheet charge.

2) Because of the large number of interlayer cation vacancies in vermiculite, there is very little sheet thinning due to shortening of diagonal shared octahedral edges. Each occupied M_{IV} cation site is surrounded by six vacant M_V cation sites, so that lateral cation-cation repulsion is at a minimum. In chlorite there is much more lateral cation—cation repulsion within the brucite sheet. This tends to thin the sheet along Z^* and to stretch it in (001) so that there is better articulation with the lateral dimensions of the talc sheet (Shirozu and Bailey, 1965).

The close average approach [O—H_2O] of the vermiculite water plane to the talc surface oxygens may be due to the slight interpenetration that is possible locally at the sites of the water vacancies. The diagonal internuclear O—H_2O distances of 2.79 Å (Table 3) are shorter than normal for the same reason. Corresponding long hydrogen bond contacts between O and OH in other layer silicates are in the range 2.9 to 3.0 Å.

The water molecules in the Llano vermiculite are shifted within the (001) plane away from their ideal positions. Because of the 30–40% vacancies the measured coordinates represent average values in a defect system. They indicate that on the average the water molecules shift slightly away from the nearest talc oxygens and toward the exchangeable cation. These shifts, illustrated in Figure 2, are believed to result from the need for the water to maintain normal bond lengths both with the talc surface oxygens and with the exchangeable cations in the thick interlayer region. The result is a rotation of the octahedral water triad about the exchangeable cation by an average angle of 3.3°, in the same direction as the rotation of the talc tetrahedral oxygens. Because the tetrahedral rotation is twice as large as the interlayer octahedral rotation, the net result is a shorter O—H_2O contact than is possible for the ideal positions of the oxygens and waters.

The metal—anion distance of 2.073 Å for the interlayer region is normal for Mg in octahedral coordination. The H_2O—H_2O unshared edges of the water triad about the exchangeable cation are shorter (2.96 Å) than normal as a result of the greater thickness of the interlayer sheet. As in dioctahedral layer silicates, the two vacant octahedra are expanded; the vacant site—H_2O distance measures 2.17 Å and the lateral edges of the water triad measure about 3.16 Å (Table 3).

GENESIS

The Llano vermiculite is reported to be formed by surface weathering of phlogopite contained in magnesite. Just a few inches below the surface the phlogopite is fresh and unaltered. The major chemical change during the alteration has been complete replacement of interlayer K by hydrated

Mg ions. Because the parent phlogopite is essentially iron free, oxidation has not contributed to the alteration. However, it is possible that the original charge of the talc sheet has been reduced slightly by hydroxylation of talc oxygens.

Single crystal study shows that the parent phlogopite in the Llano deposit is the 1M polytype. The 2-layer *s* type vermiculite from New Canaan is also derived from a regular 1M phlogopite. Aside from the chemical changes noted, two structural changes are also required to transform a 1M phlogopite into the observed vermiculite structure: 1) the 2:1 talc packets must be relatively displaced by $\pm b/3$ so that they form a regular 2-layer sequence, and 2) tetrahedral Si,Al ordering must be developed, if not already present in the parent.

The *s* vermiculite sequence is more closely related to the 1M structure than to any other mica polytype because of the presence in both of L type shifts within the talc sheets. The *s* structure can be derived from a 1M mica, therefore, by linear $b/3$ displacements without rotations. A simple 1-layer vermiculite can be postulated in which the sequence of silicate sheets is identical to that in 1M pholognite; no layer displacements would be required. This structure would have a designation I*a*-2. It is noteworthy that this structure is not adopted. It would not permit ordering or local charge balance because the space group requires that all tetrahedra be equivalent. In addition, the unique interlayer cation site lies vertically between a tetrahedron and the center of a hexagonal ring rather than between two tetrahedra.

The similarity of the *s* vermiculite structure to the parent 1M phlogopite, aside from the problem of Si,Al ordering, suggests that the relative orientations of the layers within the vermiculite polytypes may be controlled by the structure of the micaceous parent material. If this hypothesis is correct, it follows that the theoretical regular 2-layer sequences *p*, *q*, and *r* will be less abundant than the *s* sequence and, where found, will be derived from either a $2M_I$ or 3T parent mica, both of which contain M and N shifts within the talc sheets. Similar correlations can be made for chloritic parent materials having L, M, or N shifts. Most vermiculites examined in this study have irregular stacking sequences with extensive streaking of $k \neq 3n$ reflections. The parent materials of these vermiculites may have had random stacking sequences, common in trioctahedral micas and chlorites. Another possibility is that the regularity of stacking is controlled by the degree of local charge balance possible, which in turn is dependent on the degree of Si,Al ordering present in the parent material or developed during the alteration.

In interpreting the genesis of Si,Al ordering in vermiculite the observed pattern of ordering must be considered. In any individual 2:1 talc layer

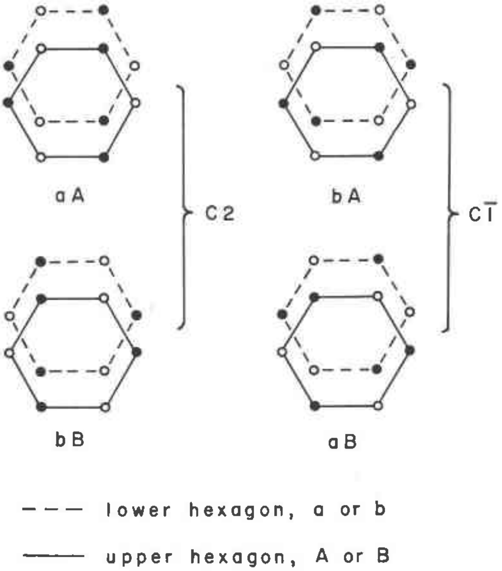

FIG. 3. Four possible Si,Al ordering patterns within one layer.

four possible ordering patterns with symmetries $C2$ or $C\bar{1}$ can be adopted. In Figure 3 these patterns are designated aA, bB, bA, and aB. The Llano vermiculite contains a quite regular sequence of aA and bB layers, related to each other by a c glide plane but with occasional mistakes in the sequence. These mistakes can be explained as an intercalation of bA or aB layers in certain positions.

$$\begin{array}{ccccccccccccccccccccccc}\cdots, & \mathrm{aA}, & & \mathrm{bB}, & & \mathrm{aA}, & & \mathrm{bB}, & & \mathrm{aA}, & & \mathrm{bB}, & & \mathrm{aA}, & & \mathrm{bB}, & & \mathrm{aA}, & & \mathrm{bB}, & & \mathrm{aA}, & \cdots \\ &&&&\uparrow&&\uparrow&&&&&&&&\uparrow&&&&&&\uparrow&& \\ &&&&\mathrm{bA}&&\mathrm{aB}&&&&&&&&\mathrm{bA}&&&&&&\mathrm{aB, aB}&& \end{array} \qquad (1)$$

The positions of intercalation have been determined by two factors.

a) The mistakes must involve the regular alternation of $+b/3$ and $-b/3$ layer displacements. Sequence (1) above can also be expressed in terms of the relative displacement directions.

$$\begin{array}{ccccccccccccccccccccccc}\cdots, & +, & & -, & & +, & & -, & & +, & & -, & & +, & & -, & & +, & & -, & & +, & \cdots \\ &&&&&&\uparrow&&\uparrow&&&&&&\uparrow&&&&&&\uparrow&& \\ &&&&&&+,&&-,&&&&&&+,&&&&&&-,-,&& \end{array} \qquad (2)$$

b) Local charge balance must be maintained so that the exchangeable cation is always between two Al-rich tetrahedra. This requires, A,b or B,a contacts between the successive layers in (1).

The accepted space group for the 1M mica polytype is $C2/m$, which requires that all eight tetrahedra in the unit cell be equivalent. Thus, we have the paradox that tetrahedral cation ordering is not permitted in the space group of the parent mica, but is observed in the alteration product. It is difficult to believe that sufficient energy would be available during surface weathering to order an original disordered Si,Al distribution. For ideal ease of conversion the parent 1M mica should be ordered and should have a regular sequence of aA and bB layers, as in (1) above. A noteworthy feature of this hypothetical mica structure is that the Si,Al ordering pattern is centrosymmetric about the alkali ion. This creates local charge balance in that a Si-rich site always superimposes on an Al-rich site, never Si on Si or Al on Al. Intensity calculations for such a 2-layer model, using layers distorted as in vermiculite but shifted into a mica sequence, indicate that the diagnostic $l=2n+1$ reflections would be extremely weak. No reflections of this type, or any other deviation from $C2/m$ symmetry, have been observed to date in either the Llano or New Canaan phlogopites. Calculations indicate that ordering to an acentric structure within an otherwise centrosymmetric framework would produce negligible change in the distribution of the $k\neq 3n$ intensities, and therefore in the N (z) test for centrosymmetry. For these reasons the problems of the true symmetry of the parent phlogopite and the genesis of the Si,Al ordering in the vermiculite remain in doubt.

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