

Mg-VERMICULITE: A REFINEMENT AND RE-EXAMINATION OF THE CRYSTAL STRUCTURE OF THE 14.36 Å PHASE

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ABSTRACT

Refinement of the crystal structure of the 14.36 Å phase of Mg-vermiculite by difference syntheses does not change the earlier general conclusions regarding the silicate layer, but reveals an electron density distribution in the interlamellar region which indicates either that the water molecules are vibrating asymmetrically or that there is a regular displacement of water sites from the hexagonal position in a direction opposite to that proposed in the earlier analysis by Mathieson and Walker. The present evidence is not decisive but tends to support the latter alternative. Additional supporting evidence is provided by a careful comparison of the structures of Mg-vermiculite and chlorite.

INTRODUCTION

The crystal structure of Mg-vermiculite at normal temperature and humidity (Mathieson and Walker, 1954) was analysed by means of orthodox ρ_0 syntheses. It has become evident recently (e.g., Cochran, 1951; Cruickshank, 1956) that in ρ_0 syntheses much detail concerning minor atomic displacements and vibrations remains hidden and can best be revealed by the use of difference syntheses (Cochran, 1951). It was considered worthwhile to attempt a refinement of the available diffraction data for this phase of Mg-vermiculite by means of $\Delta\rho$ syntheses. The additional information will be of interest with respect to triphormic layer silicates in general (for reasons, see Walker, 1957) and the improved data will assist in a current investigation of the various phases of Mg-vermiculite (Walker, 1956). It is convenient to distinguish the various phases by means of their basal spacing. Hence we shall refer to normal Mg-vermiculite as the 14.36 Å phase.

REFINEMENT

No new diffraction measurements were made; the data used were the experimental $h0l$ structure amplitudes recorded in Table 2 of the original analysis (Mathieson and Walker, 1954, hereafter referred to as I). The first difference synthesis was calculated using the recorded F_{obs} and F_{calc} values (Fig. 1a). From inspection of this distribution, it was clear that various parameter adjustments were required, in particular for D, O_3 and O_{2AB} (see Table 1 and Fig. 1c), while the region of the water molecule sites showed a gross error in the temperature factor (for which an average value, $B=1.2 \text{ \AA}^2$, was used in I) with a negative trough of

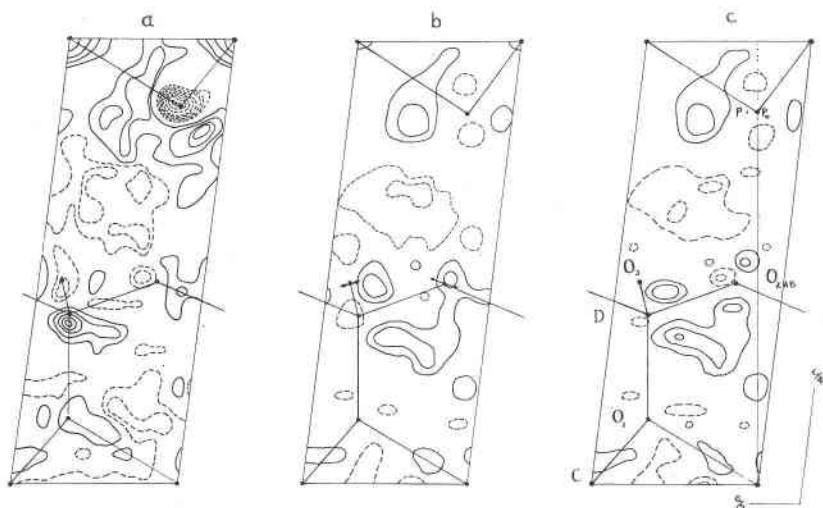


FIG. 1. Difference Fourier syntheses: *a*) first, *b*) eleventh and *c*) thirteenth. The contour levels are at intervals of $1e \cdot \text{\AA}^{-2}$, the full line representing positive, dashed line negative values, the zero level being omitted. The molecular model is outlined, the vibration directions of O_3 and O_{2AB} being indicated in *b*).

$9e \cdot \text{\AA}^{-2}$ where the peak value in the distribution was only $\approx 22e \cdot \text{\AA}^{-2}$. In subsequent calculations of structure amplitudes, improved scattering curves for O^{2-} , Si^{4+} , Al^{3+} and Mg^{2+} (MacGillavry *et al.*, 1955), tabulated since the previous analysis, were used and the three water sites we assumed to coincide in projection, leaving the question of site displacement until other features of the electron density distribution had been clarified. Adjustment of atomic parameters and isotropic temperature factors was made step by step by the iterative process of calculation of structure amplitudes, adjustment of $\sum |F_{obs}| = \sum |F_{calc}|$ and subsequent synthesis. After the eleventh $\Delta\rho$ synthesis (Fig. 1*b*) all mean atomic parameters and mean isotropic temperature factors had been determined (Table 1). In the region of O_3 , a classical type of $\Delta\rho$ distribution (Cochran and Lipson, 1953, p. 304) indicated asymmetric vibration. A similar distribution occurs around O_{2AB} , but here the mean value of B (2.0\AA^2) used for O_3 and O_{2AB} in the calculation of structure amplitudes was too high, so that in addition a positive region existed at the atom centre. The vibration directions (Fig. 1*b*) indicated by these distributions were in accord with the bonding of O_3 , O_{2A} and O_{2B} with D atoms. In three dimensions, these three oxygen atoms are structurally equivalent (Fig. 2*c*) but in the *b*-axis projection, the range of vibration of O_3 is viewed at its maximum while the superimposed vibrations of

TABLE 1. ATOMIC PARAMETERS AND TEMPERATURE FACTORS

Approximate peak value in (e. Å ⁻²)	Atom	x/a	z/c	B (Å ²)	
				11th $\Delta\rho$	13th $\Delta\rho$
21	Mg ²⁺	0.50	0.250	1.2	1.2
22	H ₂ O	0.1403	0.2104	5.4	5.4
20	O ₃	0.4322	0.1142	2.0	0.8s ² +2.4t ²
40	O _{2AB}	0.1482	0.1142	2.0	0.8s ² +1.2t ²
99	D(SiAl)	0.3967	0.0951	0.8	0.8
63	O ₁	0.3579	0.0369	1.4	1.4
136	C(Mg, Fe, Al)	0.0	0.0	1.2	1.2

s and t are defined in Cochran (1951).

O_{2A} and O_{2B} are both viewed at 30°. Hence the apparent range of vibration for O_{2AB} is smaller (i.e., smaller mean B) and the direction of vibration is different (vide Fig. 1*b*). The asymmetric vibrations of O₃ and O_{2AB} were then removed from the $\Delta\rho$ distribution by calculating the contributions of these oxygen atoms with the appropriate asymmetric temperature factors (Table 1) using Cochran's (1951) method. The resulting distribution is shown in Fig. 1*c*. Whereas in I, the final reliability index ($R = \sum |F_0 - F_c| / \sum |F_0|$) was 0.17, the index has now been reduced to 0.08. The final observed and calculated structure amplitudes are compared in Table 2.

At this stage there remained in the region of the silicate layer (i.e., $z=0$ to $c/8$) no systematic features which could be related to any error, either in the parameters or asymmetric vibrations of any of the atoms. The distribution remaining must correspond therefore to random variations arising from errors in the measurement of structure amplitudes. On this basis, it is possible, since gross features in the region $z=c/8$ to $c/4$ have also been removed, to use the region $z=0$ to $c/8$ in the 13th $\Delta\rho$ distribution (Fig. 1*c*) to estimate the standard deviations in $\Delta\rho$ and in the slope of $\Delta\rho$. These have been calculated from the relationships, $\sigma(\rho) = |\overline{\Delta\rho^2}|^{1/2}$ and $\sigma(\partial\Delta\rho/\partial z) = \{(\partial\Delta\rho/\partial z)^2\}^{1/2}$ (Cochran and Lipson, 1953). Averaged over 232* points, the standard deviation of electron density $\sigma(\rho) = 1.0 \text{ e.Å}^{-2}$ while, averaging the (slope)² over 239 points, the standard deviation $\sigma(\partial\Delta\rho/\partial z) = 4.56 \text{ e.Å}^{-3}$. With this latter value, the standard deviations for atomic parameters, $\sigma(z_n) = \partial\Delta\rho/\partial z/C_n$, can be computed when the central curvature at each atom peak, C_n , in ρ_0 has been determined. C_n may be conveniently assessed as $2p\rho_0$, p being determined from a plot of $\log \rho_0$ against r^2 (see Cochran and Lipson, 1953, p. 279, 308). The calculated values of standard deviations are listed in Table 3

* Subdivision of the unit cell axes in computing the Fourier series was as in I.

TABLE 2. COMPARISON OF OBSERVED AND FINAL CALCULATED VALUES OF h0l STRUCTURE AMPLITUDES OF 14.36 Å Mg-VERMICULITE AT ROOM TEMPERATURE

l	F ₀	F _e	l	F ₀	F _e	l	F ₀	F _e
	001		24	105	115	40	<23	10
			22	79	85	38	46	48
2	282	273	20	37	-42	36	63	66
4	62	47	18	63	-69	34	35	14
6	110	-68	16	37	32	32	<20	-22
8	211	212	14	173	185	30	<20	-22
10	342	305	12	263	259	28	<19	25
12	60	-52	10	105	101	26	52	52
14	105	-114	8	178	182	24	52	52
16	74	-79	6	116	90	22	29	24
18	86	95	4	304	316	20	29	26
20	167	172	2	205	204	18	46	40
22	84	95	0	136	139	16	150	142
24	121	114	2	16	6	14	162	154
26	42	50	4	147	-161	12	144	141
28	83	84	6	32	20	10	<16	-16
30	68	76	8	100	83	8	16	-22
32	107	109	10	147	164	6	63	64
34	61	69	12	58	63	4	167	151
36	<20	-2	14	47	-55	2	58	77
38	38	-44	16	152	144	0	110	-112
40	<22	2	18	236	218	2	87	-84
42	41	52	20	294	283	4	127	122
44	39	50	22	63	67	6	225	224
46	<24	-11	24	<16	-15	8	167	181
48	<24	-23	26	16	14	10	<16	-17
50	<25	17	28	105	110	12	58	58
52	54	63	30	89	98	14	127	132
54	39	42	32	<17	2	16	196	202
			34	52	-58	18	75	86
	201		36	<18	-9	20	<18	-8
			38	37	51	22	29	-28
52	<22	8	40	73	75	24	<18	15
50	<22	-18	42	37	31	26	52	48
48	<21	-13	44	26	13	28	58	52
46	<20	13	46	<20	12	30	17	25
44	37	46	48	47	38	32	<20	12
42	32	32	50	47	41	34	<20	3
40	<19	2	52	37	30	36	63	53
38	<18	-6				38	81	78
36	68	66		401		40	81	70
34	100	110				42	<22	8
32	105	107	48	29	34	44	<22	-14
30	<16	0	46	46	50	46	<23	10
28	16	-21	44	23	26	48	40	46
26	16	26	42	<24	-10			

TABLE 2—(continued)

1	F ₀	F _c	1	F ₀	F _c	1	F ₀	F _c
	601		20	50	-55	12	48	54
36	<22	18	22	<19	-4	14	<20	22
34	<21	-21	24	86	90	16	<20	-6
32	<20	-20	26	81	85	18	<21	-6
30	20	22	28	30	32	20	37	39
28	76	72	30	<20	-15	22	63	56
26	50	56	32	30	30	24	58	53
24	<19	16	34	60	68			
22	<19	-6	36	55	63		10.01	
20	50	50		801		14	<26	13
18	81	80				12	47	37
16	66	69	24	<24	-3	10	26	32
14	<18	-6	22	<24	5	8	<25	14
12	35	-33	20	<23	27	6	<24	-4
10	<17	-5	18	<23	21	4	<24	4
8	45	51	16	<22	1	2	<23	15
6	60	64	14	<22	-22	0	<23	22
4	35	38	12	<22	-1	2	<23	5
2	<17	-1	10	42	38	4	<22	-9
0	35	32	8	79	70	6	<22	-12
2̄	71	72	6	37	38	8	<22	13
4̄	141	142	4	<21	5	10	36	33
6̄	96	96	2	<21	1	12	42	34
8̄	35	40	0	63	57	14	<23	9
10̄	20	-22	2	74	72	16	<23	0
12̄	<18	24	4̄	32	35	18	<24	16
14̄	76	80	6̄	26	-30	20	36	39
16̄	66	70	8̄	20	-28	22	26	30
18̄	<19	-15	10̄	<20	18			

TABLE 3. (a) STANDARD DEVIATIONS OF ATOMIC PARAMETERS. (b) BOND LENGTHS

(a)		(b)	
Atom	$\sigma(z) = \sigma(x)$		
H ₂ O	0.027 Å	C—O ₁	2.071 ± 0.006 Å
O _{2AB}	0.010 Å	O ₁ —D	1.67 ± 0.01 Å
O ₃	0.019 Å	D—O ₃ —D—O _{2A} —D—O _{2B}	1.63 ± 0.02 Å
D	0.003 Å	Mg ²⁺ —H ₂ O	2.11 ± 0.03 Å
O ₁	0.006 Å	(hexagonal site)	
		O ₃ (or O _{2A} or O _{2B})—H ₂ O	2.87 ± 0.04 Å
		(hexagonal site)	

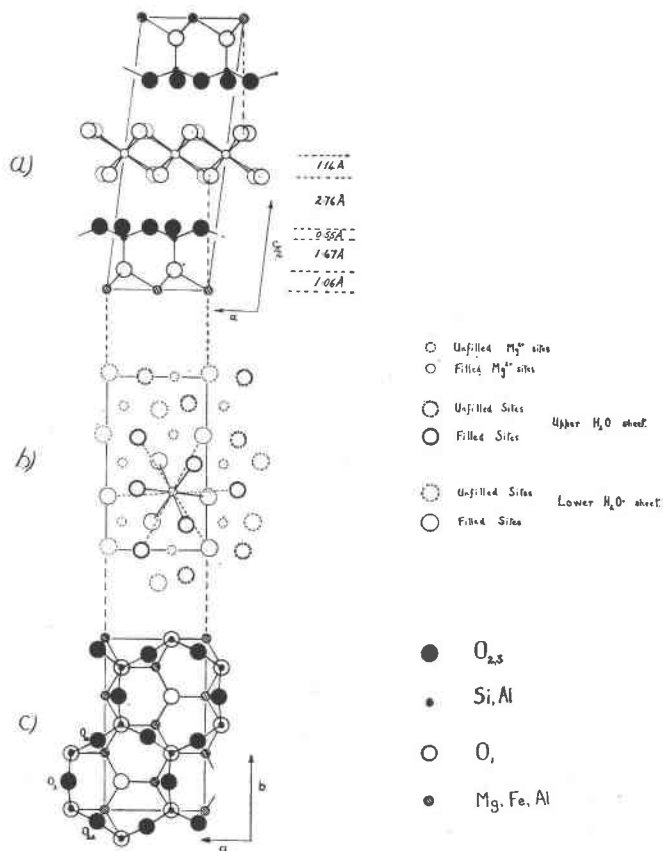


FIG. 2. The crystal structure of Mg-vermiculite involving displacement of water molecules from the hexagonal sites.

a) projection on the ac plane

b) projection of the interlamellar region normal to the ab plane

c) projection of the triphormic silicate layer from $z=0$ to $c/8$, normal to the ab plane.

The various atom species are designated on the right.

together with the bond lengths and their probable errors derived from the standard deviations. Standard deviations for O_3 and O_{2AB} were calculated on the basis of an isotropic temperature factor since, for these atoms, the direction of maximum vibration does not greatly affect the calculation of associated bond lengths.

Comparison of bond lengths (Table 3) in the silicate layer with values reported in I shows no significant change. The bond length $D-O_1$ remains greater than $D-O_{2AB}$ (O_3). The surface oxygens O_3 , O_{2A} and O_{2B} still deviate from a regular hexagon formation (Fig. 2c) and are now

observed to vibrate asymmetrically. The parameter changes all lie within the range of error quoted in I, but it is now possible to give a better estimate of the individual errors.

There appear to be changes of significance with regard to the detailed structure of the inter-lamellar region. The z parameter of the H_2O peak is considerably altered, so that whereas the inter-sheet distance $\text{Mg}-\text{H}_2\text{O}$ was previously regarded as the same as the $\text{Mg}-\text{O}$ intersheet distance (i.e., 1.06 Å), it has now been increased to 1.14 Å (Fig. 2*a*). The asymmetric electron-density distribution around the H_2O site warrants a more detailed discussion.

THE INTERLAMELLAR REGION

When the normal criteria for the correct location and mean temperature factor of a single atom have been achieved, namely $\Delta\rho=0$ and $\partial\Delta\rho/\partial z=\partial\Delta\rho/\partial x=0$ at the atom centre, there still remains a distribution of electron density around the site of the water molecules (Fig. 1*c*). Since the peak values of the distribution lie in the range -1.7 to $+2.4e.\text{Å}^{-2}$ and the standard deviation of electron density has been estimated as $1e.\text{Å}^{-2}$, it appears that the regular shape of the distribution does not arise from random errors but from the disposition of the water molecules.

So far it has been assumed in calculating the contribution of the water molecules to structure amplitudes that the three equivalent H_2O sites coincide in the b -axis projection. On this assumption, the only conclusion regarding the asymmetric distribution is that it must be ascribed to asymmetric vibrations of the three superimposed water molecules with the major vibration mode parallel to (001) (Cochran and Lipson, 1953, p. 304). If this viewpoint is correct then all H_2O sites are structurally as well as crystallographically equivalent, all $\text{Mg}-\text{H}_2\text{O}$ interatomic distances would be 2.11 Å and the particular grouping of the Mg^{2+} ions and the H_2O molecules over the hexagonal arrays of their respective sites would depend on the tendency of the Mg^{2+} ions to form hydration shells of the type shown in Fig. 3*a(ii)* (see also Fig. 7 in I).

The coincidence of the H_2O sites in the b -axis projection is not however a structural or a crystallographic necessity, but merely the simplest assumption used in the preliminary stages of the re-examination. Considering the equivalence of the [010], [310] and $[\bar{3}\bar{1}0]$ projections (see I), it is clear that the water molecules may be displaced in a regular manner from the hexagonal sites (Fig. 4*a* and *b*). In projection, one site is displaced Δ while the other two sites are displaced in the opposite direction by $\Delta/2$, the weighted mean being at the hexagonal site, Fig. 4(*iii*).

It is worth considering what effect these displacements would have on

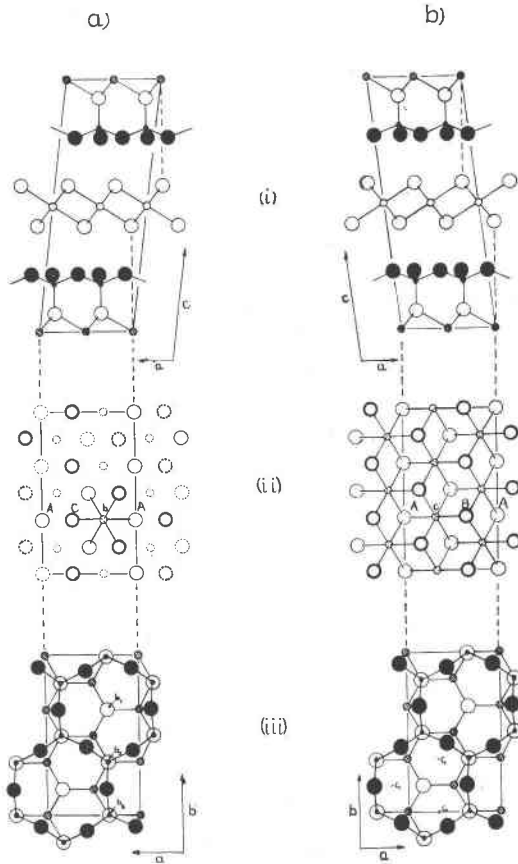


FIG. 3. Comparison of the crystal structures of *a*) Mg-vermiculite (with H_2O in hexagonal sites) and *b*) chlorite. The origin and orientation of the silicate layers is the same in both. Atom species and their levels are in Fig. 2.

- (i) projection on the ac plane
- (ii) projection of the interlamellar region normal to the ab plane
- (iii) projection of half the silicate layer normal to the ab plane.

the distribution in a difference synthesis. Consider a simple one-dimensional case where three atoms are located at $x=0$ (Fig. 5*a*). The electron density distribution for an atom can be described by a Gaussian curve (Booth, 1946). If one atom is displaced $+\Delta$ and the other two $-\Delta/2$, the resulting electron density distribution is as given in Fig. 5*b*. The $\Delta\rho$ distribution corresponding to $\rho_2-\rho_1$ is shown in Fig. 5*c*. Although intuitively the positive excursions of $\Delta\rho$ on either side of $x=0$ might have been expected to differ in magnitude, any difference is undetectable. The mean

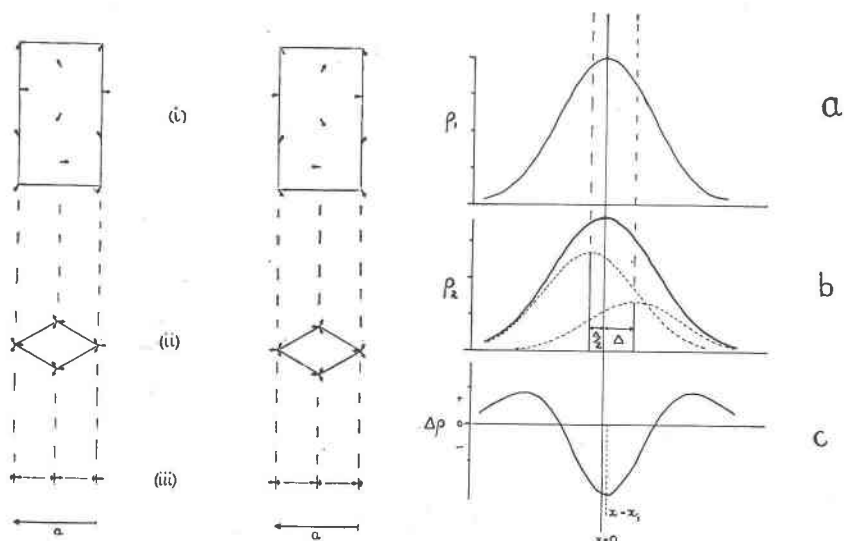


FIG. 4. (left)—The two ways in which regular displacements of the H_2O sites from the hexagonal positions in one sheet may occur.

- (i) projection on the ab plane of the full unit cell
- (ii) projection on the ab plane of the sub-cell
- (iii) projection on the ac plane.

FIG. 5. (right) Theoretical electron density distribution

- a) for three atoms superimposed at $x=0$
- b) for two atoms displaced to $+\Delta/2$ plus one atom displaced to $-\Delta$. Separate curves dashed, combined curve full line.
- c) The difference curve corresponding to $\rho_2 - \rho_1$ apparently centred at $x=x_1$.

position of the distribution is not at $x=0$ but is displaced to $x=x_1$. Hence, without prior knowledge, this distribution, Fig. 5c, could not be distinguished from the distribution of atoms superimposed at $x=x_1$ and with a major vibration mode parallel to x .

In Fig. 1c, the mean position of the asymmetric distribution is in the region of P. However, from the equivalence of the [010], [310] and $[3\bar{1}0]$ projections, the location of the mean position must be at P_0 (i.e., vertically above the origin Mg atoms). If this difference PP_0 is regarded as significant, the simple assumption that the water molecules superimpose at P_0 must be abandoned. The H_2O sites must be considered as displaced in three-dimensional space from the hexagonal sites by an amount Δ , i.e., by displacements of the type shown in Fig. 4b. No attempt to calculate further sets of structure amplitudes on this basis has been made since

the results would not have been sufficiently critical to yield a specific value of Δ .

If this evidence regarding H_2O sites being displaced from the hexagonal sites is correct, the refinement with difference syntheses has, therefore, led to the same type of structure in the interlamellar region as was suggested in I, except that the direction of displacement of the water molecules is reversed, i.e., as in Fig. 4*b* rather than Fig. 4*a* (cf. Fig. 6 in I with Fig. 2*b*). The structure with these displacements is shown in Fig. 2, the filling of available sites being based on the same premises as presented in I.

It must be realised that the present diffraction data are not sufficiently accurate to make a decisive choice between the two possible interpretations (1) that the water molecules lie in the regular hexagonal array of sites and are vibrating with their major mode in the (001) plane or (2) that the water molecules are in sites displaced by an amount Δ (probably of the order of 0.2 Å) from the hexagonal sites. The most satisfactory test as to which alternative is correct would be a structure study at low temperatures (circa 80° K.) which would differentiate the effect of asymmetric vibration at room temperature from that of displacements.

Certain evidence of a less direct nature may be offered in support of the second possibility. The mean temperature factors of the atoms in Mg-vermiculite at room temperature all have normal moderate values with the exception of the H_2O molecules, 5.4 Å², despite the fact that the temperature factor of the exchangeable Mg^{2+} remains small although sandwiched between the two sheets of water molecules. The large value of B quoted for the water molecules is associated with calculations of structure amplitudes in which the three H_2O sites are assumed superimposed. If the atoms are displaced, then values of B for individual water molecules would be smaller (say 2.5 Å²) and more in line with values for other atoms, although B for the group (regarded effectively as one atom) would remain as 5.4 Å². This can be seen more readily by inspection of Fig. 5. The value of B is the same for individual atoms in Fig. 5*b* (dashed curves) as for the superimposed atoms in Fig. 5*a*, but the effective B for the group of displaced atoms regarded as a single entity (full curve in Fig. 5*b*) would be much larger. Hence the experimental values of the temperature factors B tend to support the view that the water molecules are displaced and not merely vibrating.

Because Mg-vermiculite resembles chlorite (Brindley, 1951) structural-ly in many respects, but differs from it mainly in the reduced population of the atom species in the interlamellar region, a close comparison of the two structures throws some light upon the detailed structure of the inter-

lamellar region of vermiculite. Both minerals have similar cell dimensions and have as their major constituent and principal common feature, the triphormic silicate layer. To emphasise the basic similarities and differences, the structures are shown in Fig. 3 with the silicate layers disposed in the same orientation in both and the origins of each unit cell selected as the Mg atoms at the centre of the silicate layer. The water molecules in Mg-vermiculite are shown provisionally in the hexagonal sites, i.e., undisplaced. Comparison of Fig. 3(i) (*a* and *b*) immediately shows that the disposition of the $\text{H}_2\text{O}-\text{Mg}^{2+}-\text{H}_2\text{O}$ double sheet in vermiculite, although structurally similar to the $\text{HO}-\text{Mg}^{2+}-\text{HO}$ double sheet in chlorite, is oriented in the opposite sense.* However, we note that in both minerals, the relationship of each sheet of H_2O (or OH) sites to the adjacent related silicate layer is the same, i.e., the oxygens lie vertically over the origin Mg atoms in a hexagonal array (Fig. 3(i)(*a* and *b*)). From this viewpoint, the main difference between Mg-vermiculite and chlorite lies in the way the two silicate- H_2O (OH) halves of the sandwich are held together by the Mg^{2+} ions. There are two possible ways of close-packing the two oxygen (H_2O or OH) sheets (capital letters) with the intercalated sheet of Mg^{2+} ions (small letter)—namely AbC or AcB, Fig. 3(ii)(*a* and *b*). In chlorite, all Mg sites are occupied and so must be structurally equivalent. Both sets of *b* and *c* sites available for Mg^{2+} ions are equivalent with respect to the hexagonal array of OH groups. Whereas *c* sites are also equivalent with respect to the underlying silicate layer, the *b* sites are of two types, namely, b_1 (over the centre of the hexagon of surface oxygens) and b_2 (over the centre of triads of surface oxygens) (Fig. 3(iii)(*a* and *b*)). Complete structural equivalence is achieved in chlorite by the location of the Mg^{2+} ions in the $c_1c_1c_1$ sites. In Mg-vermiculite, if the H_2O sites are in a regular array, the Mg^{2+} ions might be expected to occupy sites $c_1c_1c_1$, but, *because they are influenced directly or indirectly by the structure of the adjacent silicate layers*, they occupy the alternative sites $b_1b_2b_2$. Since there is not a sufficiently high population of Mg^{2+} ions to fill all sites (in contrast to chlorite), the influence of the silicate layer leads them to select either b_1 or b_2 sites. We have previously deduced from the intensity distribution of the diffuse 02l spectra of Mg-vermiculite that the Mg^{2+} ions occupy only b_2 sites (see I for details). Since the H_2O sites are approximately two-thirds occupied, the water molecules tend to congregate around the Mg^{2+} ions, but, because they are not hedged around by other water molecules in the plane of the H_2O sheet (as are the hydroxyl groups in the brucite layer in chlorite), the forces acting be-

* The implications of this difference between Mg-vermiculite and chlorite may not have been fully appreciated in discussions of chlorite-vermiculite mixed crystals.

tween surface oxygen atoms and water molecules tend to displace them from the special hexagonal sites. (To visualise this, imagine Fig. 3*a(ii)* and *(iii)* superimposed). The resultant repulsive forces* tend to rotate the H₂O triads and it is suggested that the final result is as shown in Fig. 2*b*. Alternatively, we may consider that the silicate layer influences the configuration of the H₂O sheet (only partly occupied) producing a distorted network which permits Mg²⁺ ions to occupy only *b*₂ sites. This was the viewpoint presented in I (section 4). The existence of these differences between Mg-vermiculite and chlorite provides some further indirect support for preferring the second alternative, namely, that the water molecules are displaced from the hexagonal sites.

Although incidental to this study, it is of interest that the refinement by $\Delta\rho$ syntheses has revealed the reason for the small dimensional difference in *d*(001) spacing of Mg-vermiculite (14.36 Å) and chlorite (14.2 Å) (Brindley, 1951). The H₂O—Mg—H₂O intersheet distance in vermiculite is $2 \times 1.14 \text{ \AA} = 2.28 \text{ \AA}$ (Fig. 2*(a)*), while HO—Mg—OH is $2 \times 1.06 \text{ \AA} = 2.12 \text{ \AA}$, a difference of $0.16 \text{ \AA} = 14.36 - 14.2 \text{ \AA}$. It would appear, therefore, that the vertical distance between each surface oxygen and its associated H₂O (or OH), 2.76 Å, is the same in both structures, further stressing the essential similarity of the H₂O(OH)—silicate—H₂O(OH) unit and the important differentiation effected by the influence of cation and water molecule (hydroxyl group) population.

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* A similar long-range torque was invoked in I to explain the observed rotation of surface oxygen triads. In that case, the force between Mg²⁺ and O^{δ-} was attractive while here since the force is acting between O^{δ-} and H₂O^{δ-}, both of negative charge, it is repulsive and operates in the opposite sense.