ALLEVARDITE, A SWELLING DOUBLE-LAYER MICA MINERAL*

G. W. Brindley, *Research Professor of Mineral Sciences,*
Pennsylvania State University, University Park, Pa.

Abstract

The structure contains pairs of mica-like layers linked by 0.7 (K, Ca) ions/unit cell. These pairs of layers are separated by 0, 1, 2 or 3 layers of water molecules each containing 2 molecules/unit cell. One-dimensional fourier syntheses of electron density reveal the number and position of the interlayer cations and water molecules. Comparison with vermiculite shows significant differences. At high temperatures, around 900° C., the loss of (OH) groups without disruption of the layer structure is demonstrated. Organic complexes of allevardite are compared with those of montmorillonite. A fourier synthesis of the ethylene glycol complex suggests the orientation of the organic molecules between the silicate layers.

Introduction

This mineral, from a locality near Allevard, France, has a remarkable skin-like appearance. When first studied (Caillère 1934, 1936; Lemoine 1935; Déribéré, 1943) there was considerable dispute as to its true character but Caillère, Mathieu-Sicaud and Hénin (1950) showed it was a mica-type mineral with layers of water molecules separating double mica-like layers. A specimen of this mineral, presented to the writer by Mlle. Caillère, when examined by an x-ray diffractometer gave a long series of basal reflections, from which fourier syntheses of electron-density have been derived. The alumino-silicate layers have been shown to be essentially the same as in the muscovite structure, so that in calculating the signs of the structure factors used in the fourier syntheses, the silicate layer has played the same role as a heavy atom by dominating the phases of the reflections. The crystallization of the mineral is too imperfect for more general reflections to be studied so that two-dimensional syntheses have not been possible.

Chemical Composition and Structural Formula

A structural formula has been evaluated from the latest chemical analysis of allevardite (see Table 1) by Hénin, Esquevin and Caillère (1954) by assuming 12 ions of Si, Al, Fe, Mg in tetrahedral and octahedral positions, as in muscovite. Small percentages of TiO_2 and P_2O_5 have been neglected without assigning them to any particular mineral impurity, and the H_2O+ content has been taken as 6.04% as given by Caillère *et al.* (1950) which is consistent with the later analysis (see

Table 1). The formula thus obtained is:

$$\begin{pmatrix} Na & 0.62 \\ K & 0.20 \\ Ca & 0.15 \end{pmatrix} \begin{pmatrix} Al & 3.78 \\ Fe^{\cdots} & 0.07 \\ Fe^{\cdot\cdot} & 0.07 \\ Mg & 0.08 \end{pmatrix} \begin{pmatrix} Si & 6.40 \\ Al & 1.60 \end{pmatrix} O_{18.84}(OH)_{5.72}$$
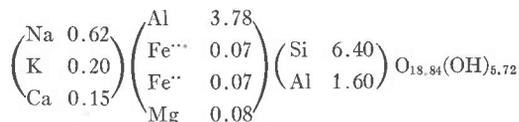
The excess of $(O+OH)$ over the 24 available sites in the layers is attributed to interlayer water and the formula can be re-written:

$$\begin{pmatrix} Na & 0.62 \\ K & 0.20 \\ Ca & 0.15 \end{pmatrix} \begin{pmatrix} Al & 3.78 \\ Fe & 0.14 \\ Mg & 0.08 \end{pmatrix} \begin{pmatrix} Si & 6.40 \\ Al & 1.60 \end{pmatrix} O_{19.40}(OH)_{4.60}(H_2O)_{0.56}$$
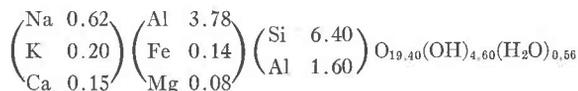
Hénin $et\ al.$ (1954), recognizing the uncertainty of the H_2O determination, evaluated a formula on the basis of $O=11$, which is equivalent to assuming a mica composition with exactly $O_{10}(OH)_2$, (this is numerically equivalent to $O_{11}+H_2O$). It is also tantamount to assuming a total negative charge, and therefore also a total positive charge, of 22 units for which there is no real justification.

TABLE 1. CHEMICAL ANALYSIS OF ALLEVARDITE

(After Hénin, Esquevin & Caillère, 1954)

SiO$_2$	45.20	MgO	0.35
Al$_2$O$_3$	32.15	K$_2$O	1.10
Fe$_2$O$_3$	0.65	Na$_2$O	2.25
FeO	0.55	P$_2$O$_5$	0.15
TiO$_2$	0.30	H$_2$O	15.80
CaO	1.00		
		Total	99.50

(After Caillère, Hénin & Mathieu-Sicaud (1950)

H$_2$O−	9.72	H$_2$O Total	15.76
H$_2$O+	6.04		

THE BASAL REFLECTIONS

The spacings and intensities have been measured using Geiger counter diffractometers (General Electric XRD3 and Philips wide range instruments). Integrated intensities have been measured from specimens consisting of thin flat rectangular sheets ranging in area from about 5 ×10 mm. to 10×15 mm. and of thickness about 0.1 mm., by (a) taking counts/second at suitably spaced angular intervals and integrating graphically, (b) direct chart recording and graphical integration. The

mineral occurs in a skin-like form with a high degree of orientation of the basal (001) planes, and it has been assumed that reflection from a flake is equivalent to reflection by an extended surface of a mosaic crystal.

LATTICE SPACINGS OF NATURAL, HYDRATED AND HEAT-TREATED ALLEVARDITE

The basal spacings of allevardite after various treatments are recorded in Table 2. Four distinct hydration states are clearly recognized corresponding to zero, one, two and three layers of water molecules be-

TABLE 2. LATTICE SPACINGS, d(001), OF HYDRATED AND HEAT-TREATED SPECIMENS OF ALLEVARDITE

λ(CuKα) = 1.5418 Å

Condition of Mineral	d(001), Å	Number of water layers per unit cell
Immersed in water	28.36 ± 0.05	3
Air-dry, natural state	24.62 ± 0.05	2
Immediately after heating to 110°–120° C.	c 21.5	1
Air-dry, after treatment with 1:10 HCl	22.00 ± 0.05	1
After 24 hr. at 450° C.	19.09 ± 0.02	0
After 24 hr. at 560° C.	19.24 ± 0.04	0
After 24 hr. at 650° C.	19.28 ± 0.04	0
After 24 hr. at 760° C.	19.33 ± 0.03	0
After 24 hr. at 900° C.	19.38 ± 0.01	0
After 24 hr. at 1000° C.	decomposed	0

tween the silicate layers. Twenty or more orders of reflection are recorded, showing that the sequence of layers is highly regular and suitable for detailed study by fourier synthesis.

The mineral is irreversibly dehydrated when heated to about 450° C. From 450° C. to 900° C. there is a small but consistent increase of d(001) which is not a thermal expansion effect, since all measurements were made after cooling the specimen to room temperature. The mineral decomposes at 1000° C., the principal product being mullite, with some cristobalite.

FOURIER SYNTHESES OF ELECTRON DENSITY NORMAL TO THE BASAL PLANE

Structure factors were derived from the integrated intensities by correcting for Lorentz and polarization factors and using the expression ap-

G. W. BRINDLEY

propriate to x-ray reflection by an extended mosaic crystal. Their signs were determined by assuming the structure consists of pairs of mica-type layers bound together by some or all of the cations K, Na and Ca, and with water layers separating pairs of bound mica layers. The best layer parameters were then determined by difference syntheses.

TABLE 3. X-RAY DATA FOR ALLEVARDITE (HEAT-TREATED SPECIMENS)

$\lambda(CuK\alpha) = 1.5418$ Å

l	560° C., 24 hr.				900° C., 24 hr.		
	$d(00l)$ Å	$d(001)$ Å	$\lvert F \rvert_{obs}$	F_{calc}	$d(00l)$ Å	$d(001)$ Å	$\lvert F \rvert_{obs}$
1	19.2	19.2*	6.1	3.6	19.4	19.4*	5.6
2	9.61	19.22*	25.9	−19.7	9.72	19.44*	16.2
3	6.417	19.25	8.2	3.5	6.487	19.46*	8.2
4	4.809	19.24	30.2	−22.7	4.848	19.39	29.4
5	3.850	19.25	6.6	3.2	3.883	19.41	5.9
6	3.186	19.12	59.4	−50.8	3.232	19.39	67.9
7	—	—	—	2.9	—	—	—
8	2.418	19.34	5.0	− 9.7	2.423	19.38	11.0
9	—	—	—	2.6	—	—	—
10	1.918	19.18	43.9	39.4	1.937	19.37	36.8
11	—	—	—	2.3	—	—	—
12	1.607	19.28	16.8	10.3	1.614	19.37	23.2
13	—	—	—	2.0	—	—	—
14	1.377	19.28	26.9	−26.7	1.386	19.40	32.0
15	—	—	—	1.8	—	—	—
16	1.202	19.23	16.5	30.5	1.211	19.38	17.3
17	—	—	—	1.7	—	—	—
18	—	—	—	− 5.4	—	—	—
19	—	—	—	1.5	—	—	—
20	0.9621	19.24	16.7	12.5	0.9691	19.38	12.5
21	—	—	—	1.3	—	—	—
22	0.8745	19.24	18.2	−26.5	0.8810	19.38	14.2

Mean $d(001)$ 19.24±0.04   Mean $d(001)$ 19.38±0.01

* Values not incorporated in the average value.

F values correspond to one-quarter of the unit cell content.

(a) *Allevardite after heat-treatment at 560° C.*

Caillère *et al.* (1950) stated that a specimen heated to 550° C. gave an x-ray pattern similar to that of ground muscovite. This is incorrect; they probably failed to observe the weak odd-order reflections, the first three of which are easily measurable with a counter diffractometer. Table 3 lists the basal spacings, and the observed and calculated struc-

ture factors. The layer parameters used in calculating the scattering factors are listed in Table 5. Figure 1 shows the electron density distributions derived from the observed and calculated scattering factors.

The close agreement between the observed and calculated data (structure factors and electron density curves) enables us to discuss the situation existing at $z=0$ and $z=9.62$ Å (i.e., $c/2$), where interlayer bonding cations would be expected to occur. The small peak at $z=0$
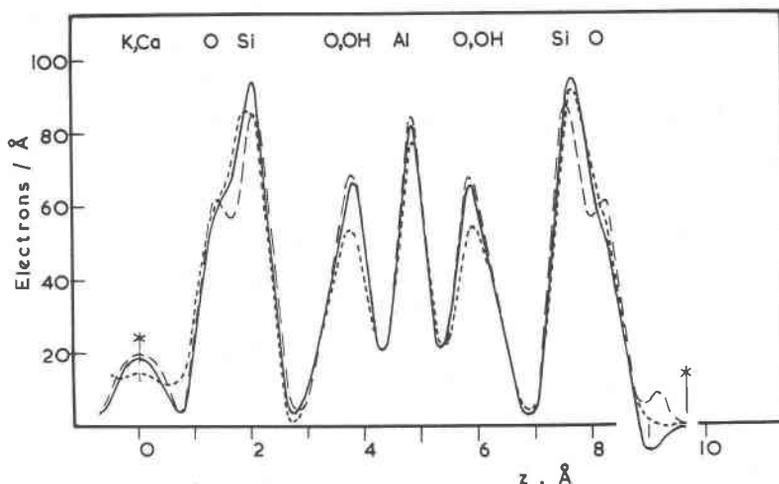
FIG. 1. Electron density distributions in allevardite: full line ——— derived from experimental structure factors after heat-treatment at 560° C. to remove water layers, dashed line – – – derived from calculated structure factors, dotted line ······ derived from experimental structure factors after heat-treatment at 900° C.; observe the diminution of the OH peaks. Symmetry centers for the one-dimensional distribution marked *.

corresponds to about 14 electrons per unit cell. It can be compared with the chemical analysis if the formula is written as follows:

$$\begin{pmatrix} Na & 1.26 \\ K & 0.40 \\ Ca & 0.30 \end{pmatrix}\left[\begin{pmatrix} Al & 3.78 \\ Fe & 0.14 \\ Mg & 0.08 \end{pmatrix}\begin{pmatrix} Si & 6.40 \\ Al & 1.60 \end{pmatrix}\begin{pmatrix} O_{19.40} \\ OH_{4.60} \end{pmatrix}\right]_2$$
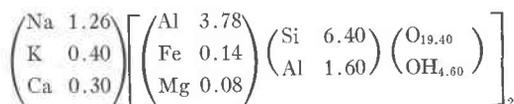
where the large bracket taken twice represents the two layers in the unit cell and the ions Na, K and Ca are available for bonding the layers together. They provide, however, a total of $12+7+5=24$ electrons, which is far in excess of the electron peak at $z=0$. The most probable explanation is that some of the cations Na, K, Ca are present as impurities and/or are adsorbed to the external surfaces of the mineral. X-rays cannot determine which of these cations are in the structure, but since

G. W. BRINDLEY

sodium micas are rare, it seems most likely that the layers are bound by the (K+Ca) ions which together furnish about the right number of electrons.

The absence of a peak at $c/2$, which is confirmed by the subsequent fourier syntheses, shows that the cations not accommodated at $z=0$ do not occur at $z=c/2$. All the evidence points to an absence of cations at this level.

(b) *Allevardite after heat-treatment at 900° C.*

Lattice spacings and structure factors are tabulated in Table 3 and the electron distribution is shown by the dotted line in Fig. 1. The main

TABLE 4. X-RAY DATA FOR ALLEVARDITE (AIR-DRY, UNTREATED MINERAL)

$\lambda(CuK\alpha) = 1.5418$ Å

l	$d(00l)$ Å	$d(001)$ Å	$|F|_{obs}$	F_{calc}
1	24.21	24.21*	45.4	45.5
2	12.28	24.56*	41.4	−43.8
3	8.27	24.81*	3.7	−13.8
4	6.16	24.64	4.7	− 1.3
5	4.941	24.70	36.0	−29.0
6	4.086	24.52	tr.	1.0
7	3.520	24.64	19.7	−17.2
8	3.089	24.71	65.4	−57.6
9	2.722	24.50	6.4	5.5
10	—	—	0.	1.4
11	2.240	24.64	14.1	−13.2
12	2.053	24.64	23.6	17.2
13	1.899	24.69	38.8	41.8
14	1.768	24.75	9.0	9.2
15	—	—	0.	− 1.4
16	1.542	24.67	16.2	16.9
17	1.446	24.58	5.4	− 5.1
18	1.370	24.66	18.0	−23.9
19	1.301	24.72	9.6	− 7.2
20	1.234	24.68	11.3	16.2
21	1.175	24.67	11.0	11.9
26	0.9469	24.62		

Mean $d(001)$ 24.65± .05

Other values $\begin{cases} 24.62 \pm .02 \\ 24.58 \pm .05 \end{cases}$

Overall mean value: 24.62±0.05

* Values not incorporated in the average value.

F values correspond to one-quarter of the unit-cell content.

effect of heating at the higher temperature is a diminution of the peaks associated with (4 O+2 OH), which can be attributed to dehydroxylation. If 4 O+2(OH) becomes 5 O+H_2O, a diminution of the O, OH peak by one-sixth of its electron content would be expected and this is consistent with the fourier synthesis. Muscovite mica has recently been studied by the writer and Mr. Vanden Heuvel in a similar way and similar results have been obtained.

(c) *Allevardite under normal air-dry conditions, without heat-treatment.*

The basal spacings and structure factors are listed in Table 4. The parameters for the atomic layers and the number of H_2O molecules per layer were determined by repeated fourier syntheses; the final parameters are given in Table 5, and the fourier syntheses in Fig. 2. The analysis shows about 12 electrons/unit cell at $z=0$ (thus confirming the result obtained with the 560° C. heated material), 2 H_2O molecules per unit cell at $z=10.85$ Å and an absence of atoms at $z=c/2$ (12.31 Å). The slightly poorer resolution of the peaks in Fig. 2 than in Fig. 1, arises from the fact that the highest order reflection used for the air-dry natural mineral, the 21st order, has a d-value of 1.175 Å whereas for the 560° C. heated material a 22nd order was used with a d-value of 0.874 Å.

(d) *Allevardite in other states of hydration.*

Allevardite after 1:10 HCl treatment, with one layer of water molecules between the silicate layers, was examined by fourier synthesis and the results confirm the presence of cations containing about 12–15 electrons/unit cell between the silicate layers and one water layer at

TABLE 5. z PARAMETERS OF ATOMIC LAYERS IN ALLEVARDITE, IN Å

Natural air-dry material		Mineral heated to 560° C.		Ethylene glycol allevardite	
$z=c/2$*	12.31	$z=c/2$*	9.62	$z=c/2$*	13.24
				$1\frac{1}{2}$ CH_2OH	12.06
				$1\frac{1}{2}$ CH_2OH	11.03
2 H_2O	10.85				
6 O	8.02	6 O	8.13	6 O	7.96
4 Si, Al	7.42	4 Si, Al	7.48	4 Si, Al	7.37
6 O, OH	5.83	6 O, OH	5.88	6 O, OH	5.75
4 Al	4.76	4 Al	4.81	4 Al	4.75
6 O, OH	3.69	6 O, OH	3.74	6 O, OH	3.75
4 Si, Al	2.10	4 Si, Al	2.14	4 Si, Al	2.13
6 O	1.50	6 O	1.49	6 O	1.54
0.7 K, Ca*	0	0.7 K, Ca*	0	0.7 K, Ca*	0

* Indicates a symmetry centre for the layer sequence.
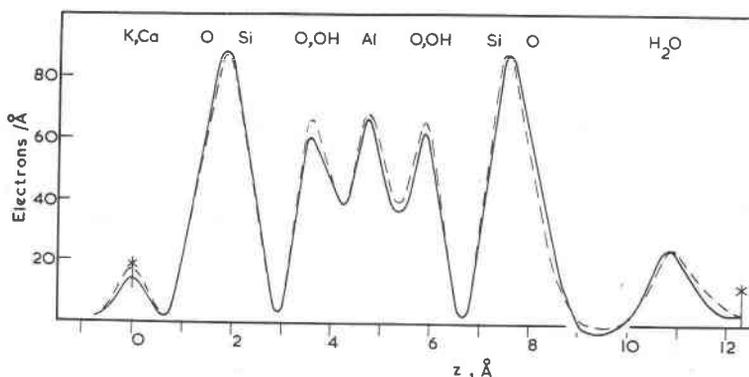
FIG. 2. Electron density distribution in natural air-dry allevardite; full line based on experimental structure factors, dashed line on calculated structure factors. Symmetry centers marked *. Note that the water layer is duplicated by the symmetry center at $z=12.31$ Å.

$z=c/2$ containing 2 water molecules/unit cell. Water wet flakes containing three water layers between the silicate layers were not suitable for accurate intensity measurements and fourier synthesis was not attempted.

DISCUSSION OF THE HYDRATION STATES OF ALLEVARDITE; COMPARISON WITH VERMICULITE

Figure 3, (a), (b), (c) and (d), represents diagrammatically the distribution of water layers in the four hydration states. In case (a), fourier
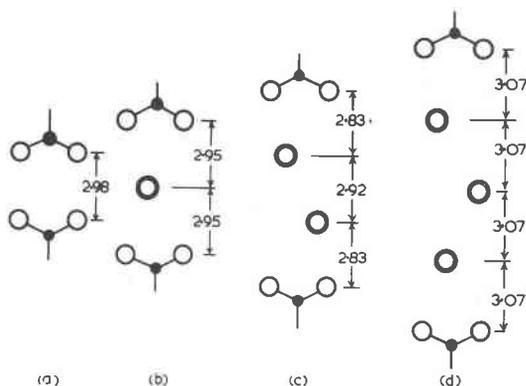
FIG. 3. Diagrammatic representation of the four hydration stages of allevardite. Heavy circles represent layers of water molecules, light circle oxygen atoms and small black circles silicon atoms.

synthesis has shown that the interlayer space at $z = c/2$ occupies 2.98 Å between centers of oxygen atoms. In case (b), if the silicate layer (about 16.1 Å thick) is substracted from $d(001) = 22.00$ Å, the interlayer space is 5.9 Å wide and the oxygen-water separation is 2.95 Å. In case (c), fourier synthesis has given the layer separations, $O - H_2O = 2.83$ Å, $H_2O - H_2O = 2.92$ Å. In case (d), we obtain after subtracting 16.1 Å from $d(001)$, 28.38 Å, a value 12.3 Å, i.e., 3.07 Å for the average $O - H_2O$ and $H_2O - H_2O$ layer separations. These separations lie within ±0.1 Å of an average value 2.95 Å.

Comparison can be made with the results obtained for the interlayer region of vermiculite by Mathieson and Walker (1954) and independently by Grudemo (1954). Vermiculite normally contains two water layers between alumino-silicate layers, and the exchangeable cations (mainly Mg in the naturally occurring mineral) lie between the water layers. Mathieson and Walker give the following layer separations, $O - H_2O = 2.84$ and $H_2O - H_2O = 2.14$. Grudemo obtains similar results. The $O - H_2O$ separation is about the same in vermiculite as in allevardite, but the $H_2O - H_2O$ layer separation is considerably less in vermiculite due to the presence of cations between the water layers. The near equality of the $O - H_2O$ and $H_2O - H_2O$ separations in allevardite is consistent with an absence of cations between the water layers, as shown by the fourier syntheses. The layer density of water molecules in vermiculite is about 4.3 H_2O per layer as compared with only 2 H_2O per layer in allevardite.

Comparison can also be made with the weight-loss measurements made by Caillère *et al.* (1950). The smaller inflections in their weight-loss versus temperature curve have no obvious structural significance, but the main 'plateaux' can be correlated with the loss of interlayer water and of hydroxyl radicals. From 200°–500° C., the weight loss is roughly constant at about $7 ± 1\%$, and from 750°–950° C. is constant at 12.8%. These weight losses, which refer to air-dry material at room temperature, will include surface adsorbed water. There is no break in the weight-loss curve at about 100° C. which would enable a distinction to be made between surface water and internal water, but if we take the weight loss at 100° C., namely 2.5%, as representing the surface water, we obtain weight losses of $4.5 ± 1.0\%$ for the range 200°–500° C. and 10.3% for the range 750°–950° C. For a mineral with two water layers each containing 2 H_2O per unit cell, a loss of 4 H_2O is equivalent to a 4.6% weight loss and dehydroxylation gives a further weight loss of 6.0%, or total loss of 10.6%. These values agree well with those obtained from the weight loss measurements.

ORGANIC COMPLEXES OF ALLEVARDITE

Caillère *et al.* (1950) showed that allevardite expands in glycerol in a manner similar to montmorillonite. In view of the precision with which the hydrated complexes could be measured, a similar study was made of complexes with dihydric alcohols. Table 6 lists results for six organic com-

TABLE 6. LATTICE SPACINGS, IN Å, OF SOME CLAY-ORGANIC COMPLEXES

1	2	3	4	5
Organic liquid	Allevardite	(2)–(4)	Mont-morillonite	Stevensite
1.2 ethane diol (ethylene glycol)	26.47±0.06	9.77	16.70	17.0
1.3 propane diol	27.72±0.04	9.56	18.16	18.2
1.4 butane diol	27.19±0.07	—	—	17.3
1.5 pentane diol	27.14±0.03	9.71	17.43	18.0
1.12 polyethylene	26.73±0.10	9.62	17.11	17.3
diethylene glycol	25.42±0.04	10.07	15.35	16.7

plexes of allevardite, together with similar data for montmorillonite (a sample from Cadouin, France) and for stevensite, a montmorillonite type mineral (see Faust and Murata, 1953; Brindley, 1955). Although the number of carbon atoms in the organic molecules increases from 2 to 12, the lattice spacings remain roughly constant, in agreement with similar observations by Bradley (1945) and by MacEwan (1948). There is an obvious similarity in the general trend of the three sets of results. In every case 1.3 propane diol gives the largest expansion. MacEwan (1948, p. 359) has commented on this result and attributed it to "the extra space taken up by the central CH_2 group." With further increase in the number of carbon atoms, the spacing progressively diminishes.

A fourier synthesis of ethylene glycol allevardite, Fig. 4, shows the same alumino-silicate layers and bonding cations at $z=0$ as the previous syntheses. In addition a broad peak corresponding to one layer of ethylene glycol occurs which appears to have two maxima at about 11.0 Å and 12.0 Å. The symmetry centre at $z=c/2$ duplicates this peak, so that there are two layers of ethylene glycol separating silica layers. From the electron content of the organic peak, there are about $1\frac{1}{2}$ molecules per layer per unit cell, which agrees with values previously given by Mac-Ewan (1948, p. 359) and by Mackenzie (1948). The double peak in the electron distribution suggests that the (OH) groups lie at two levels. If we picture a zig-zag molecule with the plane of the zig-zag at right angles to the basal plane (see inset to Fig. 4), the vertical displacement
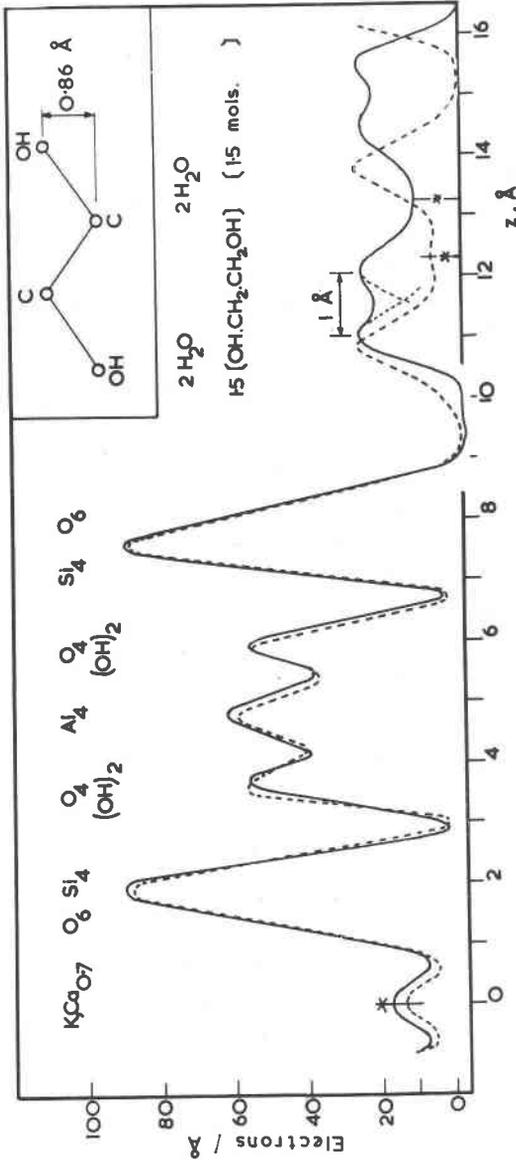
FIG. 4. Electron density distributions of ethylene glycol allevardite (full line) compared with allevardite with two water layers (dashed line). Inset shows zig-zag form of the ethylene glycol molecule. The electron distributions are continued beyond the symmetry centers, *, to show the two layers of water and of ethylene glycol.

TABLE 7. X-RAY DATA FOR ETHYLENE GLYCOL ALLEVARDITE

$\lambda(\text{CuK}\alpha) = 1.5418$ Å

l	$d(00l)$ Å	$d(001)$ Å	$\|F\|_{obs}$	F_{calc}
1	25.6	25.6*	49.0	47.5
2	13.0	26.0*	35.2	−35.2
3	8.76	26.28	20.8	−16.0
4	6.63	26.52	17.9	9.8
5	5.29	26.45	31.1	−23.5
6	4.42	26.52	20.8	−19.0
7	3.777	26.44	15.3	12.6
8	3.314	26.51	65.0	−58.9
9	2.945	26.50	39.7	−37.8
10	2.652	26.52	14.7	9.4
11	—	—	—	5.7
12	2.206	26.47	11.1	−15.1
13	2.040	26.52	30.5	23.7
14	1.895	26.53	39.7	46.6
15	1.768	26.52	9.3	15.3
16	—	—	—	− 7.0
17	1.558	26.48	16.9	13.1
18	—	—	—	2.1
19	1.395	26.50	16.2	−16.4
20	1.325	26.50	15.7	−18.4
21	—	—	—	0.8
22	1.2055	26.52	14.4	27.1

Mean 26.51 ± 0.02
Other values: 26.48 ± 0.02
              26.37 ± 0.08

* Values not incorporated in the mean value.

F values correspond to one-quarter of unit cell content.

of the (OH) groups is about 0.85 Å, and a slight tilt of the molecule would increase this separation to about 1 Å.

The evidence is fairly strong that the plane of the zig-zag of the glycol molecules does not lie parallel to (001) for if the molecules were so arranged, then the electron density peaks would be sharper than those observed. Table 7 compares the observed and calculated structure factors. The best agreement is obtained by dispersing the scattering matter of the organic molecules through a range of z-values ranging from about 11.0 to 12.0 Å. The parameters used in calculating the structure factors for this organic complex are listed in Table 5, where it is seen that $1\frac{1}{2}$ molecules of $OH \cdot CH_2 \cdot CH_2 \cdot OH$ are split equally between two levels at about 11.0 and 12.0 Å.

Figure 4 compares the electron distribution in normal allevardite with two water layers (dashed line) and ethylene glycol allevardite with two organic layers (full line). It is evident that the water layers are much more sharply defined than the organic layers and that the organic peak is about twice as large as the water peak.

REFERENCES

BRADLEY, W. F. (1945), Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Am. Chem. Soc.*, **67**, 975–981.

BRINDLEY, G. W. (1955), Stevensite, a montmorillonite-type mineral showing mixed-layer characteristics: *Am. Mineral.*, **40**, 239–247.

CAILLÈRE, S. (1934), Observations sur la composition chemique des palygorskites: *C. R. Acad. Sci., Paris*, **193**, 1795.

CAILLÈRE, S. (1936), Études de quelques silicates magnesiens à facies asbestiform ou papyracé n'appartenant pas au groupe de l'antigorite: *Bull. Soc. Franç. Min.*, **59**, 353–374.

CAILLÈRE, S., MATHIEU-SJCAUD, A., AND HÉNIN, S. (1950), Nouvel essai d'identification du minéral de La Table pres Allevard, l'allevardite: *Bull. Soc. Franç. Min. Crist.*, **73**, 193–201.

DÉRIBÉRÉ, M. (1943), Le minéral papyracé de La Table (Savoie): *Bull. Soc. Franç. Min.*, **66**, 222–237.

FAUST, G. T., AND MURATA, K. J. (1953), Stevensite, redefined as a member of the montmorillonite group: *Am. Mineral.*, **38**, 973–987.

GRUDEMO, A. (1954), An x-ray examination of the structure of vermiculite: *Sven. Forsk, f. Cement o. Betong, Handl. Nr.*, **22**, 1–56.

HÉNIN, S., ESQUEVIN, J., AND CAILLÈRE, S. (1954), Sur la fibrosité de certains minéraux de nature montmorillonitique: *Bull. Soc. Franç. Min. Crist*, **77**, 491–499.

JACKSON, W. W., AND WEST, J. (1930), The crystal structure of muscovite: *Z. Krist.*, **76**, 211–227; (1933), **85**, 160–164.

LEMOINE, E. (1935), Sur un nouveau minéral trouvé dans les calcaires bajociens de La Table: *Bull. Soc. Hist. Nat., Savoie*, **23**, 199–202.

MACEWAN, D. M. C. (1948), Complexes of clays with organic compounds, I: *Trans. Faraday Soc.*, **44**, 349–367.

MACKENZIE, R. C. (1948), Complexes of clays with organic compounds, Part II: *Trans. Faraday Soc.*, **44**, 368–375.

MATHIESON, A. McL., AND WALKER, G. F. (1954). Crystal structure of magnesium-vermiculite: *Am. Mineral.*, **39**, 231–255.