

## THE CRYSTAL STRUCTURES OF PYROPHYLLITE, 1Tc, AND OF ITS DEHYDROXYLATE

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### ABSTRACT

The crystal structures of one-layer triclinic pyrophyllite and of its dehydroxylate have been determined by X-ray powder diffraction analysis. The structures have been refined by utilizing crystal-chemical information on layer silicates generally, by comparing observed and calculated reflected intensities, and also by comparing experimental and computer-simulated diffractometer patterns. A modified reliability factor  $R'$  has been calculated for the final structures;  $R' = 10.6\%$  for pyrophyllite and  $11.2\%$  for the dehydroxylate. The Al ions in the dehydroxylate structure are in positions of five-fold coordination to oxygen with a mean Al-O distance of  $1.82 \text{ \AA}$ ; the coordination group approximates to a trigonal bipyramid. The dehydroxylation reaction is considered to be a homogeneous reaction with  $2(\text{OH})^-$  becoming  $\text{H}_2\text{O} + \text{O}^{2-}$ , and with the residual oxygen ions located at the Al level in the layer structure. The suggested structure is consistent with the 00 $l$  synthesis, with the observed reflected intensities and the diffractometer pattern, and with the  $\text{AlK}\alpha$  fluorescent wavelength.

### INTRODUCTION

Structure analyses of a one-layer triclinic pyrophyllite, (pyrophyllite, 1Tc), and of its dehydroxylate have been undertaken by X-ray powder diffraction methods. The material, originating from the Coromandel region of New Zealand, (Swindale and Hughes, 1968), is highly crystalline but crystals sufficiently large for X-ray single crystal analysis were not available. An earlier survey of pyrophyllites from many localities (Brindley and Wardle, 1970) showed that two-layer monoclinic and one-layer triclinic varieties exist, sometimes as mixtures, and that the material now studied gave the best resolved X-ray powder pattern of the triclinic variety. The dehydroxylated phase also gave a well defined powder pattern, thereby making possible a detailed structure analysis of a dehydroxylated layer silicate. An X-ray single crystal analysis of monoclinic pyrophyllite by Rayner and Brown (1966) was handicapped by structural irregularities causing diffused reflections. The sharp powder patterns of the New Zealand material may have some advantages despite the limitations imposed by the powder diffraction technique.

### EXPERIMENTAL

Crushed powder passing a 200-mesh screen was used. Diffractometer powder patterns were recorded with Ni-filtered  $\text{CuK}\alpha$  radiation at  $1/4^\circ (2\theta)/\text{min}$  and

with  $1^\circ(2\theta)$ /inch chart paper, and were calibrated with respect to silicon powder ( $a = 5.43062 \text{ \AA}$  at  $21^\circ\text{C}$ ). Some recordings were made with  $\text{FeK}\alpha$  radiation. Also Debye-Scherrer powder photographs were recorded with  $\text{CuK}\alpha$  and with  $\text{CoK}\alpha$  radiations. For intensity data, side-packed samples were used (see Brindley and Wardle, 1970). Overlapping reflections were resolved graphically and intensities obtained by measurement of the resolved areas. Basal intensities were recorded from samples oriented from a slurry. Dehydroxylations were carried out to constant weight in platinum thimbles in air at temperatures ranging from  $550^\circ\text{C}$  (500 hr) to  $950^\circ\text{C}$  (5 hr). The diffractometer traces show no differences in samples fully dehydroxylated over this temperature range.

## STRUCTURE ANALYSIS

*Unit Cells*

The unit cell parameters of pyrophyllite, 1Tc and its dehydroxylate phase previous reported (Brindley and Wardle, 1970) have been refined by the least squares refinement computer program due to Evans, Appleman, and Handwerker (1963), with the following results:

	Pyrophyllite, 1 Tc	Pyrophyllite, 1 Tc, dehydroxylate
<i>a</i>	$5.161_4 \pm 0.001_6 \text{ \AA}$	$5.191_0 \pm 0.001_3 \text{ \AA}$
<i>b</i>	$8.957_6 \pm 0.002_2$	$9.122_4 \pm 0.001_4$
<i>c</i>	$9.351_1 \pm 0.001_5$	$9.499_0 \pm 0.001_5$
$\alpha$	$91.03^\circ \pm 0.02$	$91.17^\circ \pm 0.02$
$\beta$	$100.37^\circ \pm 0.02$	$100.21^\circ \pm 0.02$
$\gamma$	$89.75^\circ \pm 0.02$	$88.62^\circ \pm 0.02$
<i>V</i>	$425.2_1 \pm 0.1_3 \text{ \AA}^3$	$442.5_8 \pm 0.1_1 \text{ \AA}^3$

These data differ only slightly from those previously given but the departure of  $\gamma$  from  $90^\circ$  is an interesting result. In particular it provides indexing for a reflection from the dehydroxylate for which no indices were found previously with  $\gamma = 90^\circ$  (see Brindley and Wardle, 1970, p. 1266).

*Idealized Structure of Pyrophyllite, 1Tc*

Previous work has shown that pyrophyllite has a 2:1 layer structure, with a dioctahedral Al, O(OH) sheet between two Si, O tetrahedral sheets. The structural arrangement can be developed with the Al ions at the zero level with respect to *c* in the unit cell and in conformity with a *C*-centered cell. In the ideal model, close packed planes of O, OH anions are placed above and below the level of Al ions. The possible arrangements within a one-layer cell (see Fig. 1) are obtained as follows: Three possible octahedral cation sites are occupied by 2 Al and one vacancy, the latter occupying one of the



1 = (1, 1'), 2 = (1, 2'), 3 = (1, 3'), 4 = (2, 1'), 5 = (2, 2'), 6 = (2, 3'), 7 = (3, 1'), 8 = (3, 2') and 9 = (3, 3'), and each combination has the A or the B anion plane arrangement. Preceding each arrangement 1, 2, ... 9, a symbol I, II, III, denotes the vacant cation site.

The ideal layer structure conforming most closely with the observed diffraction intensities was determined by calculating the intensities for the first twenty reflections of the 54 possible ideal structures using a computer program written by Smith (1963, 1967). The atomic scattering factors built into the computer program were from self-consistent field calculations for  $Al^{3+}$  and  $Si^{4+}$  and from a Suzuki curve for  $O^{2-}$ ; a temperature factor  $B = 1.0$  was used for all atoms. The results showed that only 12 different intensity distributions resulted from the 54 arrangements. Table 1 shows the equivalent Al, OH arrangements, each of which has the A and B arrangement of O, OH anion planes. Of these twelve arrangements, one gives an intensity distribution considerably nearer than the others to the observed data, namely the equivalent structures I2A, II7A, and III6A. The detailed intensity data are given elsewhere (Wardle, 1972). Projections of these equivalent structures on (001) show that they differ only in the position of the origin along the  $b$  axis. Arrangement I2A has a center of symmetry at the origin.

#### *Refined Structure of Prophyllite, 1Tc*

The idealized structure has been refined by a trial and error process on the basis of (i) the known crystal-chemical characteristics of 2:1 type layer silicates, and (ii) the fit between observed and calculated X-ray diffracted intensities, and observed and calculated diffractometer patterns.

As shown by Radoslovich and Norrish (1962), a more nearly correct

Table 1

#### Equivalent aluminum, hydroxyl arrangements

I, 1 = I, 5 = II, 1 = II, 9 = III, 5 = III, 9

I, 3 = I, 8 = II, 4 = II, 8 = III, 3 = III, 4

I, 6 = I, 7 = II, 2 = II, 6 = III, 2 = III, 7

I, 2 = II, 7 = III, 6

I, 4 = II, 3 = III, 8

I, 9 = II, 5 = III, 1

layer model is obtained by rotating the  $\text{SiO}_4$  groups in each hexagonal ring about  $c^*$  alternately in opposite directions so that the basal hexagonal ring becomes ditrigonal. The magnitude of this rotation can be estimated from the observed  $b$  parameter, an assumed value for the Si-O distance, 1.62 Å, and a regular tetrahedral geometry. For a given pair of  $\text{SiO}_4$  tetrahedra, one in the upper and one in the lower tetrahedral sheet, the rotations may be in the same or in opposite directions, and can be denoted by (+, +), (+, -), (-, +), (-, -). The basal oxygen positions were modified by rotations of  $\pm 10^\circ$  for each of these four schemes and the intensities were calculated for the first thirty reflections of the I1A,  $\dots$ , I9A structures. The results showed that the I2A and equivalent structures gave the best fit with the observed intensities with rotations (+, -), i.e., in opposite directions for the two tetrahedral sheets; the sense of the rotations is indicated in Figure 2.

For dioctahedral layer structures, it is well established (see survey by Bailey, 1966) that the Al, O(OH) dioctahedral sheets depart from the ideal arrangement depicted in Figure 1 principally in the following ways: the shared octahedral edges are shortened causing a counter-rotation of upper and lower O, OH triads, and the sheet thickness is modified so that the sheet dimensions parallel to (001) conform with the  $a$  and  $b$  parameters. It appears also that the aluminum ions do not depart from the hexagonal arrangement depicted in Figure 1. If each triad  $\text{O}_2\text{OH}$  of octahedral anions lies parallel to (001) with equal O-O and O-OH distances, then their coordinates can be related to two parameters, namely the Al-O, OH bond length and the octahedral sheet thickness.

In the first stage of refinement, the octahedral sheet thickness was held constant at the value 2.14 Å given by Rayner and Brown (1966), and the Al-O, OH bond length was varied to give projections on (001) ranging from 1.55-1.65 Å thereby covering the likely value of the bond length. Each projected distance gives possible positions for the O, OH anions, and the ideal model already selected enables the individual O and (OH) ions to be identified. The oxygen ions are the apical oxygens of the tetrahedral sheets and must be bridged by Si-O-Si bonds. When the tetrahedra are assumed to be regular with Si-O = 1.62 Å, this bridging of the apical oxygens imposes twists and tilts on the tetrahedra and also severe limitations on the projected Al-O, OH lengths which must lie in the range 1.63-1.64 Å. The twists of the tetrahedra derived from this geometrical approach are of the same magnitude,  $\pm 10^\circ$ , and in the same sense as those already obtained.

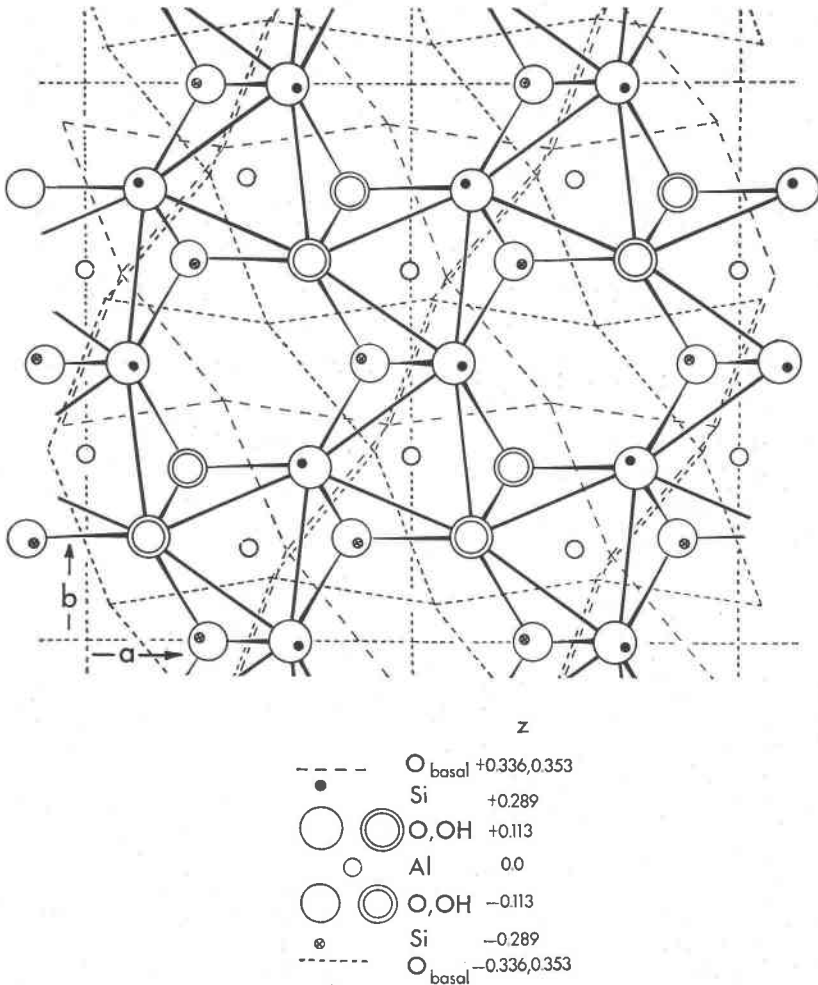


Fig. 2. Layer structure of pyrophyllite projected on (001).

Ideally the thickness of the octahedral sheet should be determinable from an  $00l$  synthesis but with 007 as the highest observable basal reflection the synthesis did not provide sufficient accuracy. Accordingly diffracted intensities were calculated for structures with octahedral sheet thicknesses ranging from 2.14 to 2.02 Å and a value 2.08 Å was selected which agrees well with the data collected by Bailey (1966). An isotropic temperature factor  $B$  was used for all atoms; values of  $B = 0.5, 1.0,$  and  $1.5$  were used and  $B = 1.0$  gave a slightly better fit to the experimental data than the other two. The calculated intensities

TABLE 2. X-RAY POWDER DATA FOR PROPHYLLITE, ITC. OBSERVED AND CALCULATED SPACINGS, Å, AND OBSERVED AND CALCULATED RELATIVE INTENSITIES; REFLECTIONS OMITTED WITH  $I(\text{CALC}) \leq 0.5$ .

hkl	d(calc)	I(calc)	d(obs)	I(obs)	hkl	d(calc)	I(calc)	d(obs)	I(obs)	hkl	d(calc)	I(calc)	d(obs)	I(obs)
001	9.197	95	9.20	90	221	2.234	1	2.222	1	241	1.6827	1	1.6827	1
002	4.598	31	4.60	32	220	2.209	1	2.209	1	240	1.6802	4	1.6802	4
110	4.419	11			114	2.193	1	2.195	1	240	1.6782	4	1.6777	12
110	4.415	90	4.42	100	132	2.175	11	2.172	14	283	1.6775	4		1.472
111	4.268	64	4.26	80	114	2.175	9	2.172	14	151	1.6736	1		
111	4.231	19	4.23		203	2.155	9	2.152	18	283	1.6666	1		
021	4.054	81	4.06	55	132	2.151	13	2.116	2	310	1.6638	2		
111	3.768	9			222	2.116	3	2.116	2	312	1.6628	1	1.661	12
111	3.749	4	3.765	8	133	2.084	14	2.063	15	310	1.6626	3		
112	3.487	16	3.490	6	221	2.078	2	2.063	15	312	1.6583	5		
112	3.450	10	3.454	6	221	2.072	2	2.070	15	134	1.6528	8	1.650	12
022	3.181	36	3.178	22	202	2.070	13	2.070	15	242	1.6500	1	1.650	12
003	3.066	82	3.068	85	024	2.060	3	2.054	16	151	1.6482	2		
112	2.973	1			133	2.049	13	2.026	3	205	1.6359	8		
112	2.952	26	2.953	17	024	2.031	2	2.026	3	134	1.6310	9	1.633	20
113	2.740	6	2.741	5	042	1.9994	5	1.998	3	152	1.6268	2		
130	2.575	8	2.710	8	223	1.9520	2	1.952	1	241	1.6210	2	1.621	2
130	2.572	8			133	1.9005	5	1.900	4	152	1.6078	2	1.607	2
131	2.551	23			204	1.8809	5	1.883	4	115	1.6066	2		
023	2.551	3	2.547	27	133	1.8758	2	1.875	4	311	1.5885	2	1.585	4
200	2.539	22	2.532	36	222	1.8743	1	1.875	4	313	1.5867	3	1.585	2
131	2.528	25			005	1.8394	11	1.841	12	152	1.5633	2	1.565	2
131	2.430	24			043	1.8234	5	1.823	2	152	1.5483	1	1.544	2
202	2.414	24	2.416	77	115	1.8074	3	1.812	3	243	1.5425	4	1.544	2
131	2.360	8			224	1.7436	3	1.744	2	225	1.5286	3	1.532	3
132	2.356	4			224	1.7248	1	1.722	1	242	1.5249	2	1.514	1
113	2.344	4	2.341	4	025	1.7120	1	1.689	12	153	1.5069	1	1.505	1
201	2.341	5			241	1.6928	4	1.691	1	331	1.4935	14	1.493	30
132	2.321	3	2.322	2	311	1.6909	1	1.689	12	060	1.4927	15		
204	2.299	4	2.300	5	150	1.6896	2	1.689	12	331	1.4878	14		
					151	1.6850	2	1.686	10	224	1.4863	1	1.487	10
								1.4834	1	312	1.4834	1		
								1.4811	1	312	1.4811	1		

for the optimum arrangement are given in the form of a comparison of observed and calculated intensities (Table 2), and also, following Smith (1968), as a comparison of the observed and computer-simulated diffraction patterns; the latter was drawn using a Calcomp Plotter (Figure 3).

The finally selected atomic coordinates which are consistent with a center of symmetry at the origin, the interatomic distances, and the bond angles are given in Table 3. Figure 2 shows a projection of the layer structure on (001), with the basal oxygen networks indicated by dashed lines. The rotations of the  $\text{SiO}_4$  groups away from the hexagonal arrangement are readily seen and are in opposite senses, as stated earlier. The angle of rotation measured from the projection is  $\pm 10^\circ$ . The tilt of the tetrahedra, indicated by the positions of the silicon atoms with respect to the apical oxygens, is close to  $4^\circ$ . Figure 4 shows a projection of adjacent basal oxygen networks viewed along  $c^*$  and the  $z$ -parameters of the oxygens are indicated.

#### *Analysis of Pyrophyllite, 1Tc, Dehydroxylate*

The similarity of the powder diffraction patterns of the initial

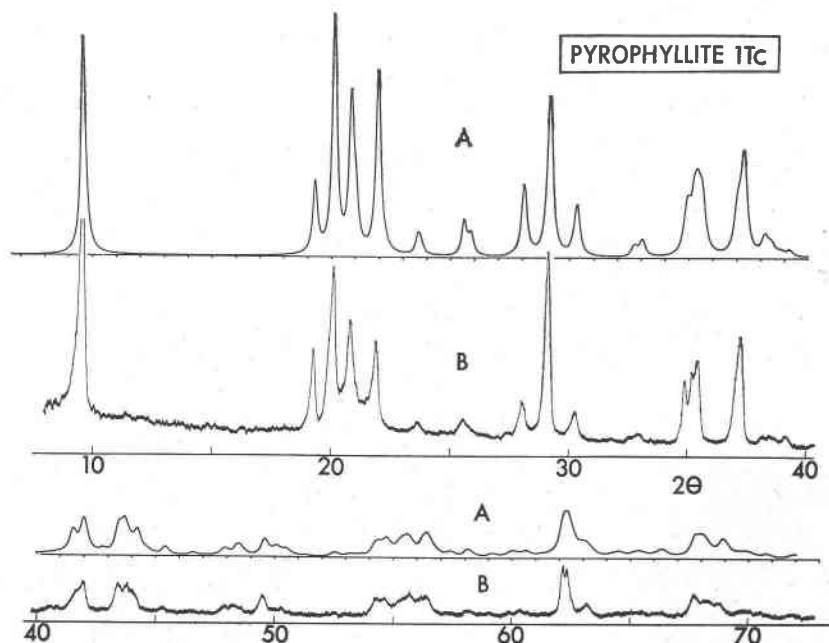


FIG. 3. Experimental (B) and computer-simulated (A) diffractometer patterns of pyrophyllite, 1Tc.



Table 3

Atomic Coordinates, Interatomic distances and angles for Pyrophyllite, 1Tc.

Atomic Coordinates  $x, y, z$ ;  $-x, -y, -z$ ;  $1/2 \pm x, 1/2 \pm y, z$ .

Center of symmetry at (0, 0, 0). Space group  $C\bar{1}$ .

O<sub>b</sub> signifies oxygens in basal networks; O are apical oxygens.

Atom	x	y	z	Atom	x	y	z
Al	0.500	0.167	0.000	OH	0.221	0.186	0.113
Si(1)	0.748	0.000	0.289	Ob(1)	0.055	0.387	0.353
Si(2)	0.759	0.331	0.289	Ob(2)	0.724	0.167	0.353
O(1)	0.671	0.004	0.113	Ob(3)	0.550	0.448	0.336
O(2)	0.721	0.319	0.113				

Interatomic distances, Å, and angles.

SiO<sub>4</sub> tetrahedra: mean Si-O, 1.62  
 mean O-O, 2.64; O-Si-O, 109.5°

AlO<sub>6</sub> octahedra: mean Al-O(OH), 1.94  
 O(OH) parallel to layers, mean O-O, 2.85; O-Al-O, 94°  
 O(OH) inclined to layers, mean O-O, 2.82; O-Al-O, 93°  
 shared octahedral edges, mean O-O, 2.49; O-Al-O, 80°

Interlayer distances: (Distances > 3.4Å are omitted)

Ob(1). . . Ob(6) correspond to oxygens labelled 1. . . .6 in Figure 4.  
 Ob(5), Ob(4) and Ob(6) are related by the center of symmetry to Ob(1),  
 Ob(2) and Ob(3) respectively.

Ob(1) - Ob(4), 3.37	Ob(2) - Ob(6), 3.12
Ob(2) - Ob(4), 3.07	Ob(3) - Ob(4), 3.12
Ob(2) - Ob(5), 3.37	Ob(3) - Ob(6), 3.32

mineral and of its dehydroxylate indicates that dehydroxylation produces only small structural changes. Two approaches to the structure analysis have been considered. (i) A direct approach examines the effect of the dehydroxylation on the 00*l* Fourier synthesis. (ii) An intuitive approach considers that adjacent pairs of (OH)<sup>-</sup> anions (see Figure 2) react to form O<sup>2-</sup> and H<sub>2</sub>O and that the residual O<sup>2-</sup> ions remain in the layer structure either distributed over the original (OH)<sup>-</sup> sites, or in midway positions at the *z*-level of the Al ions.

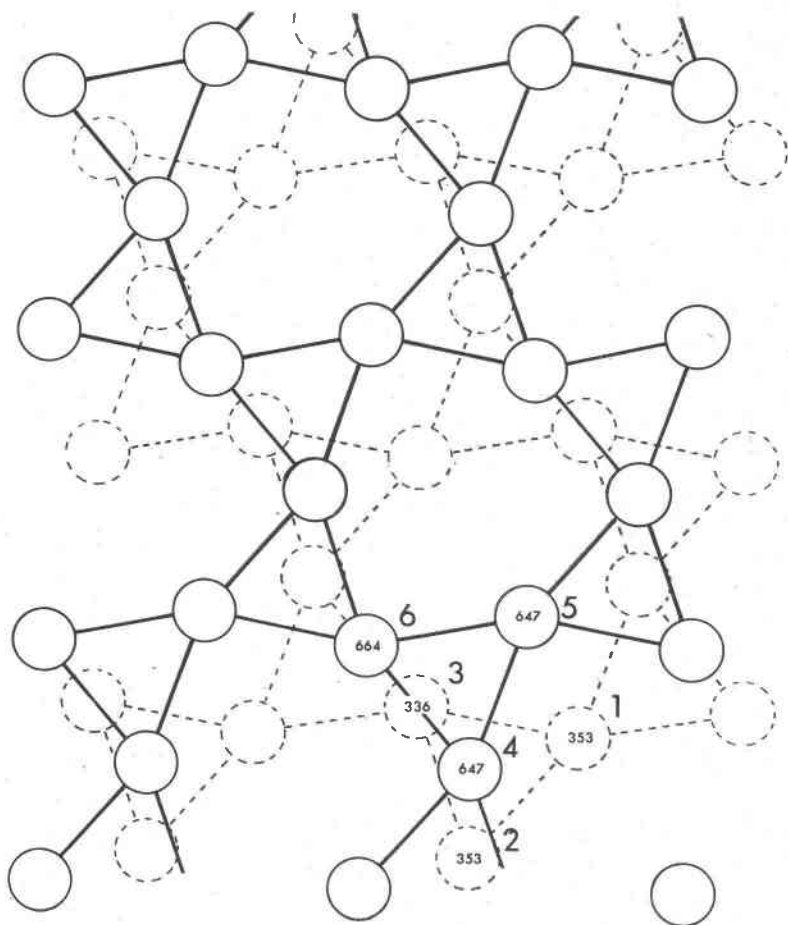


FIG. 4. Projection of adjacent basal oxygen networks viewed along  $c^*$ . Upper network solid circles, lower network dashed circles. Oxygens labelled 1, 2, ... 6 refer to Ob(1), ... , Ob(6) given in Table 3;  $z$ -coordinates ( $\times 1000$ ) are shown.

The  $00l$  syntheses of the initial and dehydroxylate forms of the mineral are shown in Figure 5. For the latter synthesis, the signs of  $F(00l)$  were taken first to be the same as those for the initial mineral. The resulting electron density curve showed a diminution of the electrons associated with the O, OH ions and a corresponding increase of electrons associated with the Al ions at  $z = 0$  which points to removal of OH ions and location of the residual oxygen at the  $z = 0$  level. This result is consistent with the intuitive approach mentioned earlier. Accordingly, the signs of  $F(00l)$  were recalculated with pairs of  $(\text{OH})^-$

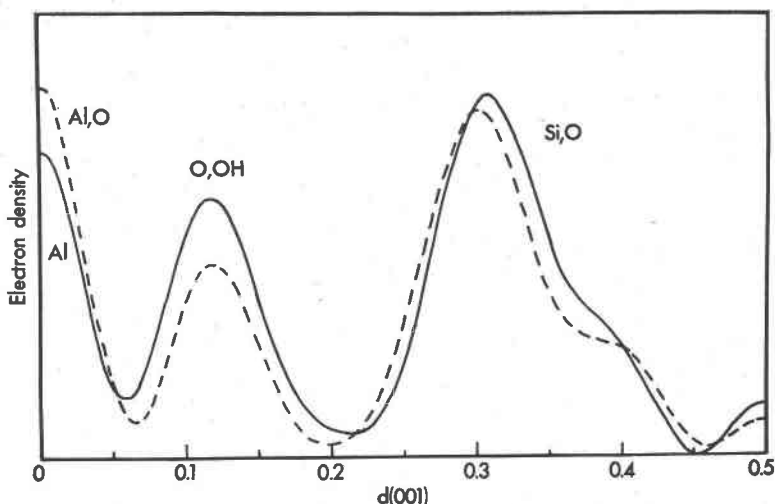


FIG. 5. One-dimensional Fourier syntheses of pyrophyllite, full line, and its dehydroxylate, dashed line.

ions replaced by a residual  $O^{2-}$  ion located in the plane  $z = 0$ . Only the sign of  $F(004)$ , a weak reflection, required changing. The resulting Fourier synthesis is shown by the broken line in Figure 5. The resolved peak areas have been normalized with respect to 100 electrons in the combined  $Si_4O_6$  peak. For the initial pyrophyllite, 55 electrons are found in the  $O_4(OH)_2$  peak and 25 electrons in the  $\frac{1}{2}(Al_4)$  peak as compared with 60 and 20 respectively from the atoms involved. The total electrons, however, are 180 as expected. For the dehydroxylate, 36 electrons are found in the  $O_4$  peak and 32 electrons in the  $\frac{1}{2}(Al_4O_2)$  peak, as compared with the expected values 40 and 30 respectively; the total electrons are 168 as compared with 170 expected.

The model which emerges from the replacement of  $2(OH)^-$  ions by  $O^{2-}$  in a midway position involves a five-fold coordination of Al by oxygen. Supporting evidence for this model has been obtained from measurements of the  $AlK\alpha$  fluorescence wavelength which has been shown to vary almost linearly with the average Al-O distance in a number of crystals for which the average Al-O distances are accurately known (Wardle and Brindley, 1971). These measurements lead to an average Al-O distance of about 1.80 Å in pyrophyllite dehydroxylate as compared with 1.70–1.74 Å for  $Al^{IV}$  and 1.90–1.94 for  $Al^{VI}$ . Evidently a mean Al-O distance of 1.80 Å could correspond with  $Al^{IV}$  or with a 1:1 mixture of  $Al^{IV}$  and  $Al^{VI}$ . A mixture of four-fold and six-fold coordinated Al ions cannot be ruled out a priori, but since the

environments of all OH-OH pairs are identical in the pyrophyllite structure, it is not unreasonable to suppose that the residual oxygens also will have identical environments.

A detailed model has been developed with the residual oxygens in the Al plane at  $z = 0$ , with five Al-O distances of approximately 1.80 Å, and O-O distances in the range 2.35–3.10 Å. These conditions involved displacements of the Al ions towards the vacant octahedral sites and related movements of the O ions; also adjustments of the SiO<sub>4</sub> tetrahedra were necessitated by the movement of the apical oxygens and the assumed regular form and size of the tetrahedra. Various atomic coordinates were derived to conform with these requirements; those finally chosen as giving the best agreement between observed and calculated intensities (Table 4) and between observed and computer-simulated diffraction patterns (Figure 6) are listed in Table 5. The resulting structure has a center of symmetry and the coordinates in Table 5 are based on axes having the origin at the center of symmetry. The labelling of the basal oxygens Ob(1), . . . , Ob(6) in Table 5 is consistent with that used in Table 3 and Figure 4. Figure 7 shows the Al-O sheet of the dehydroxylate structure projected on (001). The basal oxygen networks are similar to those depicted in Figure 2 and therefore are omitted from Figure 7 in order to show more clearly the structure of the Al-O sheet. The relations between adjacent basal oxygen planes also are similar to those shown in Figure 4.

## DISCUSSION

### *Structure Reliability*

The reliability factor  $R = \sum |F(\text{obs}) - F(\text{calc})| / \sum F(\text{obs})$  is not applicable to the present analysis because of the many unresolved reflections. A similar factor  $R'$ , defined as follows, therefore has been used:

$$R' = \sum |I(\text{obs})^{1/2} - I(\text{calc})^{1/2}| / \sum I(\text{obs})^{1/2}$$

For unresolved groups of reflections,  $I(\text{obs})$  and likewise  $I(\text{calc})$  are the sums of the intensities of the unresolved reflections.

For the pyrophyllite 1Tc structure,  $R'$  based on the first thirty-one calculated reflections for the ideal structure is 24.0 percent. For the same reflections, with the tetrahedral groups rotated  $\pm 10$  degrees but with no change in the octahedral groups,  $R' = 17.8$  percent. For the final model, with modified octahedral and tetrahedral sheets,  $R'$  for all the reflections listed in Table 2 becomes 10.6 percent. For the de-

Table 4

X-ray powder data for pyrophyllite, 17c, dehydroxylate  
 Observed and calculated spacings,  $d_o$  and  $d_c$ , and observed and calculated relative  
 intensities; reflections with  $I(\text{calc}) \leq 0.5$  omitted.

hkl	$d(\text{calc})$	$I(\text{calc})$	$d(\text{obs})$	$I(\text{obs})$	hkl	$d(\text{calc})$	$I(\text{calc})$	$d(\text{obs})$	$I(\text{obs})$	hkl	$d(\text{calc})$	$I(\text{calc})$	$d(\text{obs})$	$I(\text{obs})$
001	9.347	36	9.35	36	220	2.248	1	2.249	1	241	1.7312	3	1.4882	3
	4.674	14	4.67	15	114	2.228	2	2.232	2	150	1.7290	3	1.480	1
002	4.497	6	4.49	7	041	2.223	1	2.222	7	085	1.7198	1	1.473	1
110	4.418	100	4.42	100	221	2.223	4	2.222	7	240	1.7186	2		
111	4.339	45	4.34	42	220	2.209	2			311	1.7074	1	1.464	3
111	4.239	30	4.24	31	041	2.206	1			150	1.7063	1		
021	4.185	53	4.13	36	132	2.199	7	2.201	10	311	1.6923	1	1.453	4
021	4.072	9	4.07	9	132	2.195	1			242	1.6864	1		
111	3.816	1		2	222	2.173	1			240	1.6835	6	1.433	2
111	3.788	1		2	222	2.170	1	2.171	2	134	1.6727	2	1.422	1
112	3.543	13	3.541	10	133	2.126	16	2.126	14	310	1.6677	2		
112	3.472	3	3.470	4	221	2.109	1			134	1.6638	5	1.407	7
022	3.291	2	3.294	2	021	2.094	4	2.091	7	152	1.6629	1		
022	3.237	11	3.235	12	202	2.091	5			312	1.6628	7		
003	3.116	61	3.117	60	133	2.070	5	2.072	6	205	1.6545	2	1.394	5
112	3.004	13	3.003	11	024	2.066	1	2.063	1	115	1.6340	2	1.383	2
113	2.740	3	2.741	2	042	2.036	4	2.035	3	241	1.6274	3		
131	2.610	8	2.611	7	223	1.9840	1			135	1.6071	1	1.368	2
130	2.589	5		7	114	1.9520	1	1.942	3	311	1.5955	1		
201	2.593	7	2.584	10	223	1.9396	2			204	1.5898	1		
200	2.554	6		6	222	1.9078	4	1.906	3	313	1.5870	1		
023	2.553	3	2.548	10	222	1.8938	2	1.893	1	153	1.5626	1	1.336	3
131	2.547	7		7	005	1.8695	3	1.869	2	006	1.5579	1		
131	2.470	11	2.469	15	043	1.8543	2	1.853	2	243	1.5504	3	1.336	3
131	2.448	7	2.440	14	115	1.8361	2	1.834	2	153	1.5250	1		
202	2.429	7		7	043	1.8256	1	1.820	1	060	1.5198	3		
132	2.407	2	2.406	3	115	1.8159	1			331	1.5195	2	1.519	7
201	2.360	3	2.353	1	224	1.7717	1			224	1.5020	1		
132	2.341	2	2.341	1	025	1.7356	1			330	1.4950	2		
										312	1.4987	1	1.497	7
										061	1.4962	2		
										314	1.4959	1		
										312	1.4923	2		

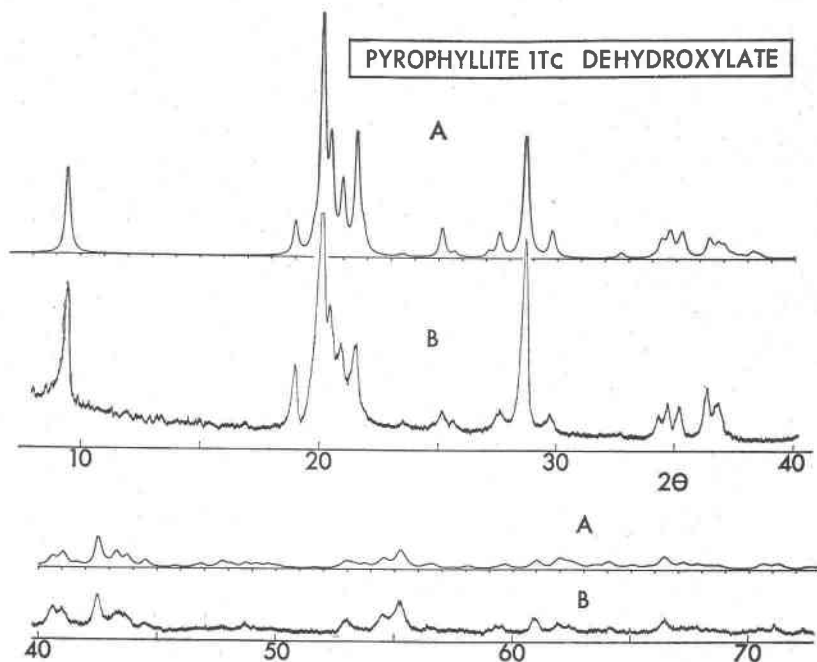


Fig. 6. Experimental (B) and computer-simulated (A) diffractometer patterns of pyrophyllite, 1Tc, dehydroxylate.

hydroxylate structure and using all the reflections listed in Table 4,  $R' = 11.2$  percent.

On the basis of these results, and the very close fit between the observed and the calculated diffractometer patterns, Figures 3 and 6, it is concluded that the derived structures approach the true structures. Further refinement on the basis of X-ray powder data is not warranted.

#### *The Structures of Pyrophyllite 1Tc and its Dehydroxylate*

In the case of pyrophyllite, the octahedral and tetrahedral sheets are similar to those of other dioctahedral layer silicates. Of particular interest are the interlayer relations illustrated in Figure 4. Because the  $\text{SiO}_4$  groups are tilted with respect to (001), one oxygen of each basal group of three is displaced within the layer defined by the other oxygens by  $0.017 \text{ \AA}$  and thereby produces corrugations running parallel to [110] on the basal oxygen surfaces. The corrugations of adjacent oxygen planes fit partially into each other (see Fig. 4) but it is questionable if this fit is the principal feature of the interlayer relations. There is a

marked tendency for oxygens of one layer to fit between two or three oxygens of the adjacent layer along lines parallel to  $[\bar{1}10]$ . This relationship may well be a consequence of attractions between  $\text{Si}^{4+}$  ions of one layer and the basal  $\text{O}^{2-}$  ions of the adjacent layer.

The twisting of the tetrahedral  $\text{SiO}_4$  groups through angles of  $\pm 10^\circ$  away from the ideal hexagonal arrangement is related approximately to the observed value of  $b$  by the relation  $\alpha = \cos^{-1}[b(\text{obs})/b(\text{ideal})]$ . In going from pyrophyllite to its dehydroxylate, the parameters  $a$  and  $b$  increase and it was suggested (Brindley, 1971) that the

Table 5

Atomic Coordinates, Interatomic distances and angles for Pyrophyllite,  
1Tc, dehydroxylate.

Atomic Coordinates.  $x, y, z; -x, -y, -z; 1/2 \pm x, 1/2 \pm y, z$ .

Center of symmetry at (0, 0, 0). Space group  $\bar{C}1$ .

Atom	x	y	z	Atom	x	y	z
Al	0.552	0.149	0.000	O(2)	0.728	0.292	0.115
Si(1)	0.225	0.486	0.286	Ob(1)	0.037	0.378	0.355
Si(2)	0.749	0.312	0.286	Ob(2)	0.717	0.152	0.355
Or	0.250	0.250	0.000	Ob(3)	0.522	0.425	0.320
O(1)	0.123	0.492	0.115				

Interatomic distances,  $\text{\AA}$ , and angles.

$\text{SiO}_4$  tetrahedra: mean Si-O, 1.62  
mean O-O, 2.65 O-Si-O,  $109.5^\circ$

$\text{AlO}_5$  trigonal bipyramid: Al-Or, 1.80  
mean Al-O, 1.82  
Or-(1) = Or-O(4), 3.11 Or-Al-O(1)(4),  $119^\circ$   
Or-(2) = Or-O(3), 2.57 Or-Al-O(2)(3),  $90^\circ$   
O(1)-O(2) = O(3)-O(4), 2.79 O(1), (3)-Al-O(2), (4),  $100^\circ$   
O(1)-O(3) = O(2)-O(4), 2.34\* O(1), (2)-Al-O(3), (4),  $80^\circ$   
O(1)-O(4), 3.18 O(1)-Al-O(4),  $123^\circ$   
O(2)-O(3), 3.66 O(2)-Al-O(3),  $180^\circ$

\* shared edge

Interlayer distances: (distances  $> 3.4\text{\AA}$  are omitted)

Ob(1)-Ob(4), 3.28 Ob(2)-Ob(5), 3.28 Ob(3)-Ob(4), 3.23  
Ob(2)-Ob(4), 3.22 Ob(2)-Ob(6), 3.23

O(3) and O(4) are related respectively to O(1) and O(2) by a center of symmetry,  
Ob(5), Ob(4) and Ob(6) are related similarly to Ob(1), Ob(2) and Ob(3).

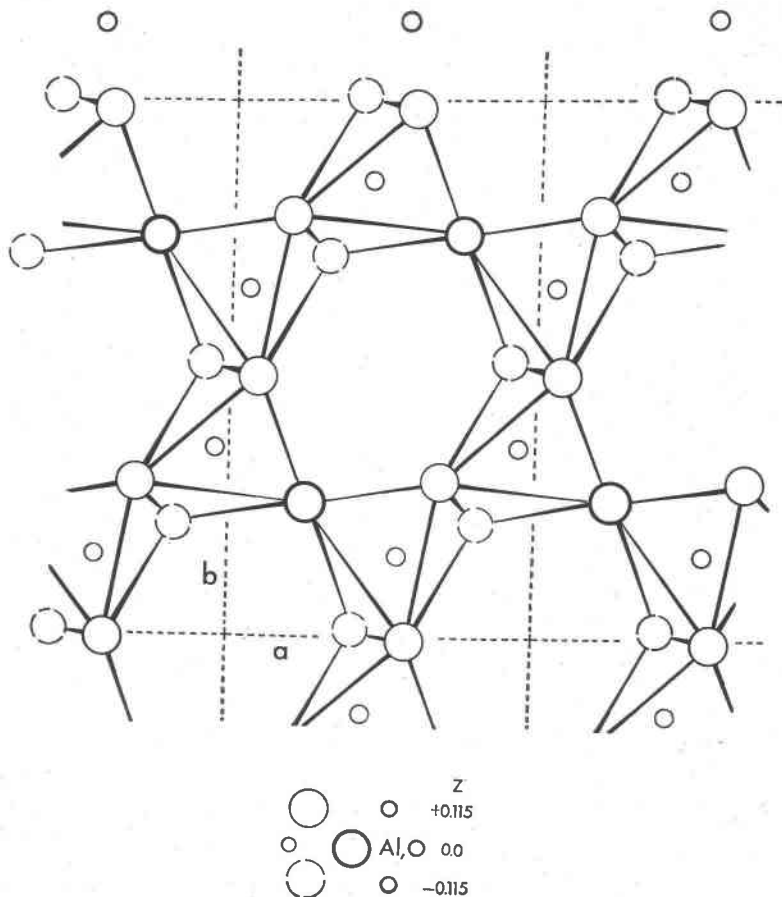


Fig. 7. The Al-O sheet of the dehydroxylate structure projected on (001).

increase indicated an untwisting of the tetrahedral sheets following the reorganization of the octahedral sheets. The present analysis indicates that the expansions arise largely from the rearrangement of the Al ions and the insertion of oxygen ions in the Al planes. Seen in projection on (001), the tetrahedral twists are not much changed.

The five-fold coordination of Al is an interesting result. Previous discussions involving pyrophyllite dehydroxylate (Heller *et al.*, 1962; Brett *et al.*, 1970) have mentioned the possibility of a five-fold coordination but definite evidence has been lacking. Heller *et al.* (1962) stated that infra-red evidence precludes four-fold coordination but "does not exclude five-fold coordination". The form of the five-fold group now found is approximately a trigonal bipyramid and is similar



to that found in andalusite (Taylor, 1929; Burnham and Buerger, 1961) for which the latter authors found an average Al<sup>V</sup>-O distance of 1.836 Å and a 'bent' pyramidal axis with O-Al-O = 162°. In the present case, essentially as a result of the geometrical approach to the problem, the axis is a straight line. The details of the Al coordination group found in the dehydroxylate are listed in Table 5; the average Al-O distance, 1.81<sub>8</sub> Å, is close to that found by Burnham and Buerger.

### *The Dehydroxylation Reaction*

There has been considerable argument (see review by Brett *et al.*, 1970) whether dehydroxylation of hydrous layer silicates proceeds by homogeneous or inhomogeneous processes. The reaction in pyrophyllite appears to be homogeneous with pairs of (OH)<sup>-</sup> ions reacting locally to form O<sup>2-</sup> and H<sub>2</sub>O. An inhomogeneous reaction is visualized as a migration of protons to favorable reaction sites with a counter-migration of cations, Al<sup>3+</sup> ions, to maintain electrical neutrality. On this hypothesis, oxygen ions are not lost from that part of the structure which forms the dehydroxylate, but only from reaction zones where they combine with protons to form water and liberate Al<sup>3+</sup> ions for counter-migration.

These mechanisms have been discussed particularly by Nicol (1964) in relation to a comparable problem involving the dehydroxylation of muscovite, which had been studied earlier by Eberhart (1963). The latter also obtained 001 syntheses of muscovite and its dehydroxylate, and concluded that a homogeneous reaction replaced 2(OH)<sup>-</sup> by O<sup>2-</sup> in the plane of the Al ions. Nicol (1964) criticized the conclusion of Eberhart and concluded that the inhomogeneous mechanism "explains the observed data at least as well as the homogeneous one". It is difficult to reconcile the inhomogeneous mechanism with a coordination of Al other than six-fold. The AlK<sub>α</sub> wavelength measurements clearly indicate a decrease in coordination; four-fold coordination is precluded by the infrared data. The available data, including the present structure analysis, all indicate a five-fold coordination and on this basis it is considered that the pyrophyllite dehydroxylation reaction (and probably also that of muscovite) is homogeneous.

The increase in *c* and *d*(001) on dehydroxylation is related partly to the increased tilt of the SiO<sub>4</sub> tetrahedra, which increases the effective thickness of each tetrahedral sheet by 0.037 Å, and partly to the increased thickness of the Al, O sheet by 0.071 Å. The total increase, 0.037 + 0.071 + 0.037 = 0.145 Å, in the layer thickness is about identical with the observed increase of 0.150 Å in *d*(001). In other

words, the separation of adjacent basal oxygens shows little change; the average separations of near basal oxygens in Table 3, (3.23 Å), and in Table 5, (3.25 Å) are nearly identical. The net result of the parameter changes is a 3.9 percent increase in unit cell volume with dehydroxylation.

In trioctahedral layer silicates, dehydroxylation generally occurs at higher temperatures than in dioctahedral silicates, and recrystallization generally occurs at about the same temperature. The present results for pyrophyllite, and the probability that a similar process occurs in muscovite, suggest a possible structural reason for the different thermal behaviors, namely that in the trioctahedral minerals there is less freedom of movement for cation and oxygen reorganization when reaction occurs. Consequently higher temperatures and major structural changes are involved with the trioctahedral minerals.

#### Nomenclature

Previously (Brindley and Wardle, 1970) the dehydroxylated phase was described as an anhydride, but following the recommendation of Brett *et al.* (1970) the term "dehydroxylate" is now preferred as being a more accurate term. Anhydride is a term more aptly used when structural water is removed.

The one-layer triclinic structure of pyrophyllite is now labelled "pyrophyllite, 1Tc". Similarly the two-layer monoclinic structure can be labelled "pyrophyllite, 2M". By placing 1Tc and 2M *after* rather than *before* the name of the mineral, the indexing of the mineral under "P" rather than "T" or "M" is assured.

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