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The Crystal Structures of Warwickite, Ludwigite and Pinakiolite

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The crystal structures of warwickite, $(Mg_3Ti)B_2O_8$, ludwigite, $(Mg, Fe)_4B_2O_8(MgO)_2$, and pinakiolite, $(MgMn_3)B_2O_8(MgO)_2$, have been completely worked out. The unit cells and space groups are as follows:

	a (A.)	*b* (A.)	*c* (A.)	β	Space group
Warwickite	9·20	9·45	3·01	—	V_h^{16}–*Pnam*
Ludwigite	9·14	12·45	3·05	—	V_h^{9}–*Pbam*
Pinakiolite	5·36	5·98	12·73	120° 34′	C_{2h}^{2}–$P2_1/m$

The three minerals are structurally closely related, each containing similarly packed layers or strips of oxygen atoms. Morphotropical relationships are discussed in some detail.

Warwickite, ludwigite and pinakiolite are all boron-bearing minerals whose mutual relationship may be grasped when their empirical chemical formulae are compared:

Warwickite	$3(Mg,Fe)O.TiO_2.B_2O_3$
Ludwigite	$3MgO.(Fe,Mg)O.B_2O_3.Fe_2O_3$
Pinakiolite	$3MgO.MnO.B_2O_3.Mn_2O_3$

Optical and other physical properties as well as paragenesis strongly suggest that they may also be closely related structurally. The following is the result of our studies undertaken to find out the common principle, if any, governing their morphotropical relations.

For Weissenberg–Buerger and oscillation photographs Mo $K\alpha$ radiation ($\lambda = 0{\cdot}710$ A.) was used throughout these studies.

1. The structure of warwickite

(i) *Material*

Warwickite crystals from Edenville, N.Y., U.S.A., were used as material for X-ray examination.* They are brownish black prismatic crystals, about $1{\cdot}5 \times 0{\cdot}6$ mm., embedded in limestone, from which they were carefully separated using HCl (1 : 1) solution. The analysis of this mineral by Bradley (1909) may be well expressed, allowing for the small amount of magnetite and spinel contained as impurities, by the formula $(Mg, Fe)_3TiB_2O_8$.

(ii) *Unit cell and space group*

The orthorhombic unit cell has the dimensions

$$a = 9{\cdot}2_0, \quad b = 9{\cdot}4_5, \quad c = 3{\cdot}01 \pm 0{\cdot}01 \text{ A.},$$

giving the axial ratio, $a:b:c = 0{\cdot}972:1:0{\cdot}318$, in agreement with one obtained by Des Cloizeaux (1874), namely, $a:b = 0{\cdot}977$ (c missing owing to lack of pyramidal faces). There are two molecules of $(Mg, Fe)_3TiB_2O_8$ in the cell.

The space group has been determined to be either V_h^{16}–*Pnam* or C_{2h}^{9}–*Pna*, with the reflexions $h0l$ occurring only when h is even and the reflexions $0kl$ only when $k+l$ is even. These have been deduced from observed spectra in the zero, first- and second-level Weissenberg–Buerger photographs about the c axis. On account of the absence of sufficient morphological data we were unable to decide which of these space groups to adopt before we started the analysis.

(iii) *Analysis*

An outstanding feature of the c-axis Weissenberg–Buerger photographs is that the intensity distribution in the zero level is virtually identical with, and almost indistinguishable from, that in the second level. This suggests immediately that z co-ordinates of all the atoms in the cell must be either $\frac{1}{4}$ or $\frac{3}{4}$, whether we conceive the structure as based on V_h^{16}–*Pnam* or on C_{2h}^{9}–*Pna*. Such positions of atoms will give rise to symmetry (reflexion) planes passing through them and parallel to (001), provided that we assume the spherical symmetry of each ion. This reasoning has led us to prefer V_h^{16}–*Pnam* to C_{2h}^{9}–*Pna* as the working space group. The possibility of the latter, however, is, in the course of analysis, not to be entirely set aside, since we are here arguing not, as

Table 1. *Co-ordinates of atoms in warwickite*

Co-ordinates are given in decimal fractions of the axial lengths: $a = 9{\cdot}20$, $b = 9{\cdot}45$, $c = 3{\cdot}01$ A. Space group V_h^{16}–*Pnam*. Two molecules of $(Mg, Fe)_3TiB_2O_8$ per cell. Origin at a centre of symmetry.

Atom	x/a	y/b	z/c	No. of atoms in the cell
O_I	0	0·125	0·250	4
O_{II}	0·250	0	0·250	4
O_{III}	0·236	0·250	0·750	4
O_{IV}	0·016	0·375	0·750	4
$(Mg, Ti)_I$	0·110	0·056	0·750	4
$(Mg, Ti)_{II}$	0·370	0·201	0·250	4
B	0·160	0·375	0·750	4

* Also prepared artificially with the ideal composition $3MgO.TiO_2.B_2O_3$. Powder photographs show that it is identical with the natural mineral. A melting with the excess of MgO gave spinel in addition to the said mineral.

usual, in terms of absent spectra but in terms of intensity estimation, which is, of course, not absolute.

The dimensions of the unit cell, together with the volume per oxygen atom, suggest further that the structure may be built on the closest packing. The hexagonal closest packing of oxygen with 1·32 A. as its radius has the orthorhombic dimensions $a=2{\cdot}64$, $b=4{\cdot}58$, $c=4{\cdot}31$ A. If we double the b and c lengths and exchange the c and a axes, we can approximate them very closely to those of warwickite, thus:

Hexagonal closest packing	$a=8{\cdot}62, b=9{\cdot}16, c=2{\cdot}64$ A.
Warwickite	$a=9{\cdot}20, b=9{\cdot}45, c=3{\cdot}01$ A.

Table 2. *Intensity of the X-ray spectra of warwickite*

Intensities were estimated visually in Weissenberg–Buerger photographs. Mo $K\alpha$ radiation ($\lambda=0{\cdot}710$ A.). Camera radius 34·1 mm.; coupling constant 1 mm. to 1°. Rotation axis c.

hkl	$I_{obs.}$	$F_{calc.}$
400	—	15·5
600	*vw*	−10·0
800	*ms*	84·0
10,0,0	*vw*	6·2
12,0,0	—	6·9
14,0,0	*vw*	8·0
040	*vw*	13·3
060	—	−9·6
080	—	3·8
0,10,0	—	1·3
0,12,0	*vw*	−28·7
0,14,0	—	9·1
0,16,0	*m*−	31·2
120	*w*	−16·1
130	*m*+	36·2
140	*mw*	−21·2
150	*m*	−32·5
160	*m*	−27·2
170	*w*	−5·4
180	—	−1·5
190	—	12·7
1,10,0	—	−6·9
230	*s*	−62·3
240	*s*	−70·0
250	*m*	−25·8
260	—	2·1
270	*vw*	−1·5
280	—	−4·0
290	—	−25·0
2,10,0	—	−3·6
2,11,0	*m*−	33·3
320	*m*	−38·6
330	*m*	−33·2
340	—	−3·5
350	*w*	24·6
360	*m*+	−40·6
370	*w*	28·3
380	—	2·0
390	—	17·0
410	—	−4·2
420	—	3·4
430	—	−6·2
440	*vw*	21·0
450	—	−2·0
460	—	−7·3
470	—	10·3
480	*s*	80·1
490	—	5·1
510	*mw*	−26·3
520	*mw*	−25·0
530	*m*+	−36·4
540	—	−13·8
550	*m*−	21·2
560	*vw*	−21·0
570	—	6·1
580	—	−7·8
590	—	3·0
5,10,0	—	−2·4
610	—	31·0
620	—	−9·0
630	*m*+	36·8
640	*m*+	−48·0
650	*w*	−20·0
660	—	9·4
670	—	−0·1
680	—	9·7
690	—	13·5
710	*vw*	−8·2
720	*ms*	38·5
730	—	17·9
740	—	8·9
750	—	−17·1
760	*w*	26·2
770	—	−11·3
780	—	1·0
790	—	−9·5
810	—	3·0
820	—	−2·0
830	—	1·0
840	—	−11·1
850	*w*	28·2
860	—	−8·2
870	—	10·4
880	—	−0·8
890	—	0·0
910	*vw*	21·0
920	—	−3·1
930	—	14·3
940	—	−18·9
950	*w*	−18·1
960	*vw*	−23·6
970	—	−5·3
980	—	3·2
990	—	−13·0
601	*m*	−37·8
801	*w*	−4·7
10,0,1	*mw*	37·9
12,0,1	*w*	−9·5
14,0,1	*w*	13·0
051	*m*+	−43·5
071	*mw*	16·0
091	*vw*	−34·5
0,11,1	*w*	−35·8
131	—	8·0
141	—	−5·2
151	*m*+	−40·0
161	*s*	−68·3
171	*mw*	−3·0
181	—	−9·6
191	*w*	−21·7
1,10,1	*m*	33·4
231	*mw*	−24·4
241	*w*	8·6
251	—	7·6
261	—	−0·6
271	—	−16·9
281	*m*+	−41·4
291	—	10·0
311	*ms*	41·0
321	*s*	62·4
331	*s*	61·8
341	*w*	−8·4
351	*m*	30·7
361	—	18·2
371	—	7·6
381	—	−10·5
391	—	−19·7
411	*m*	−31·5
421	*w*	13·7
431	*s*	62·3
441	—	5·3
451	*mw*	19·1
461	—	−7·2
471	—	8·5
481	—	−6·3
491	—	7·8
511	*mw*	−9·6
521	*s*	63·8
531	*mw*	−42·6
541	—	9·8
551	—	7·9
561	—	−8·7
571	—	−14·3
581	—	−2·1
591	—	6·1
611	*vw*	19·8
621	—	7·3
631	—	−4·2
641	—	6·1
651	*mw*	26·7
661	—	2·8
671	—	3·6
681	*m*	41·8
691	—	−9·2
711	*vw*	−10·0
721	*vw*	10·4
731	*vw*	−14·0
741	—	15·8
751	*w*	24·6
761	*w*	−39·3
771	—	7·3
781	—	12·6
791	—	21·7
811	—	5·8
821	—	−16·4
831	—	14·8
841	—	−5·4
851	*mw*	−25·2
861	—	8·5
871	—	−13·6
881	—	10·2
891	—	−12·0

Both cells contain the same number (sixteen) of oxygen atoms.

Starting from this arrangement we tried to obtain a structure consistent with the assumed space group and also with the usual conceptions regarding ionic environment of each constituent atom, and we then adjusted the positions of the atoms by trial and error. We give in Table 1 co-ordinates of atoms of the structure thus finally arrived at. Since there are in the space group V_h^{16}–*Pnam* no twofold equivalent positions for two Ti atoms in the cell, we have merged them with six Mg atoms and distributed them statistically over two sets of fourfold equivalent points. We could not find experimentally enough ground for splitting them into two Ti and two Mg atoms on the one hand and four Mg atoms on the other. Table 2 gives a comparison of calculated and observed intensities.

(iv) *Description of structure*

The structure of warwickite is illustrated in Fig. 1, projected on (001). Although largely built on the hexagonal closest packing of oxygen atoms, the structure retains but partially the oxygen arrangement characteristic of it. The hexagonal layers of packed

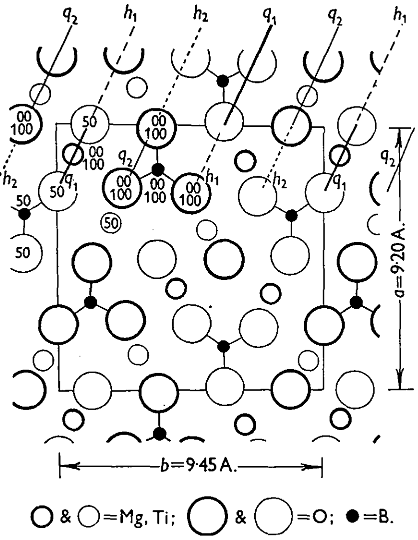

Fig. 1. The structure of warwickite, $(Mg_3Ti)B_2O_8$, projected on (001). Numbers give the height of atoms in the cell expressed as a percentage of the c translation. Part of the hexagonal and quadratic strips of oxygen atoms (cf. Figs. 2 and 6) are traced and marked h_1, h_2 and q_1, q_2 respectively.

oxygen which, piled on top of each other, make up the closest packing in three dimensions, are no longer to be seen in full extension in the structure. Instead, a band may be thought of, which consists of two strips, each forming part of the hexagonally close-packed layer and extending indefinitely only in one direction (Fig. 2 (*a*)). Such a band lies at about 64° to the b axis and is stretched parallel to the c direction (see also Fig. 6 (*c*)). Lying upon and underneath this band there are bands slanting and stretched in the same way, each being composed of two strips taken from a quadratic layer (Fig. 2 (*b*)), just like the above-described strips from the hexagonal layer of oxygen atoms. These superimposed bands make up the bulk of the structure. Magnesium and titanium atoms surrounded octahedrally by oxygen atoms, and boron atoms in the middle of nearly regular triangles of oxygen atoms, unite these bands to form a structure bound in every direction. The oxygen octahedra around magnesium and titanium share either an O–O edge or an O corner with the neighbouring ones. Oxygen triangles around boron share an oxygen atom with the

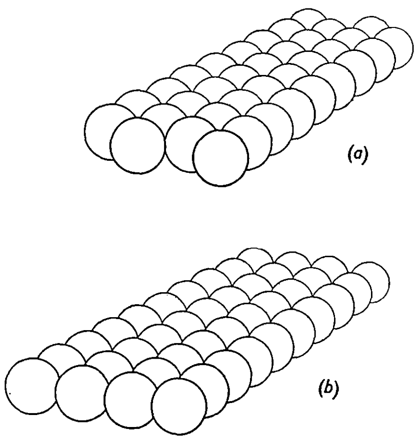

Fig. 2. Strips of oxygen atoms packed (*a*) in the hexagonal form, and (*b*) in the quadratic form.

adjoining oxygen octahedra. Each oxygen atom lies either between one B and two Mg, Ti; or between one B and three Mg, Ti; or between four Mg, Ti. The interatomic distances are given in Table 3.

Table 3. *Interatomic distances in warwickite*

Atom	Co-ordination	Neighbour	Distance (A.)
B	3	O_{III}	1·30
	(triangle)	O_{IV}	1·35
		$O_{II'}$	1·45
(Mg, Ti)$_I$	6	O_I, O_I^*	1·95
	(octahedron)	O_{II}, O_{II}^*	2·05
		$O_{I'}^*$	1·96
		O_{III}	2·25
(Mg, Ti)$_{II}$	6	O_{III}, O_{III}^*	2·00
	(octahedron)	$O_{IV'}$, $O_{IV'}^*$	2·20
		O_{II}	2·15
		$O_{I''}$	2·15
O_{III}		O_{IV}	2·35
O_{IV}		$O_{II'}$	2·45
$O_{II'}$		O_{III}	2·32

Primes denote the equivalent atoms and asterisks atoms in the adjacent cell.

2. The structure of ludwigite

(i) *Material*

The specimen used in the following investigation was from the Hol Kol mine, Suan, Korea. It was a radiated aggregate of acicular crystals of about 5 mm. in length. A perfect single crystal was difficult to obtain, since individual crystals for the most part had a sort of fibrous arrangement with c as the fibre axis. (The maximum deviation was about 5°.) This did not, however, interfere much with our measurement. When powdered, the crystal showed evident magnetism. An analysis by Shannon (1921) may best be expressed by the formula

$$Mg_3(Fe, Mg)Fe_2B_2O_{10}, \text{ with } (Fe : Mg) = (3 : 2).$$

(ii) *Unit cell and space group*

The orthorhombic unit cell has the dimensions

$$a = 9{\cdot}1_4, \quad b = 12{\cdot}4_5, \quad c = 3{\cdot}05 \pm 0{\cdot}02 \text{ A}.$$

with the axial ratio,

$$a : b : c = 0{\cdot}755 : 1 : 0{\cdot}252.$$

This gives the value $(340)\wedge(3\bar{4}0) = 88° \, 44'$ in agreement with $(110)\wedge(1\bar{1}0) = 89° \, 20'$ as observed by Mallard (1888). The specific gravity is 3·86 (Watanabé, 1939) and there are two molecules of $Mg_3(Fe, Mg)Fe_2B_2O_{10}$ in the cell.

Since $h0l$ and $0kl$ reflexions are absent when h and k respectively are odd, the space group of ludwigite is either C_{2v}^8–Pba or V_h^9–$Pbam$, between which, lacking morphological and other evidence, we again could not choose before we set out to determine the atomic parameters.

(iii) *Analysis*

Similar considerations to those made with regard to warwickite apply also to ludwigite. In addition to the apparent identity of the zero- and second-level c-axis Weissenberg–Buerger photographs, we have found that the first- and third-level c-axis Weissenberg–Buerger photographs are nearly identical in intensity distribution. The formulae for structure amplitude, then, allow no other positions than $z = 0$ or $\frac{1}{2}$ for every atom in the cell. Ensuing reflexion planes m go through these points and are parallel to (001). The space group of ludwigite becomes automatically V_h^9–$Pbam$ instead of C_{2v}^8–Pba, which should, however, be retained for further consideration until we have successfully finished the analysis.

The orthorhombic dimensions of the hexagonal closest packing of oxygen atoms may again be approximated to those of the unit cell of ludwigite; if we take double its a length and two and half times its b length we have

Hexagonal closest packing	$a = 8{\cdot}62, b = 11{\cdot}45, c = 2{\cdot}64$ A.
Ludwigite	$a = 9{\cdot}14, b = 12{\cdot}45, c = 3{\cdot}05$ A.

The number of oxygen atoms per cell is twenty in both cells.

Starting with this ideal arrangement of oxygen atoms we tried to allot other atoms to appropriate positions, adjusting also those of oxygen atoms, when necessary, by trial and error. There were few alternatives for positions satisfying the requirements of the space group as well as the geometrical conditions of the constituent atoms. We give in Table 4 co-ordinates of atoms in the structure finally arrived at. Calculated intensities of reflexions are listed with those observed in Table 5. In calculation the presence of Fe^{2+} replacing Mg was ignored, since it did not much influence the result.

Table 4. *Co-ordinates of atoms in ludwigite*

Co-ordinates are given in decimal fractions of the axial length: $a = 9{\cdot}14$, $b = 12{\cdot}45$, $c = 3{\cdot}05$ A. Space group V_h^9–$Pbam$. Two molecules of $Mg_4Fe_2^{3+}B_2O_{10}$ in the cell. Origin at a centre of symmetry.

Atom	x/a	y/b	z/c	No. of atoms in the cell
O_I	0·125	−0·056	0	4
O_{II}	0·112	0·145	0·500	4
O_{III}	0·136	0·349	0	4
O_{IV}	0·375	0·058	0·500	4
O_V	0·361	0·250	0	4
Mg_I	0	0	0·500	2
Mg_{II}	0	0·275	0·500	4
Mg_{III}	0·500	0	0	2
Fe^{3+}	0·250	0·114	0	4
B	0·288	0·352	0	4

(iv) *Description of structure*

Based like warwickite on a modified hexagonal closest packing of oxygen atoms, the structure (Fig. 3) may be described in a similar way. The band, which consists of two strips of hexagonally close-packed oxygen atoms, is

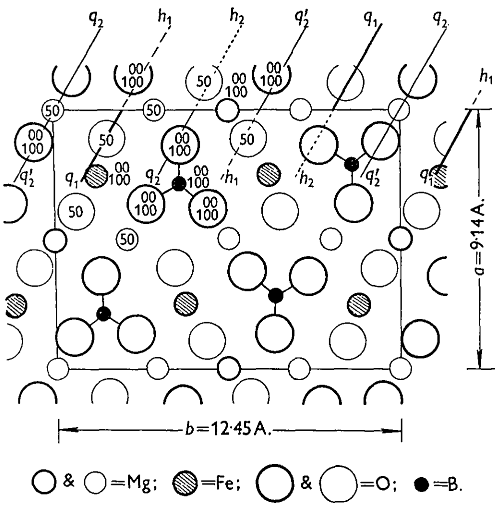

Fig. 3. The structure of ludwigite, $(Mg, Fe)_4B_2O_8(MgO)_2$, projected on (001). Numbers give the height of atoms in the cell expressed as a percentage of the c translation. Part of the hexagonal and quadratic strips of oxygen atoms (cf. Figs. 2 and 6) are traced and marked h_1, h_2, and q_1, q_2, q_2' respectively.

slanting, as found earlier in warwickite, at 60° to the b direction and is stretched along the c direction. Above and below this band lie bands also stretched along the same c direction. They are composed, however, of three strips, instead of two as in warwickite, in which oxygen atoms are packed together in quadratic form (see Fig. 6 (b) below). Magnesium and iron atoms occupy the centres of octahedra of oxygen atoms formed by the stacking of these strips, and, together with boron atoms in the middle of the oxygen triangles, unite the structure.

The linkage of metallic and oxygen atoms in ludwigite is almost the same with that in warwickite, oxygen atoms being either between one B, one Fe^{3+} and two Mg; or between one B, and three Mg; or between two

Table 5. *Intensity of the X-ray spectra of ludwigite*

Intensities were estimated visually in Weissenberg–Buerger photographs. Mo $K\alpha$ radiation ($\lambda = 0{\cdot}710$ A.). Camera radius 34·1 mm.; coupling constant 1 mm. to 1°. Rotation axis *c*.

hkl	$I_{obs.}$	$F_{calc.}$
400	*m*+	62·2
600	—	19·4
800	*s*	149·3
10,0,0	—	24·0
12,0,0	*vw*	53·5
14,0,0	—	− 6·0
040	—	19·9
060	*mw*	60·3
080	*s*	108·2
0,10,0	—	13·3
0,12,0	—	− 4·2
0,14,0	—	14·5
140	—	−29·2
150	—	−23·0
160	*m*	63·7
170	—	26·0
180	*vw*	36·9
190	—	−23·1
1,10,0	*vw*	40·0
240	*s*	143·0
250	*ms*	−104·0
260	—	−13·2
270	—	0·8
280	—	−16·3
290	—	− 1·7
2,10,0	—	− 3·1
320	*ms*	68·5
330	—	21·2
340	—	19·9
350	*m*−	34·7
360	*m*−	−52·2
370	—	−12·4
380	—	−28·7
390	—	−24·4
3,10,0	—	38·0
410	—	− 5·1
420	—	−17·7
430	—	− 1·8
440	—	−11·0
450	—	6·1
460	*mw*	40·0
470	—	− 1·3
480	*m*+	80·9
490	—	− 4·5
4,10,0	*m*+	97·6
510	—	− 4·8
520	*m*	−60·0
530	—	12·0
540	—	−16·0
550	—	−19·6
560	*w*	49·8
570	*vw*	28·1
580	—	21·0
590	—	−22·8
5,10,0	*w*−	37·0
610	—	7·2
620	—	11·5
630	—	2·5
640	*s*	102·6
650	*mw*	−57·3
660	—	−10·5

hkl	$I_{obs.}$	$F_{calc.}$
670	—	− 1·5
680	—	−14·7
690	—	5·5
710	—	− 7·2
720	*mw*	53·0
730	—	17·3
740	—	14·6
750	—	−15·7
760	*vw*	−45·4
770	—	12·5
780	—	19·6
790	—	−11·4
810	—	− 4·9
820	—	14·0
830	—	− 1·9
840	—	−11·4
850	—	− 5·9
860	*vw*	25·8
870	—	− 0·1
880	*m*	59·9
890	—	3·2
910	—	0·3
920	*vw*	48·9
930	—	− 4·5
940	—	12·0
950	—	12·7
960	*vw*	−40·5
970	—	−16·0
980	—	−17·6
10,1,0	—	3·1
10,2,0	—	6·3
10,3,0	—	−10·5
10,4,0	*m*	67·0
10,5,0	—	26·5
601	*mw*	−77·2
801	—	34·8
10,0,1	*mw*	−66·5
12,0,1	—	14·2
061	—	20·0
081	*mw*	54·6
0,10,1	—	22·6
0,12,1	—	−27·4
141	—	−20·7
151	—	− 8·0
161	*w*	54·6
171	*s*−	−84·6
181	*w*+	57·7
191	—	−24·2
1,10,1	*vw*	−38·4
241	*m*	47·2
251	—	12·8
261	*w*	− 8·2
271	—	−12·6
281	*m*−	−57·9
291	—	22·1
2,10,1	*m*−	−58·5
321	*s*	106·2
331	*s*	−92·5
341	*vw*	39·7

hkl	$I_{obs.}$	$F_{calc.}$
351	—	− 8·5
361	*m*+	−58·2
371	*vw*	−20·1
381	—	− 7·4
391	—	− 0·4
3,10,1	*vw*	43·5
411	—	− 4·9
421	*m*−	28·5
431	—	− 1·8
441	*ms*	−78·3
451	—	5·8
461	*m*−	36·9
471	—	− 2·9
481	*w*−	25·6
491	—	− 4·2
4,10,1	*w*	39·0
511	—	−19·8
521	*ms*	91·7
531	*ms*	−77·7
541	—	−18·3
551	—	− 7·5
561	*w*	47·3
571	—	− 4·1
581	—	5·9
591	—	5·7
5,10,1	*w*−	−35·7
611	—	1·8
621	*vw*	32·4
631	—	17·1
641	*m*	53·2
651	—	−17·4
661	—	−33·5
671	—	11·1
681	*w*	−46·7
691	—	− 7·7
711	*vw*	−17·6
721	—	28·0
731	—	− 4·6
741	—	7·4
751	—	− 6·1
761	*w*−	−44·0
771	*m*+	−60·9
781	*vw*	−40·1
791	—	− 5·2
811	—	− 4·7
821	—	3·2
831	—	− 1·9
841	*w*+	−49·6
851	—	5·9
861	—	22·1
871	—	− 0·1
881	*w*	38·1
911	*vw*	−21·1
921	—	−29·3
931	—	−13·4
941	—	− 5·0
951	—	− 5·8
961	*vw*	40·1
971	*w*−	−41·4
981	—	30·8

Fe^{3+} and two Mg; or between two Fe^{3+} and three Mg. The interatomic distances are given in Table 6.

Table 6. *Interatomic distances in ludwigite*

Atom	Co-ordination	Neighbour	Distance (A.)
B	3	O_{III}	1·40
	(triangle)	$O_{I''}$	1·40
		O_{V}	1·50
Fe^{3+}	6	O_{I}^{*}	2·45
	(octahedron)	O_{V}	2·00
		O_{II}, O_{II}^{*}	2·05
		O_{IV}, O_{IV}^{*}	1·98
$(Mg, Fe)_{I}$	6	O_{I}^{*} (2), $O_{I'}^{*}$ (2)	2·03
	(octahedron)	O_{II}, $O_{II''}$	2·02
$(Mg, Fe)_{II}$	6	O_{II}	2·00
	(octahedron)	O_{III} (2)	2·19
		$O_{IV'}^{*}$	2·35
		$O_{V'}^{*}$ (2)	2·01
$(Mg, Fe)_{III}$	6	O_{IV} (2), $O_{IV'}^{*}$ (2)	2·01
	(octahedron)	$O_{III'}$, $O_{III''}^{*}$	2·25
O_{III}		O_{V}	2·43
O_{III}		$O_{I'}$	2·40
O_{V}		$O_{I'}$	2·50

Primes denote equivalent atoms and asterisks atoms in the adjacent cell.

3. The structure of pinakiolite

(i) *Material*

The specimen used in the experiment came from Långban, Sweden. It was a fine plate of the dimensions $5 \times 5 \times 0{\cdot}5$ mm. According to Flink (1891) its chemical composition may be expressed as $Mg_3Mn^{2+}Mn_2^{3+}B_2O_{10}$.

(ii) *Unit cell and space group*

The unit cell has been found to be, not orthorhombic as assumed earlier (Flink, 1891), but monoclinic with the following dimensions:

$$a = 5{\cdot}36 \pm 0{\cdot}05, \quad b = 5{\cdot}98 \pm 0{\cdot}02 \text{ A.},$$
$$c = 12{\cdot}73 \pm 0{\cdot}04 \text{ A.}, \quad \beta = 120^\circ\ 34'.$$

There are two molecules of $Mg_3Mn^{2+}Mn_2^{3+}B_2O_{10}$ in the cell. The transformation from the orthorhombic (Flink) to the new monoclinic axes may be effected with the matrix $004/200/03\bar{3}$. The corresponding face indices are:

Orthorhombic	Monoclinic
100	010
010	001
001	$40\bar{3}$
310	021
011	100

The space group is either C_{2h}^2–$P2_1/m$ or C_2^2–$P2_1$, since the only absent reflexions were $0k0$ with k odd. Lacking morphological and other evidence we again could not choose between these groups before we began to determine the atomic parameters.

(iii) *Analysis*

We note again that the zero- and fourth-level Weissenberg–Buerger photographs about the b axis display almost identical intensity distribution. This, taken strictly, would require that every atom in pinakiolite should have y parameter either 0, $\frac{1}{4}$, $\frac{1}{2}$ or $\frac{3}{4}$. This would in turn give rise to reflexion planes passing through these points and parallel to (010). Since, however, we observed in the oscillation photographs about the b axis a few, although very faint and almost negligible, spots that belong to the first and third layer-lines, there should be no reflexion planes through $y = 0$ and $\frac{1}{2}$, leaving only those through $y = \frac{1}{4}$ and $\frac{3}{4}$. Consequently the most probable space group of pinakiolite is

$$C_{2h}^2\text{–}P2_1/m.$$

Packing and other relations suggest that this structure too, may be built on a scheme akin to the closest packing of oxygen atoms, and that it may be closer to the structure of ludwigite rather than to that of warwickite.

These considerations have led us to test a tentative structure of pinakiolite similar to that of ludwigite, due regard having been taken of the difference in symmetry and nature of the constituent atoms.

The final result has been obtained as usual by the trial-and-error method. The atomic co-ordinates are given in Table 7. Calculated and observed intensities are given in Table 8.

Table 7. *Co-ordinates of atoms in pinakiolite*

Co-ordinates are given in decimal fractions of the axial lengths: $a = 5{\cdot}36 \pm 0{\cdot}05$, $b = 5{\cdot}98 \pm 0{\cdot}02$, $c = 12{\cdot}73 \pm 0{\cdot}04$ A., $\beta = 120^\circ\ 34'$. Space group C_{2h}^2–$P2_1/m$. Two molecules of $Mg_3Mn^{2+}Mn_2^{3+}B_2O_{10}$ in the cell. Origin at a centre of symmetry.

Atom	x/a	y/b	z/c	No. of atoms in the cell
O_{I}	0·239	0·250	−0·011	2
O_{II}	0·239	0·750	−0·011	2
O_{III}	0·175	0	0·175	4
O_{IV}	0·638	0	0·366	4
O_{V}	0·643	0	0·180	4
O_{VI}	0·202	0·250	0·396	2
O_{VII}	0·202	0·750	0·396	2
Mg_{I}	0	0	0	2
Mg_{II}	−0·053	0·250	0·197	2
Mg_{III}	0	0·250	0·500	2
Mn^{2+}	−0·053	0·750	0·197	2
Mn_{I}^{3+}	0·500	0	0	2
Mn_{II}^{3+}	0·500	0	0·500	2
B	0·500	0	0·250	4

(iv) *Description of structure*

The structure of pinakiolite is illustrated in Fig. 4. In packing and co-ordination it is essentially the same as that of ludwigite. The strips of packed oxygen atoms found in the latter crystal may be traced also here, but stretched along the b direction. They are joined, however, with the neighbouring similar ones to form two-dimensional layers. The framework of the structure is, therefore, made up actually of hexagonal and quadratic layers of packed oxygen atoms, piled on top of one another and not of joined strips of packed oxygen atoms, as in ludwigite and warwickite. Magnesium and manganese atoms unite oxygen atoms within each layer and those of the adjacent layers. Boron atoms are

Table 8. *Intensity of the X-ray spectra of pinakiolite*

Intensities were estimated visually in Weissenberg–Buerger photographs. Mo $K\alpha$ radiation (λ=0·710 A.). Camera radius 34·1 mm.; coupling constant 1 mm. to 1°. Rotation axis *b*.

hkl	$I_{obs.}$	$\frac{1}{2}F_{calc.}$
200	*mw*	40·1
300	—	− 7·6
400	*m*	41·6
500	—	− 8·2
600	*w*	29·1
040	*vs*	84·4
060	*vw*	17·4
080	*m*+	44·6
004	*s*	49·6
005	*s*	53·7
006	*ms*	64·0
007	*vw*	−13·4
008	*m*	33·2
009	*vw*	− 5·6
0,0,10	*s*	50·9
0,0,11	*vw*	13·3
0,0,12	*m*	33·0
0,0,13	—	− 6·9
0,0,14	*m*	20·0
0,0,15	—	8·4
0,0,16	*mw*	21·7
0,0,17	—	11·1
0,0,18	*mw*	18·8
0,0,19	—	1·3
0,0,20	*w*	18·0
103	*w*	−25·0
104	*vw*	22·8
105	—	9·5
106	—	− 3·1
107	—	− 3·8
108	*vw*	−28·7
109	*w*	−24·5
201	*w*	−31·0
202	*ms*	35·2
203	—	− 4·5
204	*ms*	50·0
205	*w*	7·2
206	*w*	30·1
207	—	2·7
208	*vw*	21·3
301	*vw*	−20·0
302	*w*	−14·0
303	—	− 2·5
304	*vw*	20·1
305	—	0·4
306	*w*	15·3
307	—	1·5
401	*vw*	23·0
402	*mw*	41·7
403	—	2·7
404	*vw*	23·8
405	—	− 1·6
406	*w*	34·4
501	—	2·8
502	—	− 0·1
503	—	− 2·9
504	*vw*	−19·9
505	—	8·3
601	—	3·7
602	*w*	27·5
603	—	− 1·2
604	—	15·8
$20\bar{1}$	*w*	10·6
$20\bar{2}$	*m*	26·6
$20\bar{3}$	*vw*	−16·2
$20\bar{4}$	*vs*	78·6
$20\bar{5}$	*m*	−26·8
$20\bar{6}$	*vs*	71·0
$20\bar{7}$	*mw*	−31·9
$20\bar{8}$	*m*+	43·5
$30\bar{1}$	—	17·3
$30\bar{2}$	*w*	−27·2
$30\bar{3}$	—	2·6
$30\bar{4}$	—	− 2·3
$30\bar{5}$	*w*	13·1
$30\bar{6}$	*w*	20·2
$30\bar{7}$	—	−20·9
$30\bar{8}$	—	−18·2
$30\bar{9}$	*mw*	18·2
$40\bar{1}$	—	−14·5
$40\bar{2}$	*m*	38·2
$40\bar{3}$	*vw*	10·1
$40\bar{4}$	*vs*	78·0
$40\bar{5}$	*w*	8·0
$40\bar{6}$	*w*	14·8
$40\bar{7}$	*vw*	2·9
$40\bar{8}$	*ms*	−46·3
$40\bar{9}$	*m*	23·2
$4,0,\overline{10}$	*ms*	54·8
$50\bar{1}$	—	− 5·0
$50\bar{2}$	—	9·4
$50\bar{3}$	—	14·5
$50\bar{4}$	—	−12·9
$50\bar{5}$	—	4·7
$50\bar{6}$	—	− 7·0
$50\bar{7}$	—	− 9·7
$50\bar{8}$	—	−13·1
$50\bar{9}$	—	2·5
$5,0,\overline{10}$	—	− 3·2
$5,0,\overline{11}$	—	− 2·5
$60\bar{1}$	—	− 7·8
$60\bar{2}$	*vw*	15·3
$60\bar{3}$	—	− 0·1
$60\bar{4}$	*w*	27·2
$60\bar{5}$	—	2·4
$60\bar{6}$	*w*	17·9
$60\bar{7}$	*w*	−13·3
$60\bar{8}$	*mw*	34·8
$60\bar{9}$	—	− 4·5
$6,0,\overline{10}$	*w*	27·1
$6,0,\overline{11}$	—	− 1·9
$6,0,\overline{12}$	—	17·8
$70\bar{1}$	—	5·4
$70\bar{2}$	—	− 3·2
$70\bar{3}$	*w*	22·0
$70\bar{4}$	—	− 4·0
$70\bar{5}$	—	2·2
$70\bar{6}$	—	7·6
$70\bar{7}$	—	4·2
$70\bar{8}$	—	− 7·4
$70\bar{9}$	—	5·1
$7,0,\overline{10}$	*vw*	−17·6
$7,0,\overline{11}$	—	11·2
$7,0,\overline{12}$	—	−11·3
220	*w*	27·8
320	*mw*	−24·8
420	—	7·6
520	—	−16·3
620	*w*	22·6
720	—	− 7·6
820	*w*	23·6
024	*m*	28·9
025	—	− 0·6
026	*mw*	35·3
027	—	12·2
028	*m*	27·3
029	—	− 1·1
0,2,10	*mw*	15·3
0,2,11	*w*	17·5
0,2,12	*vw*	16·9
0,2,13	—	6·2
0,2,14	*vw*	12·1
0,2,15	—	− 9·5
0,2,16	—	16·1
0,2,17	—	6·2
0,2,18	—	15·8
0,2,19	—	3·1
0,2,20	—	3·7
123	*ms*	24·2
124	*ms*	31·9
125	—	2·6
126	*vw*	−29·7
127	—	11·0
128	*vw*	−15·9
129	—	12·5
221	—	13·1
222	*ms*	32·5
223	*ms*	40·0
224	*m*	45·2
225	—	10·9
226	—	2·9
227	*w*	6·4
$32\bar{1}$	—	− 4·6
$32\bar{2}$	*vw*	−21·9
$32\bar{3}$	—	20·8
$32\bar{4}$	*mw*	−24·5
$32\bar{5}$	—	4·8
$32\bar{6}$	*mw*	−33·0
421	—	1·0
422	*vw*	20·6
423	—	7·5
424	*vw*	29·4
425	—	− 6·4
222	*vs*	78·4
223	*ms*	37·6
224	*mw*	20·0
225	—	− 3·1
226	*s*	42·8
321	*mw*	−15·4
322	*mw*	8·9
323	*m*	23·9
324	*ms*	−49·5
325	—	− 8·1
326	*w*	24·9
327	*w*	11·4
421	—	12·9
422	*w*	21·8
423	—	9·8
424	*mw*	23·8
425	—	− 3·5
426	*w*	35·9
427	—	− 9·5
428	*w*	24·4

always in the centres of triangles, and magnesium and manganese atoms in the middle of octahedra, both formed of oxygen atoms. Each oxygen atom is either between one B and three Mg; or between one B, two Mg and one Mn^{3+}; or between two Mg and two Mn^{3+}. The interatomic distances are listed in Table 9.

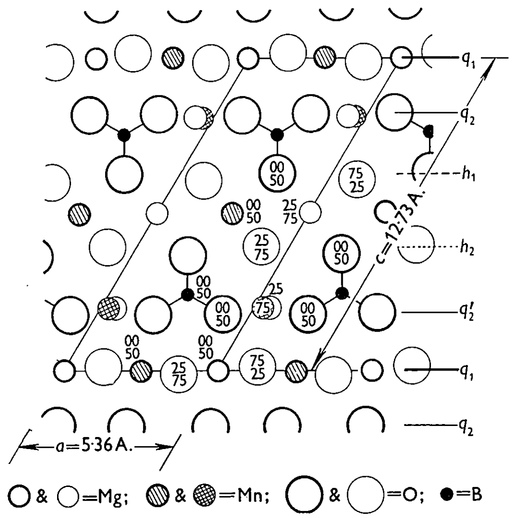

Fig. 4. The structure of pinakiolite, $(MgMn_3)B_2O_8(MgO)_2$, projected on (010). Numbers give the height of atoms in the cell expressed as a percentage of the b translation. Mn and Mg_{II} atoms are displaced slightly from their true positions so as to be seen. Part of the hexagonal and quadratic layers of oxygen atoms are traced and marked h_1, h_2 and q_1, q_2, q_2' respectively in order to facilitate comparison with Fig. 6.

Table 9. *Interatomic distances in pinakiolite*

Atom	Co-ordination	Neighbour	Distance (A.)
B	3	O_{III}	1·29
	(triangle)	O_{IV}	1·58
		O_{V}	1·37
Mg_{I}	6	O_{I}, $O^{*}_{I'}$	2·00
	(octahedron)	O_{II}, $O^{*}_{II'}$	2·00
		O_{III}, $O^{*}_{III'}$	1·94
Mg_{II}	6	O^{*}_{II}	2·06
	(octahedron)	O_{III}, $O_{III'}$	2·00
		O^{*}_{V}, $O^{*}_{V'}$	2·16
		O_{VI}	2·22
Mg_{III}	6	O^{*}_{IV}, $O^{*}_{IV'}$	2·46
	(octahedron)	$O_{IV''}$, $O_{IV'''}$	2.46
		O^{*}_{VI}, $O_{VII'}$	2·00
Mn^{2+}	6	$O^{*}_{I'}$	2·06
	(octahedron)	O_{III}, $O_{III'}$	2·00
		O^{*}_{V}, $O^{*}_{V'}$	2·16
		O_{VII}	2·22
Mn^{3+}_{I}	6	O_{I}, $O_{I'}$	2·00
	(octahedron)	O_{II}, $O_{II'}$	2·00
		O_{V}, $O^{*}_{V'}$	2·00
Mn^{3+}_{II}	6	O_{IV}, $O_{IV'}$	2·09
	(octahedron)	O_{VI}, $O_{VI'}$	2·13
		O_{VII}, $O_{VII'}$	2·13
O_{II}		O_{III}	2·39
O_{III}		O_{IV}	2·40
O_{IV}		O_{II}	2·30

Primes denote the equivalent atoms and asterisks atoms in the adjacent cell.

4. The atomic morphotropical relationship between warwickite, ludwigite and pinakiolite

The a and c lengths of warwickite are approximately equal to the a and c lengths of ludwigite, while the b length of ludwigite is longer than the b length of warwickite by about the diameter of an oxygen ion. Further, the b length of pinakiolite is nearly twice the c length of warwickite or of ludwigite. These dimensional relations are easily explicable in terms of the structures of these minerals. If we conceive of the unit structure of warwickite as divided into, and composed of, a part A and its counterpart A' (Fig. 5 (a, b)), each representing the same composition M_2BO_4 (M = Mg, Ti, Mn or Fe), the unit structure of ludwigite may be promptly obtained by inserting between them slabs, B and B', each representing the composition MgO (Fig. 5 (c)). The structure of pinakiolite may also be derived in a similar way from that of warwickite. The component main blocks (designated $\bar{A}$ and $\bar{A}'$) are a little modified in this case owing to the presence of manganese in place of titanium or magnesium, with the result that the symmetry of the crystal is lowered from orthorhombic to monoclinic. The structure of pinakiolite may be thought of as partitioned into rectangular patches in contrast to the parallel slabs in warwickite and ludwigite (as viewed in projections, Fig. 5 (d)) in such a way that one patch is a little shifted in the c direction relative to the next patch. Diagrammatically, the three structures, extending the notations adopted by Taylor & West (1928) (see also Bragg (1937, p. 152)), may be represented by the two-dimensional orthogonal and oblique matrices shown in Table 10.

Table 10. *Representation of the structures*

		No. of oxygen layers or strips	Composition
Warwickite	$AA'AA'A$ $AA'AA'A$ $AA'AA'A$	4, parallel to (120)	$Mg_3TiB_2O_8$
Ludwigite	$ABA'B'A$ $ABA'B'A$ $ABA'B'A$	5, parallel to (250)	$(Mg, Fe)_4B_2O_8(MgO)_2$
Pinakiolite	$\bar{A}B\bar{A}'B'\bar{A}$ $\bar{A}B\bar{A}'B'\bar{A}$ $\bar{A}B\bar{A}'B'\bar{A}$	5, parallel to (001)	$MgMn_3B_2O_8(MgO)_2$

The relations that exist among warwickite, ludwigite and pinakiolite will be clearer if we ignore the metallic ions and consider the arrangement of oxygen atoms only. The structure of pinakiolite is composed, as described above, of five layers of packed oxygen atoms, of which two are after the hexagonal and the remaining three after the quadratic pattern (see Fig. 4). We now divide these piled layers by cutting them parallel to (100) into blocks of the size of two unit cells (Fig. 6 (a)) and then let them slip stepwise parallel to (100) by an amount $\frac{2}{5}b$ (Fig. 6 (b)). The resulting arrangement will be exactly the arrangement of oxygen atoms underlying the structure of ludwigite (see Fig. 3). From the point of view of the arrangement of oxygen atoms, the

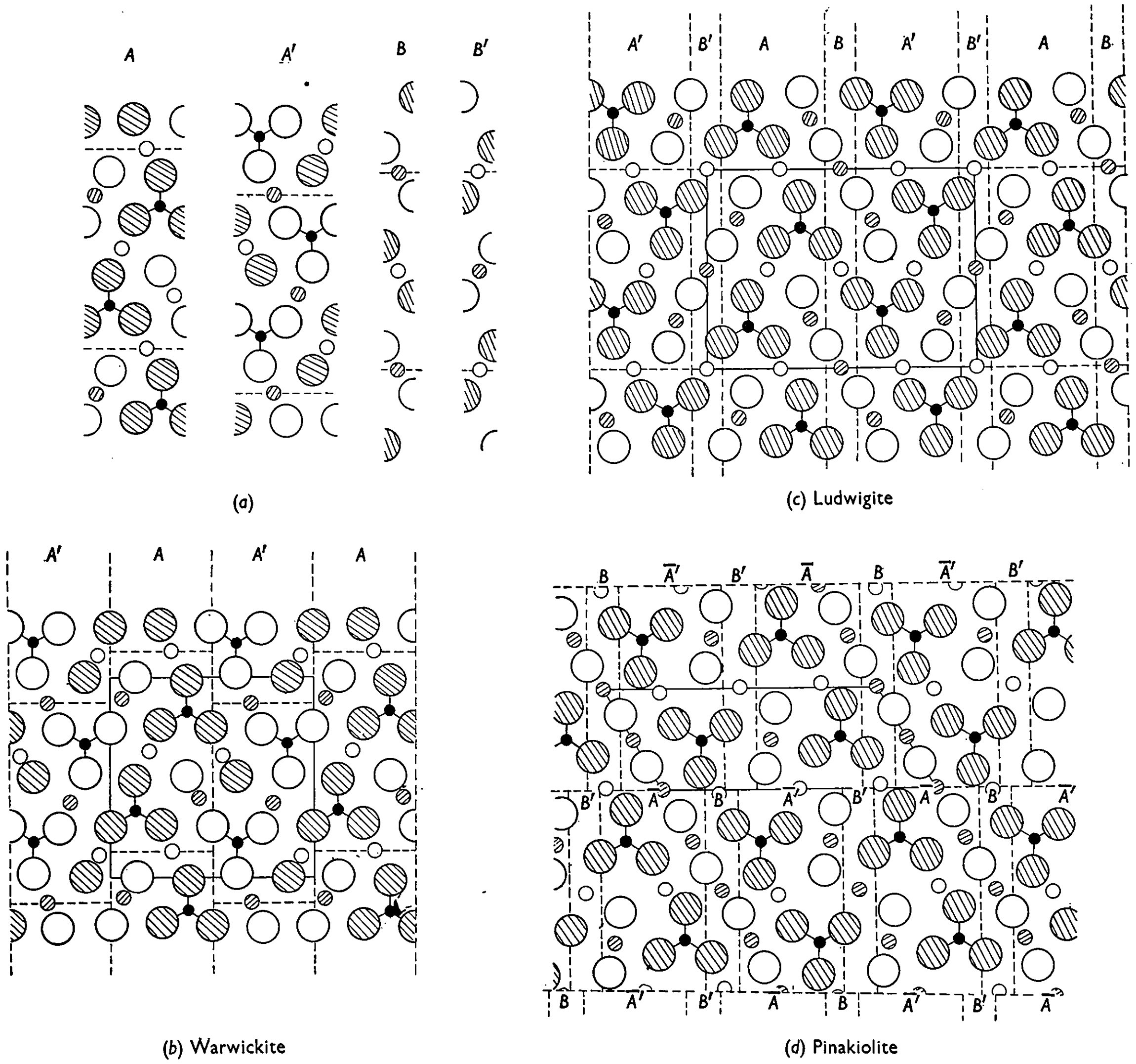

Fig. 5. The structures of warwickite (*b*), ludwigite (*c*) and pinakiolite (*d*) projected respectively on (001), (001) and (010). Notation as in the previous figures. (*a*) shows the unit blocks M_2BO_4 and MgO from which the respective structures may be constructed by stacking them together in the order indicated in each figure.

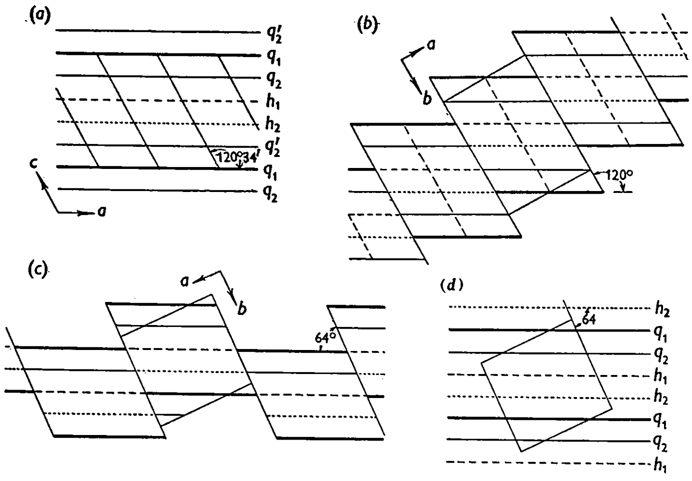

Fig. 6. Diagrams illustrating the relationship that exists between the arrangements of oxygen atoms in pinakiolite (*a*) and ludwigite (*b*) on the one hand, and between those in a hypothetical structure (corresponding to pinakiolite) (*d*) and warwickite (*c*) on the other. The lines h_1 and h_2 represent the traces of layers or strips of oxygen atoms packed in the hexagonal fashion and the lines q_1, q_2 and q_2' those of layers or strips of oxygen atoms packed in the quadratic fashion. The unit cells are also shown in projections in the respective figures. (In the hypothetical structure (*d*) the unit cell of warwickite is traced.)

structure of warwickite is slightly different from those of pinakiolite and ludwigite. Let us picture to ourselves a hypothetical arrangement of oxygen atoms which consists of only four piled layers (two hexagonal and two quadratic), instead of five as in pinakiolite. If now we outline in this arrangement the unit cell of warwickite in the position shown in Fig. 6 (*d*) and then let it slip alternately upwards and downwards by an amount $\frac{1}{2}b$ parallel to (100), making an angle of about 64° with the plane of layers (Fig. 6 (*c*)), we shall obtain the very arrangement of oxygen atoms characteristic of the structure of warwickite (see Fig. 1). It is interesting to note that the cleavage of pinakiolite occurs parallel to the layers, i.e. (001), while that of warwickite is parallel to the plane of slips, i.e. (100).

These relationships between various arrangements of oxygen atoms underlying the structures of warwickite, ludwigite and pinakiolite are all the more interesting, since we have previously found similar phenomena in the wollastonite group (Ito, 1949, p. 110). One of the present writers in collaboration with R. Sadanaga and Y. Takéuchi, basing his argument on the experimental evidences obtained by him as well as by Barnick, has demonstrated that we can derive the structure of monoclinic as well as triclinic wollastonite from another monoclinic wollastonite, protowollastonite, by slipping its cells alternately or stepwise. Although analogy here is only partial and the mechanism applies in this case only to the arrangements of oxygen atoms, and not to the entire structures as in wollastonite, it is nevertheless very interesting in view of the dominant role of oxygen in the genesis of minerals (see, for example, Barth (1948)).

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The Interpretation of Diffuse X-ray Diagrams of Carbon

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Measurements on a carbon prepared by pyrolysis of polyvinylidene chloride at 1000° C. have been used to study methods of interpretation of the diffuse X-ray diagrams given by non-graphitic carbons. Results obtained from a Fourier integral analysis are in satisfactory agreement with those deduced from a comparison of the experimental intensity curve with an intensity curve calculated for a hypothetical structure. For the high-angle part of the diagram the latter method is found to be preferable; it is less tedious, and gives the results with greater precision. The Fourier transform of the low-angle scattering is, however, of value.

It is concluded that, in the carbon investigated, 65 % is in the form of highly perfect and planar graphite-like layers of mean diameter 16 A., and 35 % is in a much less organized state, giving only a gas-like contribution to the X-ray scattering. About 55 % of the graphite-like layers are grouped in pairs of parallel layers with an interlayer spacing of 3·7 A., and the remaining 45 % show no mutual orientation. There is a mean interparticle distance of about 26 A.

Introduction

The general form of the X-ray diagrams given by non-graphitic carbons is well known. Diffuse bands are observed corresponding approximately to the positions of the (002), (100) and (110) reflexions of graphite, and there is often strong low-angle scattering. The degree of sharpening of the bands is frequently considered as a measure of progress towards graphite. The general trend of the phenomenon has been extensively investigated by Riley and his collaborators (Blayden, Gibson & Riley, 1944) who have studied the influence of temperature on many different carbons. Warren (1934), in a quantitative study of a carbon black, confirmed by Fourier integral analysis the existence of interatomic distances close to those within a single graphite layer. A further important advance was made by Warren