Zeitschrift für Kristallographie, Bd. 127, S. 21—33 (1968)

The crystal structure of wavellite

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(Received December 14, 1967)

Auszug

An einem nadelförmigen Wavellit-Kristall von Arkansas wurden die Gitterkonstanten $a = 9{,}62$ Å, $b = 17{,}36$ Å, $c = 6{,}99$ Å und die Raumgruppe *Pcmn* bestimmt. Die Intensitäten von 765 Interferenzen wurden mit einem Diffraktometer und Cu$K\alpha$-Strahlung gemessen.

Auf der Grundlage von dreidimensionalen Pattersondiagrammen wurde die Struktur mit Hilfe der Minimumfunktions-Methode und anschließender Fourier-Synthese bestimmt. Die Atomkoordinaten wurden zuerst mit isotropen, dann mit anisotropen Temperatur-Faktoren verfeinert. Für R ergab sich aus allen Interferenzen 5,5%.

Die Al-Atome der beiden Lagen sind oktaedrisch koordiniert; das eine ist an zwei O, zwei OH und zwei H_2O gebunden, das andere an drei O, zwei OH und ein H_2O. Die Phosphor-Atome sind vom Sauerstoff tetraedrisch umgeben. Die Al-Oktaeder bilden, durch gemeinsame, mit OH besetzte Ecken verbunden, Ketten parallel zur c-Achse. Die P-Tetraeder sind mit den Ketten durch O-Atome aufeinanderfolgender Oktaeder verknüpft. Ein H_2O-Molekül besetzt den großen Hohlraum zwischen den Ketten und ist, worauf der hohe Temperatur-Faktor hinweist, statistisch über den Hohlraum verteilt.

Abstract

A needle-like crystal of wavellite from Arkansas was used for this investigation. The lattice constants of $a = 9.62$ Å, $b = 17.36$ Å, and $c = 6.99$ Å and the space group of *Pcmn* were obtained. Intensities of 765 reflections were collected with an equi-inclination, single-crystal diffractometer, using Cu$K\alpha$ radiation.

Three-dimensional Patterson maps were prepared and the structure was determined by using the minimum-function method and subsequent Fourier syntheses. The atomic coordinates were refined, first with isotropic then with anisotropic temperature factors, using a full-matrix least-squares method. A final R of 5.5% was obtained for all reflections.

The two aluminum atoms in the structure are octahedrally coordinated: one is bonded to two O, two (OH), and two H_2O; and the other to three O, two (OH),

and one H_2O. The phosphorus is in tetrahedral coordination with oxygen. The Al octahedra, linked through (OH) corners, form chains parallel to the *c* axis, and the P tetrahedra are attached to this chain by sharing O atoms of subsequent octahedra. An extra H_2O molecule occupies the large cavity between the chains and, as indicated by a high temperature factor, it has a statistical distribution within this cavity.

Introduction

Wavellite, $Al_3(PO_4)_2(OH)_3 \cdot 4.5{-}5H_2O$, is known to occur with other basic aluminum phosphates in many localities. The structures of two hydrous minerals in that group have been determined: eosphorite by HANSON (1960) and turquois by CID-DRESDNER (1964). The structure of wavellite, however, was expected to be different from these two because it contains no metallic ions other than aluminum.

The unit-cell dimensions of a wavellite crystal from Llallagua were determined by GORDON (1950) as $a = 9.60$, $b = 17.31$ and $c = 6.98$ Å. A differential thermal-analysis curve of wavellite was obtained by MAULY, JR. (1950). He reported the endothermic points of the dehydration and of the final conversion to the tridymite structure of berlinite. No detailed structure model has yet been proposed, however.

Experimental procedures

A specimen from Montgomery County, Arkansas, was used for the investigation of the wavellite structure. A light green-colored globular aggregate was crushed and several apparently single-crystal fragments were examined. A needle-like piece, measuring 0.043, 0.053, and 0.45 mm along the *a*, *b*, *c* axes, was accepted as a single crystal from its optical and x-ray characteristics.

The orthorhombic unit-cell dimensions obtained from the *c*-axis rotation Weissenberg photographs, and from a^*c^* and b^*c^* precession photographs were $a = 9.62 \pm 0.01$, $b = 17.34 \pm 0.02$, and $c = 7.01 \pm \pm 0.01$ Å. These values were further refined by a least-squares method using powder-diffractometer data yielding the following unit translations:

$$\begin{aligned} a &= 9.621 \pm 0.002 \text{ Å} \\ b &= 17.363 \pm 0.004 \text{ Å} \\ c &= 6.994 \pm 0.003 \text{ Å}. \end{aligned}$$

The systematic absences of $l = 2n + 1$ in $0kl$ and $h + k = 2n + 1$ in $hk0$ planes in the single-crystal photographs indicated two possible

space groups: $Pcmn$ and $Pc2_1n$. This conclusion confirms GORDON's (1950) observations.

For the collection of three-dimensional intensities a single-crystal equi-inclination diffractometer, scintillation counter and copper radiation with balanced Ni—Co filters were used. The crystal was mounted with c axis parallel with the rotation axis of the instrument. The usual Lorentz-polarization and absorption corrections were made after calculating these factors with CHARLES W. BURNHAM's computer program written for polyhedral specimens. Within the instrumental limit of $2\theta = 110°$, 765 reflections were scanned, of which 63 had intensities below the detection level of the equipment. Structure factors equal to the square roots of the lowest observed ones within corresponding $\sin\theta$ ranges were assigned for these unobserved reflections.

Structure determination

The three-dimensional Patterson synthesis maps calculated with the University of Minnesota CDC 1604 computer showed a number of prominent peaks at $\frac{1}{2}\frac{1}{2}\frac{1}{4}$, and $0\frac{1}{3}0$ positions and on the $z = 0$, 1/4, and 1/2 levels. Several peaks on the $z = 1/4$ level were found to be equivalent to peaks on the $z = 1/2$ level by the operation of a mirror plane located at $x = 1/4$. From this it was concluded that the density of atoms on or close to the $z = 1/8$ level must be significantly high.

In the consideration of candidates for P—P, Al—Al, and P—Al peaks to be used in the minimum-function method the expected concentration of atoms on the $z = 1/8$ level was utilized and led to the location of three inversion peaks. Two were assumed to be Al—Al vectors and one a P—P vector. Three sets of M_2 function maps were then prepared by the superposition of Patterson maps separated by $z = 1/2$ levels and shifted by $x = 1/2$ and $y = 1/2$ in accordance with the n-glide operation.

The three M_2 function maps were combined to yield a set of M_6 function maps which in turn produced a set of M_{12} function maps by superimposing the mirror equivalent halves of the same maps. This set of M_{12} function maps disclosed the positions of three oxygen atoms and two hydroxyl groups in the asymmetric unit and the locations of aluminum and phosphorus atoms, approximately at the sites indicated by the initial inversion peaks. However, the positions of one oxygen atom and of the water molecules were ambiguous.

Successive Fourier syntheses were calculated with the starting coordinates thus obtained, until all of the atomic positions were clearly defined. During this procedure, the R factor dropped from 53.5% to 22.6%. Several cycles of full-matrix least-squares refinement were completed with isotropic temperature factors at the

Table 1. *Final atomic parameters and anisotropic temperature factors in wavellite and their standard deviations (lower rows)* ($\times 10^5$)

Atom	Number of atoms in the unit cell	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al(1)	4	22384	25000	12326	219	52	316	0	70	0
		23	0	26	31	8	37	0	31	0
Al(2)	8	75605	01638	14186	88	45	124	−2	39	1
		19	8	16	16	5	24	10	19	10
P	8	06061	09221	10399	139	51	78	−5	−27	−13
		14	8	17	16	5	22	8	18	10
O(1)	8	90525	08349	06432	282	102	227	−21	−143	52
		38	22	36	45	13	56	21	43	23
O(2)	8	08916	17642	15555	323	81	796	−53	93	−84
		40	23	41	48	14	75	22	50	26
O(3)	8	10095	04183	27355	272	122	285	1	56	16
		40	23	40	48	14	57	22	44	26
O(4)	8	36037	07246	42258	358	98	234	−10	99	81
		38	21	40	45	14	59	19	44	24
OH(1)	4	27997	25000	36925	210	62	415	0	102	0
		50	0	58	69	17	76	0	69	0
OH(2)	8	82173	01851	39490	245	99	530	−24	−85	20
		36	20	40	38	14	60	21	49	27
$H_2O(1)$	8	37060	17055	09551	438	205	1337	57	−106	−38
		45	26	54	51	18	77	24	63	35
$H_2O(2)$	8	64979	11144	19740	457	133	455	74	42	8
		41	23	40	50	15	59	23	46	27
$H_2O(3,1)$	2	81314	25000	23453	1660	239	3935	0	309	0
		277	0	427	343	74	599	0	477	0
$H_2O(3,2)$	2	78308	25000	11326	1644	147	3432	0	994	0
		262	0	393	371	60	498	0	450	0

Table 2. *Ellipsoids of thermal vibration*

Atom	B		r	$\langle r \rangle$		φ (a)		φ (b)		φ (c)	
Al(1)	0.684	.048	1	.080 Å	.007 Å	122°	10°	90°		32°	10°
			2	.089	.007	90		0		90	
			3	.108	.007	32	10	90		58	10
Al(2)	0.371	.033	1	.046	.008	124	10	92	± 8	34	10
			2	.071	.006	146	10	92	24	124	10
			3	.083	.005	92	22	2	20	90	14
P	0.425	.030	1	.040	.007	79	7	82	6	14	6
			2	.082	.005	17	22	79	29	103	7
			3	.089	.004	78	29	166	24	84	9
O(1)	0.904	.071	1	.054	.014	67	7	100	7	26	6
			2	.113	.010	44	14	48	15	101	10
			3	.137	.008	125	14	44	15	67	6
O(2)	1.242	.076	1	.092	.012	64	15	31	9	75	11
			2	.118	.009	40	14	102	15	127	11
			3	.158	.007	63	8	118	6	41	8
O(3)	1.011	.072	1	.080	.010	107	12	94	8	17	12
			2	.115	.010	163	12	86	20	106	12
			3	.137	.008	87	19	6	15	85	9
O(4)	0.989	.074	1	.053	.015	104	6	112	6	27	6
			2	.130	.008	58	76	145	59	102	33
			3	.134	.008	35	72	65	72	67	19
OH(1)	0.777	.097	1	.081	.017	137	16	90		47	16
			2	.097	.013	90		0		90	
			3	.116	.013	47	16	90		43	16
OH(2)	1.045	.068	1	.096	.010	35	18	80	19	57	17
			2	.114	.009	73	20	45	21	131	23
			3	.132	.008	120	12	46	20	58	16
$H_2O(1)$	2.237	.087	1	.135	.009	21	7	108	8	80	8
			2	.173	.008	97	10	137	15	132	15
			3	.192	.007	110	6	127	15	44	15
$H_2O(2)$	1.395	.080	1	.105	.007	100	17	87	19	11	22
			2	.121	.010	131	9	42	9	99	25
			3	.165	.008	43	8	48	8	85	6
$H_2O(3,1)$	5.575	.543	1	.191	.030	90		0		90	
			2	.271	.028	23	30	90		113	30
			3	.319	.028	69	30	90		23	30
$H_2O(3,2)$	4.856	.510	1	.150	.031	90		0		90	
			2	.217	.031	42	10	90		132	10
			3	.339	.031	48	10	90		42	10

B is the equivalent isotropic temperature factor; $\langle r \rangle$ is the root-mean-square displacement along principal axis, r; φ's are the angles between r and the crystallographic axes. Second values in each column are corresponding standard deviations.

Table 3. *List of calculated and observed structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	2	0	115.0	149.1	2	0	1	59.7	- 63.8	8	2	1	11.5	- 11.1	4	8	2	14.2	12.5
	4		54.6	55.4		1		32.7	- 36.3		3		64.5	- 66.0		9		71.3	- 73.5
	6		92.7	- 93.1		2		16.3	- 14.9		4		20.5	23.0		10		11.8	- 13.5
	8		44.4	37.2		3		47.4	- 53.4		5		14.2	- 13.8		11		32.5	- 32.8
	10		45.3	46.6		4		65.6	61.3		6		14.7	15.0		12		41.4	- 41.0
	12		170.2	170.9		5		52.7	- 48.6		7		2.0	- 4.0		13		26.1	- 24.8
	14		91.8	- 91.5		6		21.7	22.9		8		29.2	- 28.2		14		33.3	- 33.6
	16		19.7	- 17.8		7		35.6	38.8		9		26.7	25.7		15		44.0	- 44.0
	18		66.0	- 63.6		8		1.9	3.2		10		36.2	- 35.5		16		2.0	- 2.2
1	1	0	97.8	-103.1		9		13.1	11.8		11		20.5	- 23.2	5	0	2	19.1	- 20.8
	3		63.2	65.3		10		20.0	- 18.4	9	0	1	7.7	9.0		1		28.0	27.0
	5		7.6	3.1		11		12.6	- 12.5		1		2.0	- 3.9		2		36.4	39.2
	7		14.0	20.6		12		30.1	30.3		2		13.1	- 12.3		3		14.7	11.5
	9		72.5	72.3		13		31.7	- 31.3		3		14.9	14.5		4		114.5	115.2
	11		155.5	156.6		14		56.1	54.8		4		56.2	56.4		5		12.3	- 11.1
	13		19.3	18.7		15		9.1	- 8.3		5		15.7	- 13.1		6		151.9	155.7
	15		86.6	85.1		16		17.5	17.5		6		16.4	16.8		7		13.5	- 14.0
	17		36.7	36.4		17		12.2	- 12.7		7		17.9	- 19.2		8		42.4	41.3
2	0	0	113.9	-107.8	3	0	1	32.8	31.0		8		33.4	33.8		9		11.5	- 11.5
	2		7.3	1.2		1		40.5	- 34.4	10	0	1	26.2	27.0		10		18.4	- 16.5
	4		196.3	-214.6		2		30.6	31.9		1		6.0	5.0		11		14.4	- 16.1
	6		50.7	- 53.8		3		66.2	- 63.0		2		10.5	9.7		12		23.8	- 23.2
	8		154.9	-153.7		4		26.4	- 26.9	0	1	2	156.3	-179.4		13		14.0	- 13.5
	10		53.0	53.4		5		53.1	51.2		2		2.7	2.7		14		20.2	19.4
	12		24.7	- 22.1		6		69.1	65.4		3		62.5	- 64.9		15		23.6	- 23.0
	14		12.0	15.3		7		52.0	49.8		4		35.0	- 40.9	6	0	2	7.1	8.3
	16		69.4	- 65.7		8		11.9	10.5		5		47.9	32.9		1		61.7	62.3
	18		16.9	20.5		9		58.7	60.0		6		49.7	- 51.4		2		22.2	20.0
3	1	0	77.0	- 72.1		10		41.7	43.0		7		40.8	46.2		3		43.0	62.1
	3		123.5	-130.2		11		1.9	2.2		8		42.4	- 41.8		4		46.7	46.2
	5		4.1	- 8.4		12		7.6	- 9.2		9		44.1	41.8		5		60.0	60.1
	7		154.3	-149.3		13		1.8	4.4		10		25.8	28.9		6		49.4	47.8
	9		11.6	14.3		14		19.2	- 19.5		11		13.4	- 13.4		7		18.2	22.4
	11		69.8	- 70.2		15		2.0	5.8		12		63.4	61.3		8		14.9	- 13.2
	13		87.6	- 84.1		16		35.6	- 34.8		13		151.9	-153.4		9		4.3	- 2.0
	15		67.7	- 64.7		17		23.0	21.5		14		45.9	45.3		10		25.9	- 25.5
	17		7.2	8.4	4	0	1	114.3	-115.8		15		27.7	- 26.8		11		23.1	23.7
4	0	0	110.0	- 90.0		1		2.0	- 6.2		16		12.5	- 13.8		12		13.5	- 12.5
	2		30.4	- 23.4		2		38.0	- 42.3		17		7.9	- 8.5		13		98.8	98.9
	4		162.8	156.7		3		19.4	- 24.2	1	0	2	34.4	29.9		14		2.0	- 3.6
	6		19.4	16.7		4		31.4	- 27.0		1		29.8	- 27.9	7	0	2	86.6	- 85.8
	8		135.8	136.9		5		50.5	49.1		2		89.0	96.3		1		22.9	- 21.2
	10		1.9	- 3.5		6		10.2	- 9.3		3		16.6	- 12.3		2		111.5	-114.3
	12		18.3	16.3		7		8.2	10.8		4		36.5	34.6		3		28.8	- 25.8
	14		1.8	1.7		8		20.3	23.0		5		25.4	19.6		4		45.1	- 44.8
	16		19.2	18.4		9		53.6	58.0		6		41.3	- 29.8		5		16.5	- 16.0
5	1	0	57.0	- 57.2		10		15.9	- 16.8		7		44.2	42.9		6		1.8	- 3.6
	3		12.2	- 13.6		11		12.5	- 11.1		8		31.5	32.3		7		9.7	8.9
	5		1.9	- 1.8		12		33.3	- 34.2		9		8.3	7.4		8		32.9	- 34.6
	7		135.1	134.3		13		23.1	- 21.8		10		17.0	19.6		9		14.1	10.5
	9		39.0	35.3		14		17.1	18.0		11		8.5	- 7.9		10		53.4	- 53.0
	11		1.8	2.4		15		13.2	- 13.7		12		20.3	- 23.0		11		9.5	9.4
	13		39.7	- 37.2		16		29.0	29.6		13		14.1	- 13.4		12		22.4	- 20.0
	15		42.1	41.8	5	0	1	37.8	- 38.9		14		44.8	42.2	8	0	2	18.6	- 22.0
6	0	0	134.4	-134.5		1		19.4	17.7		15		2.0	- 3.8		1		12.5	10.2
	2		35.8	- 35.0		2		67.1	- 66.0		16		8.7	9.5		2		26.6	- 26.0
	4		43.5	- 38.2		3		46.7	47.5		17		7.9	- 9.6		3		44.3	42.5
	6		12.4	14.0		4		48.3	48.2	2	0	2	29.8	29.1		4		2.0	- 5.5
	8		1.9	2.3		5		1.9	- 1.3		1		25.1	- 21.8		5		2.0	- 3.5
	10		22.7	- 22.9		6		12.6	13.5		2		7.1	7.5		6		2.0	2.7
	12		65.9	- 65.0		7		21.3	21.1		3		73.3	- 74.4		7		74.6	- 72.8
	14		30.7	29.4		8		38.4	40.0		4		18.3	- 15.2		8		13.6	- 14.6
7	1	0	26.3	26.0		9		34.3	- 34.7		5		27.7	29.5		9		92.2	- 88.7
	3		53.1	- 50.4		10		52.0	- 51.1		6		26.1	- 26.9		10		17.7	- 16.3
	5		14.2	- 12.4		11		1.8	- 3.2		7		38.0	35.2	9	0	2	72.3	69.9
	7		33.9	34.7		12		13.5	- 13.8		8		22.6	22.1		1		20.8	- 21.1
	9		33.9	31.7		13		6.1	- 6.9		9		111.8	114.0		2		57.6	57.2
	11		33.5	- 33.4		14		22.2	- 22.8		10		26.7	27.0		3		31.3	- 30.8
	13		29.4	- 27.1		15		9.8	- 11.3		11		25.0	25.5		4		27.4	27.3
8	0	0	16.1	20.6	6	0	1	4.8	- 7.0		12		17.5	17.9		5		12.9	- 11.7
	2		12.2	12.9		1		54.9	- 55.1		13		7.0	6.8		6		23.7	24.8
	4		56.1	56.1		2		20.7	20.5		14		1.8	1.6		7		13.7	- 14.3
	6		65.3	64.3		3		6.6	- 3.5		15		10.7	- 8.6	1	0	3	11.7	- 9.8
	8		9.8	12.1		4		38.8	37.5		16		10.5	- 7.5		1		30.1	- 29.7
	10		38.7	- 35.2		5		11.2	- 12.8		17		52.2	48.6		2		45.2	41.4
9	1	0	6.4	7.4		6		37.2	39.8	3	0	2	126.0	-124.0		3		66.6	- 68.7
	3		11.8	11.3		7		31.0	31.7		1		12.1	8.7		4		2.5	2.7
	5		2.0	2.9		8		23.4	23.3		2		17.0	- 24.1		5		8.3	- 4.6
	7		16.9	18.4		9		7.9	6.0		3		19.3	16.5		6		1.9	- 7.1
10	0	0	54.0	- 53.2		10		10.1	- 13.0		4		6.2	- 2.9		7		91.6	93.7
	2		46.0	- 46.9		11		13.1	13.9		5		40.1	37.8		8		13.6	13.9
1	0	1	111.2	124.1		12		42.8	- 42.2		6		84.1	- 81.5		9		54.2	58.1
	1		49.4	- 52.2		13		56.6	- 55.3		7		50.7	50.2		10		11.7	- 10.0
	2		34.6	35.9		14		8.2	- 9.1		8		15.8	- 10.7		11		29.6	- 28.9
	3		46.4	- 52.4	7	0	1	97.8	-101.0		9		24.2	24.4		12		34.2	- 34.8
	4		64.5	- 65.7		1		74.3	72.0		10		75.7	- 76.9		13		63.5	- 63.8
	5		65.4	- 61.4		2		23.4	20.8		11		1.9	4.3		14		11.8	12.9
	6		128.3	-134.9		3		55.4	56.3		12		54.9	- 56.2		15		44.2	- 44.3
	7		34.7	- 28.5		4		9.0	8.5		13		1.8	1.2		16		4.8	3.3
	8		42.5	- 40.6		5		17.4	16.7		14		25.9	24.4	2	0	3	136.4	127.7
	9		14.8	15.5		6		31.0	32.3		15		2.0	- 1.4		1		65.3	63.3
	10		48.1	47.7		7		22.7	- 20.2		16		42.9	40.0		2		77.4	72.2
	11		1.9	- 1.2		8		25.4	- 25.6	4	0	2	2.0	- 3.8		3		28.6	29.5
	12		66.9	70.8		9		18.5	- 21.2		1		27.5	25.9		4		15.5	13.0
	13		48.7	- 48.5		10		22.4	- 22.1		2		6.2	- 5.9		5		17.4	- 16.2
	14		1.8	6.6		11		2.0	- 0.7		3		15.4	- 12.6		6		22.0	24.1
	15		16.8	- 16.0		12		54.3	- 56.1		4		5.0	- 4.9		7		34.3	- 35.8
	16		27.0	- 26.3		13		56.6	52.0		5		110.6	-108.6		8		36.1	- 36.5
	17		8.8	9.1	8	0	1	12.4	16.2		6		3.6	4.7		9		25.7	- 26.2
	18		37.9	- 36.1		1		10.7	11.1		7		12.4	- 13.9		10		27.5	- 29.9

Table 3. *(Continued)*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	11	3	5.2	5.3	0	1	4	1.9	- 4.1	6	3	4	59.5	60.3	6	3	5	18.0	18.6
	12		5.7	- 7.3		2		19.4	- 20.6		4		11.8	12.1		4		2.0	3.6
	13		42.8	42.9		3		8.4	- 10.1		5		27.9	28.4		5		2.0	2.7
	14		9.7	9.4		4		60.3	- 58.1		6		14.2	- 11.8		6		7.6	- 7.3
	15		6.3	- 7.2		5		12.0	- 11.1		7		46.9	- 47.4		7		46.7	- 45.9
	16		15.8	16.0		6		9.9	8.1		8		34.9	35.4		8		5.8	6.0
3	0	3	35.0	- 37.3		7		31.5	30.6		9		30.5	- 31.3	7	0	5	54.5	51.1
	1		29.4	- 30.3		8		55.4	- 55.3		10		35.5	36.9		1		10.5	- 8.4
	2		45.6	- 42.9		9		42.0	43.2		11		3.8	- 5.8		2		11.0	- 9.9
	3		30.0	- 31.8		10		46.6	- 48.0	7	0	4	19.0	- 17.8		3		15.9	17.9
	4		48.1	47.3		11		34.3	35.0		1		2.0	- 1.9		4		2.0	1.9
	5		1.9	- 2.5		12		124.5	-125.2		2		5.2	6.1		5		6.2	8.0
	6		1.9	1.7		13		5.1	- 4.3		3		48.9	51.4	0	1	6	38.4	38.7
	7		4.8	- 3.4		14		31.1	31.9		4		33.2	33.4		2		31.6	- 31.9
	8		7.9	5.0		15		6.1	- 7.2		5		25.8	27.9		3		18.3	17.7
	9		55.6	54.7	1	0	4	53.2	- 53.7		6		31.5	33.5		4		40.4	41.1
	10		32.2	- 33.9		1		75.6	76.2		7		6.9	6.9		5		41.2	42.8
	11		45.5	45.9		2		28.1	- 29.9		8		7.3	9.5		6		81.3	81.4
	12		11.9	13.1		3		50.7	- 48.7		9		2.0	4.5		7		18.9	16.6
	13		4.1	4.3		4		26.4	- 25.0	8	0	4	9.7	4.7		8		40.7	39.8
	14		2.0	1.8		5		15.7	- 18.2		1		9.3	10.6		9		10.6	10.3
	15		6.0	- 5.1		6		38.1	- 39.0		2		2.0	1.2		10		11.1	- 9.4
4	0	3	81.3	- 80.6		7		96.9	- 99.9		3		35.2	38.8	1	0	6	43.9	43.6
	1		9.7	12.0		8		53.9	- 56.2		4		47.6	- 50.2		1		16.1	16.4
	2		43.0	- 44.2		9		50.5	- 52.6		5		16.9	18.6		2		22.8	- 21.7
	3		28.4	28.3		10		21.0	- 20.4	1	0	5	87.9	- 87.9		3		40.7	39.4
	4		36.9	36.2		11		94.7	- 97.7		1		13.0	14.3		4		38.6	- 38.3
	5		23.6	- 22.8		12		13.1	14.4		2		43.6	- 44.5		5		18.3	20.0
	6		16.0	16.3		13		5.5	3.7		3		16.8	- 16.1		6		55.9	- 56.1
	7		17.9	15.9		14		30.7	31.5		4		52.1	49.9		7		6.5	5.7
	8		9.7	- 10.3		15		64.7	- 64.9		5		23.2	- 23.4		8		12.4	- 12.8
	9		53.1	- 54.0	2	0	4	74.5	73.8		6		102.7	101.7		9		2.0	1.8
	10		68.0	- 67.0		1		20.8	- 21.4		7		10.5	9.9		10		10.2	- 8.4
	11		1.8	- 5.2		2		20.6	23.0		8		1.8	5.4	2	0	6	50.9	- 49.6
	12		38.4	- 36.2		3		65.5	- 67.1		9		10.8	- 11.5		1		1.8	3.5
	13		18.6	19.9		4		136.9	141.3		10		42.3	- 40.4		2		40.8	- 40.6
	14		4.5	6.0		5		32.6	- 34.6		11		6.4	- 6.7		3		34.5	33.1
	15		24.0	25.4		6		43.7	44.6		12		26.4	- 26.4		4		5.3	0.8
5	0	3	19.9	- 22.2		7		9.6	9.7		13		14.5	14.9		5		24.2	- 22.2
	1		3.7	- 5.1		8		76.7	79.4	2	0	5	44.3	44.4		6		16.9	16.8
	2		1.9	- 2.7		9		3.3	3.8		1		9.0	7.5		7		24.5	- 22.7
	3		17.7	18.8		10		43.0	- 44.5		2		16.0	- 15.3		8		17.8	- 16.5
	4		39.9	- 37.6		11		28.8	- 29.6		3		41.9	39.9		9		51.4	- 49.2
	5		20.9	- 23.2		12		15.7	14.0		4		37.4	- 37.3		10		36.6	- 33.2
	6		40.3	41.4		13		34.3	- 34.7		5		74.5	74.0	3	0	6	105.6	103.7
	7		54.3	- 57.4		14		8.1	- 11.0		6		26.5	- 27.0		1		13.7	14.1
	8		27.9	- 28.4		15		37.6	- 37.0		7		12.5	- 9.2		2		77.7	74.4
	9		62.1	- 63.5	3	0	4	25.4	25.0		8		29.3	- 29.1		3		31.7	31.9
	10		29.3	26.9		1		19.9	23.2		9		5.7	- 5.3		4		6.8	- 9.1
	11		8.8	- 8.9		2		14.9	15.6		10		17.0	17.8		5		10.3	12.0
	12		4.1	- 4.8		3		86.1	88.7		11		2.0	- 4.2		6		2.0	- 1.8
	13		2.0	2.9		4		25.8	29.5		12		45.7	44.9		7		37.4	- 35.0
	14		5.4	3.1		5		29.6	- 28.7		13		18.9	19.6		8		7.5	- 8.4
6	0	3	101.7	-104.7		6		21.6	21.0	3	0	5	1.9	- 1.2		9		28.6	- 26.5
	1		25.0	23.4		7		34.3	34.9		1		1.8	- 5.8	4	0	6	63.3	60.4
	2		10.2	- 13.2		8		1.8	- 5.3		2		15.8	- 15.6		1		16.2	15.4
	3		10.0	- 9.2		9		50.7	- 50.9		3		1.8	- 0.3		2		52.3	48.2
	4		47.1	48.0		10		1.8	1.1		4		5.3	- 3.4		3		12.9	10.5
	5		26.2	29.0		11		55.9	56.6		5		6.1	- 5.8		4		28.0	25.4
	6		65.8	66.0		12		24.1	25.5		6		43.4	- 40.2		5		24.7	22.5
	7		21.0	- 21.4		13		67.0	68.2		7		7.3	- 6.4		6		8.8	3.8
	8		29.8	29.8		14		24.7	24.7		8		8.4	8.4		7		19.8	- 16.9
	9		2.0	2.6	4	0	4	67.9	- 68.3		9		2.0	- 2.0		8		5.9	- 5.6
	10		12.6	- 13.5		1		8.4	- 8.4		10		26.5	- 25.4	5	0	6	18.3	- 19.1
	11		24.6	- 26.4		2		35.5	- 37.8		11		5.3	6.0		1		2.0	- 1.0
	12		46.7	- 44.3		3		1.9	- 2.2		12		20.0	- 17.1		2		39.4	- 37.9
7	0	3	80.7	81.8		4		84.1	- 86.1	4	0	5	29.8	28.7		3		24.1	24.2
	1		56.4	56.7		5		11.2	12.9		1		19.4	17.8		4		40.1	- 37.5
	2		14.8	- 13.5		6		11.6	12.7		2		3.1	4.6		5		20.8	19.4
	3		51.7	50.4		7		33.8	36.4		3		71.4	68.2		6		69.1	- 64.7
	4		1.8	4.8		8		72.1	- 72.4		4		11.4	- 11.8	6	0	6	9.4	- 8.0
	5		28.2	27.9		9		17.7	19.7		5		15.8	- 14.4		1		32.9	- 30.1
	6		20.3	- 18.5		10		9.1	8.3		6		10.3	9.4	1	0	7	9.1	5.8
	7		25.6	- 27.2		11		11.7	12.8		7		41.2	- 40.3		1		19.4	20.7
	8		25.9	26.0		12		6.6	- 8.0		8		7.0	- 8.7		2		13.6	- 13.4
	9		48.7	- 47.7		13		15.5	16.5		9		56.5	- 54.8		3		50.6	50.1
	10		10.6	9.4	5	0	4	23.8	- 24.2		10		25.8	24.6		4		14.7	14.8
	11		33.4	- 31.0		1		33.5	34.0		11		21.0	18.8		5		25.2	24.2
8	0	3	2.0	1.1		2		37.9	- 39.8	5	0	5	27.0	27.7		6		32.4	33.5
	1		24.8	- 25.2		3		1.8	4.3		1		1.8	- 0.7	2	0	7	2.0	9.8
	2		25.2	- 23.9		4		14.0	- 15.0		2		63.2	61.9		1		15.5	- 13.0
	3		36.4	37.1		5		16.8	17.5		3		25.6	23.5		2		11.1	13.2
	4		2.0	0.4		6		28.5	29.0		4		13.5	- 12.7		3		16.7	14.7
	5		2.0	- 0.8		7		74.7	- 76.0		5		38.4	37.6		4		14.4	- 13.2
	6		5.0	4.3		8		7.0	8.1		6		12.3	- 12.9		5		9.2	- 4.7
	7		7.6	9.5		9		37.6	- 41.0		7		5.6	- 7.2	3	0	7	23.7	- 18.7
	8		13.1	13.9		10		14.3	- 15.8		8		16.6	- 16.8		1		7.3	5.7
9	0	3	19.6	- 20.8		11		31.7	- 33.3		9		17.2	16.8		2		10.0	8.7
	1		17.2	19.3		12		26.9	- 28.3		10		28.8	28.3		3		15.7	14.9
	2		15.8	15.8	6	0	4	76.8	75.6	6	0	5	14.5	- 15.1					
	3		52.4	53.0		1		23.7	24.9		1		55.2	52.8					
	4		36.7	- 37.1		2		1.8	1.3		2		13.4	- 12.3					

beginning and with anisotropic temperature factors in the final cycles, using LARRY W. FINGER's program and the Control Data Corporation 1604 computer of the University of Minnesota. The

weighting factors used in these calculations were reciprocals of the variances of the observed structure factors. Neutral atomic-scattering factors were assumed for all atoms.

In the final three cycles of the full-matrix least-squares refinement, however, only 684 of the reflections whose $(\sin\theta)/\lambda$ were larger than 0.25 were used. The contribution of the hydrogen atoms to the structure factors was neglected in these calculations.

In the Fourier sections a broad oval-shaped pattern appeared where the water molecule, $H_2O(3)$ was expected to be. When the position of this water molecule was assumed to be at the center of that peak the calculations gave an extraordinarily high anisotropic temperature factor. When the water molecule was split into two positions within the oval-shaped peak both the temperature factors and the R factor were improved.

The final R factors were 4.7% and 5.5% respectively for the reflections with $(\sin\theta)/\lambda > 0.25$ and for all reflections. Both sets of calculations included the unobserved reflections. The final atomic coordinates and the anisotropic temperature factors are tabulated with their standard deviations in Table 1. The displacements and the orientation of the ellipsoids of thermal vibration are given in Table 2. A comparison of the observed and calculated structure factors are shown in Table 3.

Description of the structure

The c axis projection of the wavellite structure and a stereoscopic drawing of its polyhedral model are illustrated in Figs. 1 and 2, while the bond distances and angles with the corresponding standard deviations are listed in Table 4 and 5 respectively.

Two different octahedral coordinations of the aluminum atoms were observed in this structure. Al(1) is bound to two oxygen atoms, to two water molecules, and to two hydroxyl groups. Bond distances range from 1.78 to 1.98 Å with an average of 1.87 Å. Al(2) is bound to three oxygen atoms, to two hydroxyl groups, and to one water molecule. Bond distances range from 1.88 to 1.98 Å with an average of 1.91 Å. The average O—M—O bond angle is near 90°. The coordination octahedron of Al(1) is slightly more distorted than that of Al(2). The octahedra form two independent zigzagging chains, parallel to the c axis by sharing the hydroxyls at opposite corners.

The Al(1) and Al(2) octahedral chains are linked together by phosphate tetrahedra through sharing oxygen atoms. This scheme

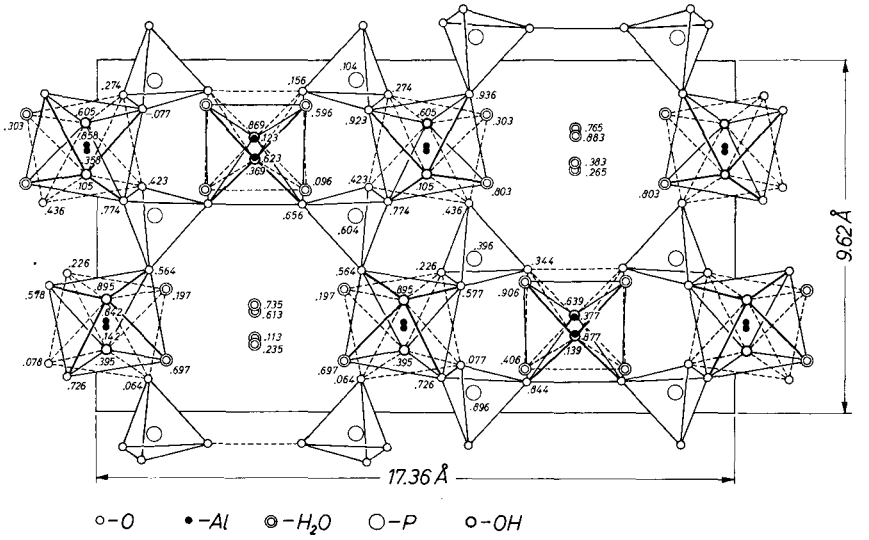

Fig. 1. The structure of wavellite projected along the c axis. Numbers indicate relative heigths of the positions

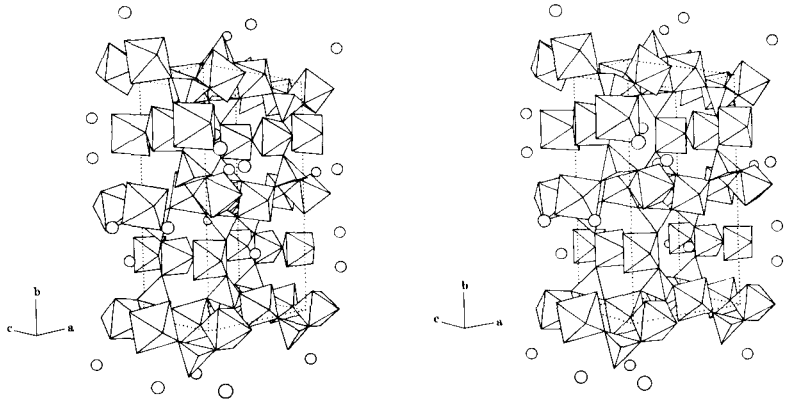

Fig. 2. A stereoscopic view of the wavellite structure

of linkage creates a dense layer of octahedra and tetrahedra in the (010) plane at intervals of $y = 1/2$. These layers are in turn connected by alternating Al(1) octahedra and water molecules. While the Al(1) octahedra form a chain, the water molecules connecting these layers occupy a broad channel parallel with the c axis. Although the temperature factors of this water molecule decreased after it was split into two positions, it is still reasonably high indicating a possible

incomplete occupation and/or statistical distribution of water molecules in these sites.

The strong octahedral chains in the structure are clearly responsible for the fibrous habit of wavellite. The relative weakness of the structure in the (110) plane, through the channel containing H_2O and

Table 4. *Selected bond distances and their standard deviations*

PO_4 tetrahedron				
P	— O(1)	1.5277 Å	.0041 Å	
P	— O(2)	1.5308	.0042	
P	— O(3)	1.5238	.0037	
P	— O(4)	1.5183	.0037	
O(1)	— O(2)	2.4781	.0055	
O(1)	— O(3)	2.4918	.0046	
O(1)	— O(4)	2.4706	.0054	
O(2)	— O(3)	2.4809	.0054	
O(2)	— O(4)	2.4796	.0050	
O(3)	— O(4)	2.5389	.0038	
Al(1) octahedron				
Al(1)	— O(2)	1.8336 Å	.0042 Å	*
Al(1)	— $H_2O(1)$	1.9835	.0046	*
Al(1)	— OH(1)	1.8031	.0045	
Al(1)	— $OH(1)^3$	1.7768	.0044	
OH(1)	— O(2)	2.6899	.0056	
OH(1)	— $H_2O(1)$	2.5156	.0056	*
$OH(1)^3$	— O(2)	2.6882	.0050	*
$OH(1)^3$	— $H_2O(1)$	2.5506	.0054	
O(2)	— $O(2)^5$	2.5551	.0080	
$H_2O(1)$	— $H_2O(1)^5$	2.7590	.0091	
O(2)	— $H_2O(1)$	2.7419	.0057	*
* 2 ×				

Al(2) octahedron			
Al(2)	— OH(2)	1.8795 Å	.0032 Å
Al(2)	— O(1)	1.9268	.0039
Al(2)	— $OH(2)^3$	1.8826	.0032
Al(2)	— $O(3)^4$	1.8969	.0041
Al(2)	— $O(4)^4$	1.8947	.0041
Al(2)	— $H_2O(2)$	1.9799	.0043
OH(2)	— O(1)	2.6952	.0040
OH(2)	— $O(3)^4$	2.6452	.0052
OH(2)	— $O(4)^4$	2.7502	.0046
OH(2)	— $H_2O(2)$	2.6921	.0046
$OH(2)^3$	— O(1)	2.7286	.0051
$OH(2)^3$	— $O(3)^4$	2.6509	.0041
$OH(2)^3$	— $O(4)^4$	2.6821	.0043
$OH(2)^3$	— $H_2O(2)$	2.6747	.0046
O(1)	— $O(4)^4$	2.7436	.0050
O(1)	— $H_2O(2)$	2.6725	.0055
$O(3)^4$	— $O(4)^4$	2.7565	.0054
$O(3)^4$	— $H_2O(2)$	2.7099	.0055
Others			
OH(2)	— O(3)	2.8461 Å	.0049 Å
$H_2O(1)$	— O(4)	2.8535	.0049
$H_2O(1)$	— $H_2O(2)$	2.9624	.0053
$H_2O(2)^3$	— O(1)	2.6647	.0037
$H_2O(2)$	— $H_2O(3,1)$	2.8853	.0155
$H_2O(2)$	— $H_2O(3,2)$	2.7890	.0112
$H_2O(3,1)$	— $H_2O(3,2)$	2.8961	.0229
$H_2O(3,2)^3$	— $H_2O(3,1)$	2.8058	.0205

Superscripts identify symmetrically identical atoms in different sites.

1.	$x, \quad y, \quad z$	2.	$-x, \quad -y, \quad -z$
3.	$\frac{1}{2}-x, \quad y, \quad \frac{1}{2}+z$	4.	$\frac{1}{2}+x, \quad -y, \quad \frac{1}{2}-z$
5.	$x, \quad \frac{1}{2}-y, \quad z$	6.	$-x, \quad \frac{1}{2}+y, \quad -z$
7.	$\frac{1}{2}-x, \quad \frac{1}{2}-y, \quad \frac{1}{2}+z$	8.	$\frac{1}{2}+x, \quad \frac{1}{2}+y, \quad \frac{1}{2}-z$

(Superscript 1 is omitted from the tables.)

the oxygen atoms shared between the P tetrahedra and the Al(1)-octahedra, explains the corresponding perfect cleavage of the mineral. The other good and distinct cleavages of wavellite in the (101) and (001) planes can also be explained by similar arguments.

Table 5. *Selected bond angles and their standard deviations*

O(1)	— P	— O(2)	108.2°	.2°
O(1)		O(3)	109.5	.2
O(1)		O(4)	108.4	.2
O(2)		O(3)	108.6	.2
O(2)		O(4)	108.8	.2
O(3)		O(4)	113.2	.2
OH(1)	— Al(1)	— O(2)	95.4	.2 (×2)
OH(1)		$H_2O(1)$	83.1	.2 (×2)
OH(1)[3]		O(2)	96.2	.2 (×2)
OH(1)[3]		$H_2O(1)$	85.2	.2 (×2)
O(2)		O(2)[5]	88.3	.3
$H_2O(1)$		$H_2O(1)$[5]	88.1	.3
O(2)		$H_2O(1)$	91.8	.2 (×2)
O(2)		$H_2O(1)$[5]	178.5	5.1 (×2)
OH(1)		OH(1)[3]	163.8	.2
Al(1)	— OH(1)	— Al(1)[3]	161.4	.4
OH(2)	— Al(2)	— O(1)	90.2	.2
OH(2)		O(3)[4]	88.9	.2
OH(2)		O(4)[4]	93.6	.2
OH(2)		$H_2O(2)$	88.4	.1
OH(2)[3]		O(1)	91.5	.2
OH(2)[3]		O(3)[4]	89.1	.2
OH(2)[3]		O(4)[4]	90.5	.2
OH(2)[3]		$H_2O(2)$	87.6	.1
O(1)		O(4)[4]	91.8	.2
O(1)		$H_2O(2)$	86.3	.2
O(3)[4]		O(4)[4]	93.3	.2
O(3)[4]		$H_2O(2)$	88.7	.2
O(1)		O(3)[4]	174.9	1.4
O(4)[4]		$H_2O(2)$	177.3	3.2
OH(2)		OH(2)[3]	175.6	.9
Al(2)	— OH(2)	— Al(2)[3]	136.9	.3
P	— O(2)	— Al(1)	139.8	.3
P	— O(1)	— Al(2)	137.5	.3
P	— O(3)	— Al(2)[4]	138.5	.3
P[3]	— O(4)	— Al(2)[4]	130.4	.3

Table 5. (*Continued*)

O(2)	— $H_2O(1)$ —	O(4)	82.3°	.1°
O(2)		$H_2O(1)^5$	87.9	.1
O(2)		$H_2O(2)$	150.6	.5
OH(1)		$H_2O(2)$	108.7	.2
OH(1)		O(4)	73.8	.1
$OH(1)^3$		O(4)	143.2	.4
$OH(1)^3$		OH(1)	88.8	.1
$OH(1)^3$		$H_2O(2)$	148.4	.4
$H_2O(1)^3$		$H_2O(2)$	110.3	.2
O(2)		OH(1)	61.4	.2
O(2)		$OH(1)^3$	60.9	.1
OH(1)		$H_2O(1)^5$	56.7	.3
$OH(1)^3$		$H_2O(1)^5$	57.3	.3
O(4)		$H_2O(1)^5$	126.6	.3
O(4)		$H_2O(2)$	68.4	.1
$H_2O(1)$	— $H_2O(2)$ —	OH(2)	152.7	.4
$H_2O(1)$		$OH(2)^3$	96.4	.2
$H_2O(1)$		$H_2O(3,1)$	103.1	.4
$H_2O(1)$		$H_2O(3,2)$	93.9	.5
$H_2O(1)$		O(1)	144.4	.4
$H_2O(1)$		$O(3)^4$	101.6	.2
$H_2O(1)$		$O(1)^3$	96.6	.2
O(1)		$O(1)^3$	119.0	.2
O(1)		$O(3)^4$	90.4	.2
O(1)		OH(2)	60.3	.1
O(1)		$OH(2)^3$	61.4	.2
O(1)		$H_2O(3,1)$	71.5	.4
O(1)		$H_2O(3,2)$	70.1	.3
$O(1)^3$		$O(3)^4$	73.4	.1
$O(1)^3$		$H_2O(3,1)$	100.0	.6
$O(1)^3$		$H_2O(3,2)$	116.9	.6
$O(1)^3$		OH(2)	61.2	.1
$O(3)^4$		OH(2)	58.6	.2
$O(3)^4$		$OH(2)^3$	59.0	.1
$O(3)^4$		$H_2O(3,1)$	155.0	1.7
$O(3)^4$		$H_2O(3,2)$	160.5	1.5
OH(2)		$OH(2)^3$	88.9	.2
OH(2)		$H_2O(3,1)$	96.8	.6
OH(2)		$H_2O(3,2)$	110.0	.7
$OH(2)^3$		$H_2O(3,1)$	121.2	.7
$OH(2)^3$		$H_2O(3,2)$	107.8	.6
$OH(2)^3$		$O(1)^3$	132.2	.3
$H_2O(2)$	— $H_2O(3,1)$ —	$H_2O(2)^5$	112.9	1.4
$H_2O(2)$	— $H_2O(3,2)$ —	$H_2O(2)^5$	119.2	1.2

The only known crystal structure resembling that of wavellite is the structure of laueite determined by MOORE (1965). The chain of Al(2) octahedra and *P* tetrahedra of wavellite corresponds to a similar chain of Fe octahedra and P tetrahedra in laueite. The Al(1)-octahedral chain of wavellite, however, is replaced by single Mn octahedra in the laueite structure where every second octahedron of the chain is in the large open channel of the former structure. Thus the broad single channel of wavellite is replaced by two narrower channels in laueite parallel with the *a* and *b* unit translations.

The authors wish to acknowledge the National Science Foundation for the support of this investigation.

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