

The structure of wadeite.

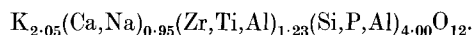
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[Taken as read January 27, 1956.]

INTRODUCTION.

WADEITE has been found only in a suite of leucite-lamproites from the West Kimberley area of Western Australia. The leucite-bearing rocks occur at a number of isolated volcanic vents that have in every instance broken through sedimentary deposits of Permian age.¹ The nature of the mineral, wadeite, has been described by Prider.² It is a potassium-zirconium silicate occurring as highly birefringent prisms up to 1 mm. in length with hexagonal-shaped basal sections. It is invariably replaced in part along the poor pyramidal cleavages by calcite. These cleavages, intersecting at angles of nearly 90°, are rendered visible because of the presence of the secondary calcite which has entered along these directions. The mineral is colourless, uniaxial, optically positive, and has ϵ 1.655, ω 1.625, and $\epsilon - \omega$ 0.030. It has a specific gravity of 3.10, is non-magnetic, and insoluble in hot acids. Prider, on the basis of a chemical analysis (table I), calculated the formula to be



X-ray powder and Laue diffraction work, carried out in this department by Shearer, Robinson, and Jefferies,³ showed the diffraction symmetry to be $6/m (C_{6h})$ and the unit-cell dimensions to be a 6.89 and c 10.18 Å. On the basis of this information and the chemical data, the formula ascribed to wadeite was $(\text{K}(\text{Zr,Ca})\text{Si}_2\text{O}_6)_3$. The purpose of the present work was to confirm these earlier observations and to attempt a complete structure determination of what appeared to be a unique mineral structure.

¹ A. Wade and R. T. Prider, *Quart. Journ. Geol. Soc. London*, 1940, vol. 96, p. 39. [M.A. 8-28.]

² R. T. Prider, *Min. Mag.*, 1939, vol. 25, p. 379.

³ J. Shearer, E. T. Robinson, and J. T. Jefferies, *Min. Mag.*, 1952, vol. 29, Proc. p. lxi.

TABLE I. Chemical analysis of wadeite.

	Molecular proportions (Prider).	No. of metal atoms on basis of 18(O).	Valency.	Ionic radii (Å.).	Grouping.
P ₂ O ₅	0.022	0.34	5	0.34	6(Si, Al, P) ⁴⁺
SiO ₂	0.657	5.06	4	0.39	
Al ₂ O ₃	0.059	0.91	3	0.57	
MgO	0.007	0.06	2	0.78	
TiO ₂	0.020	0.15	4	0.64	2(Zr, Ti, Mg, Al, Na) ⁴⁺
ZrO ₂	0.173	1.33	4	0.87	
Na ₂ O	0.045	0.69	1	0.98	
CaO	0.093	0.73	2	1.06	
K ₂ O	0.196	3.02	1	1.33	4(K, Ca, Ba, Na) ⁺
BaO	0.008	0.06	2	1.43	
		12.35			
Oxygen		18	-2	1.32	18O ²⁻

EXPERIMENTAL.

The crystal used was of the shape and size shown in fig. 1. The direction of the *c*-axis was reasonably well defined but there was only one 120° interfacial angle that could be distinguished.

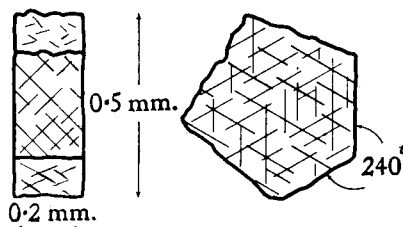


FIG. 1. Size of the crystal used and general appearance of the cleavage cracks.

Single-crystal oscillation and Weissenberg diffraction patterns were prepared using copper and molybdenum $K\alpha$ radiations. The unit-cell dimensions were determined by the θ -method¹ to be a 6.893 ± 0.004 Å. and c 10.172 ± 0.002 Å. The intensities of the X-ray reflections were estimated visually on a series of Weissenberg photographs and the appropriate absorption, Lorentz, and polarization corrections were applied. The observed structure amplitudes (F_0) so obtained are listed in tables II and III. In order to check the accuracy of the visual estimation of intensity, a number of reflection intensities were measured on a Geiger-counter spectrometer. As can be seen from table IV, the agree-

¹ O. Weisz, W. Cochran, and W. F. Cole, Acta Cryst., 1948, vol. 1, p. 83. [M.A.]

ment is quite reasonable, except for some of the weaker reflections and the strong reflection ($2\bar{1}\bar{1}2$). Inaccuracy in the visual method is to be expected for such very strong and weak reflections.¹

TABLE II. Observed and calculated structure amplitudes $F(hki0)$.

h	k	i	l	F_o	F_c	h	k	i	l	F_o	F_c
0	0	0	0	—	356	5	3	$\bar{8}$	0	35	36
1	0	$\bar{1}$	0	—	41	6	2	$\bar{8}$	0	10	13
2	$\bar{1}$	$\bar{1}$	0	68	68	7	1	$\bar{8}$	0	37	37
2	0	$\bar{2}$	0	< 8	7	8	0	$\bar{8}$	0	50	46
3	$\bar{1}$	$\bar{2}$	0	42	48	9	$\bar{1}$	$\bar{8}$	0	22	18
4	$\bar{2}$	$\bar{2}$	0	81	86	10	$\bar{2}$	$\bar{8}$	0	23	29
2	1	$\bar{3}$	0	< 5	7	11	$\bar{3}$	$\bar{8}$	0	< 11	1
3	0	$\bar{3}$	0	95	95	12	4	$\bar{8}$	0	< 11	8
4	$\bar{1}$	$\bar{3}$	0	75	80	13	$\bar{5}$	$\bar{8}$	0	< 11	8
5	$\bar{2}$	$\bar{3}$	0	8	9	5	4	$\bar{9}$	0	40	32
6	$\bar{3}$	$\bar{3}$	0	46	51	6	3	$\bar{9}$	0	56	60
3	1	$\bar{4}$	0	< 6	3	7	2	$\bar{9}$	0	< 9	1
4	0	$\bar{4}$	0	38	40	8	1	$\bar{9}$	0	< 10	3
5	$\bar{1}$	$\bar{4}$	0	65	67	9	0	$\bar{9}$	0	27	28
6	$\bar{2}$	$\bar{4}$	0	31	28	10	$\bar{1}$	$\bar{9}$	0	< 11	5
7	$\bar{3}$	$\bar{4}$	0	37	36	11	$\bar{2}$	$\bar{9}$	0	< 11	5
8	$\bar{4}$	$\bar{4}$	0	48	50	12	$\bar{3}$	$\bar{9}$	0	< 11	14
3	2	$\bar{5}$	0	13	$\bar{12}$	13	4	$\bar{9}$	0	22	11
4	1	$\bar{5}$	0	106	111	6	4	$\bar{10}$	0	< 10	4
5	0	$\bar{5}$	0	33	27	7	3	$\bar{10}$	0	< 10	0
6	$\bar{1}$	$\bar{5}$	0	25	19	8	2	$\bar{10}$	0	28	34
7	$\bar{2}$	$\bar{5}$	0	60	60	9	1	$\bar{10}$	0	< 11	3
8	$\bar{3}$	$\bar{5}$	0	< 8	7	10	0	$\bar{10}$	0	< 11	5
9	4	$\bar{5}$	0	< 9	1	11	$\bar{1}$	$\bar{10}$	0	30	29
10	$\bar{5}$	$\bar{5}$	0	18	24	12	$\bar{2}$	$\bar{10}$	0	< 12	11
4	2	$\bar{6}$	0	21	14	13	$\bar{3}$	$\bar{10}$	0	< 12	0
5	1	$\bar{6}$	0	33	23	6	5	$\bar{11}$	0	< 11	2
6	0	$\bar{6}$	0	33	37	7	4	$\bar{11}$	0	16	26
7	$\bar{1}$	$\bar{6}$	0	< 8	4	8	3	$\bar{11}$	0	15	12
8	$\bar{2}$	$\bar{6}$	0	< 8	2	9	2	$\bar{11}$	0	21	23
9	$\bar{3}$	$\bar{6}$	0	42	45	10	1	$\bar{11}$	0	< 11	18
10	4	$\bar{6}$	0	18	14	11	0	$\bar{11}$	0	< 11	1
11	$\bar{5}$	$\bar{6}$	0	15	12	12	$\bar{1}$	$\bar{11}$	0	< 12	9
12	$\bar{6}$	$\bar{6}$	0	32	29	7	5	$\bar{12}$	0	18	12
4	3	$\bar{7}$	0	16	17	8	4	$\bar{12}$	0	< 11	6
5	2	$\bar{7}$	0	39	51	9	3	$\bar{12}$	0	25	30
6	1	$\bar{7}$	0	< 8	3	10	2	$\bar{12}$	0	< 12	9
7	0	$\bar{7}$	0	23	22	11	1	$\bar{12}$	0	< 12	0
8	$\bar{1}$	$\bar{7}$	0	51	65	12	0	$\bar{12}$	0	15	18
9	$\bar{2}$	$\bar{7}$	0	< 9	8	7	6	$\bar{13}$	0	< 12	0
10	3	$\bar{7}$	0	23	15	8	5	$\bar{13}$	0	< 12	13
11	4	$\bar{7}$	0	28	32	9	4	$\bar{13}$	0	< 12	4
12	5	$\bar{7}$	0	< 11	10	10	3	$\bar{13}$	0	< 12	1
13	6	$\bar{7}$	0	< 12	6						

¹ W. Cochran, Acta Cryst., 1950, vol. 3, p. 268

TABLE III. Observed and calculated structure amplitudes $F(2h\bar{h}l)$.

The letter d indicates that the reflection could be detected but not measured.

$$R = (F_c - F_0)/F_c$$

h	l	F_0	F_c	R	h	l	F_0	F_c	R
0	0	—	356	—	4	15	—	1	—
0	2	—	9	—	4	16	—	26	—
0	4	77	82	0.06	4	17	—	1	—
0	6	61	64	0.05	4	18	—	16	—
0	8	91	87	0.05	4	19	—	1	—
0	10	d	20	—	6	0	47	52	0.10
0	12	45	41	0.10	6	1	—	3	—
0	14	—	8	—	6	2	64	58	0.10
0	16	55	54	0.02	6	3	23	20	0.15
0	18	d	18	—	6	4	33	39	0.15
0	20	d	21	—	6	5	d	15	—
2	0	63	68	0.07	6	6	32	22	0.45
2	1	50	43	0.16	6	7	—	0	—
2	2	103	110	0.06	6	8	—	12	—
2	3	19	19	0.00	6	9	—	6	—
2	4	59	54	0.09	6	10	—	5	—
2	5	—	2	—	6	11	—	12	—
2	6	50	41	0.22	6	12	—	14	—
2	7	35	32	0.09	6	13	—	4	—
2	8	—	13	—	6	14	—	24	—
2	9	d	14	—	6	15	—	1	—
2	10	d	14	—	6	16	—	18	—
2	11	—	3	—	6	17	—	4	—
2	12	—	14	—	6	18	—	14	—
2	13	—	8	—	8	0	51	50	0.02
2	14	—	37	—	8	1	—	3	—
2	15	—	12	—	8	2	59	57	0.04
2	16	—	23	—	8	3	—	3	—
2	17	—	1	—	8	4	—	5	—
2	18	—	22	—	8	5	—	3	—
2	19	—	2	—	8	6	d	18	—
2	20	—	13	—	8	7	—	2	—
4	0	78	86	0.09	8	8	—	4	—
4	1	—	4	—	8	9	—	2	—
4	2	58	63	0.08	8	10	—	16	—
4	3	—	4	—	8	11	—	1	—
4	4	65	59	0.10	8	12	—	1	—
4	5	—	3	—	8	13	—	0	—
4	6	d	13	—	8	14	—	15	—
4	7	—	2	—	8	15	—	0	—
4	8	—	9	—	8	16	—	14	—
4	9	—	1	—	10	0	22	24	0.08
4	10	—	6	—	10	1	—	11	—
4	11	—	1	—	10	2	35	41	0.15
4	12	—	24	—	10	3	—	16	—
4	13	—	1	—	10	4	—	13	—
4	14	—	24	—	10	5	—	12	—

TABLE III (contd.)

h	l	F_0	F_c	R	h	l	F_0	F_c	R
10	6	—	17	—	12	1	—	5	—
10	7	—	7	—	12	2	—	21	—
10	8	—	8	—	12	3	—	5	—
10	9	—	8	—	12	4	—	12	—
10	10	—	6	—	12	5	—	4	—
10	11	—	8	—	12	6	—	2	—
10	12	—	4	—	12	7	—	4	—
10	13	—	5	—	12	8	—	20	—
10	14	—	16	—	12	9	—	4	—
12	0	31	29	0.07	12	10	—	1	—

TABLE IV. Comparison of counter intensities (I_c) with visual intensities (I_v).

h	k	i	l	I_c	I_v	h	k	i	l	I_c	I_v
4	2	2	0	51	51	0	0	0	8	36	36
6	3	3	0	12	10	0	0	0	10	6	—
8	4	4	0	10	8	0	0	0	12	6	3
10	5	5	0	1.2	0.8	0	0	0	16	6	4.5
12	6	6	0	1.8	1.9	2	1	1	2	152	133
0	0	0	4	50	50	4	2	2	4	28	32
0	0	0	6	21	21	6	3	3	6	4	3.5

An interesting feature of the oscillation photographs was the occurrence of a number of powder diffraction lines superimposed on the single-crystal pattern. Reference to the American Society for Testing Materials index showed that the spacings of these lines corresponded to those of calcite, thus confirming the presence of this mineral in the surface cracks of the crystal.

SOLUTION OF STRUCTURE.

Examination of the zero-level and first-level Weissenberg photographs of the crystal taken with the c -axis and the $(2\bar{1}\bar{1}0)$ -axis (perpendicular to the a - and c -axes) as the axes of rotation, confirmed the diffraction symmetry of $6/m$ (C_{6h}). This, together with the systematically absent reflections, $000l$ when l is odd, indicated that wadeite belongs either to the space group $P6_3$ (C_6^6) or $P6_3/m$ (C_{6h}^2).

Consideration of the unit-cell dimensions and the measured density shows there is one molecule, containing eighteen oxygen atoms, per unit cell (table I). Furthermore, general considerations of symmetry and chemical data, together with the failure of tests for non-centrosymmetry, suggest the formula to be $Zr_2K_4Si_6O_{18}$ and that it belongs to the $P6_3/m$ (C_{6h}^2) space group. It is obvious from table I that this is only an idealized formula, since there has been considerable substitution of the metal atoms.

It has been noted that the cleavage cracks in the prism faces of the

crystal cross at nearly 90° . This is a typical property of pyroxenes which have, in general, a somewhat similar type of chemical formula to wadeite. However, it is impossible to fit a pyroxene type of silicon-oxygen chain into the symmetry of the $P6_3/m$ space group.

Wadeite, then, appears to be based on a silicon-oxygen framework of six silicon and eighteen oxygen atoms in the unit cell. By constructing

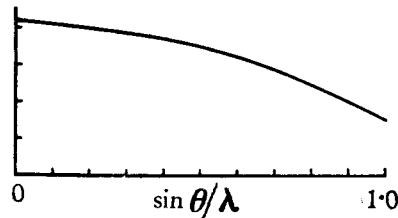


FIG. 2. Form of the temperature factor plotted against $(\sin \theta)/\lambda$.

a model of wooden spheres, representing oxygen atoms, within the confines of a unit cell of appropriate dimensions, it was found that there were two, not very different, frameworks that fulfilled the required symmetry conditions. The structure based on either of these two frameworks defined the x , y coordinates of the zirconium and

potassium atoms; i.e. $(0,0,z)$ for zirconium and $(2/3,1/3,z)$ and $(1/3,2/3,z)$ for potassium.

Two heavy atoms, such as zirconium, at the origin of the two-dimensional projection along the c -axis, provide a large, positive contribution to the structure factors corresponding to reflections of the type $(hki0)$. There would therefore be very few errors in assuming all these structure factors to be positive. A Fourier synthesis of this projection was carried out using the values of F_0 in table II and taking them all to be positive. This synthesis showed the positions of all the atoms except for six oxygens, and established which of the two model structures was to be accepted.

In order to calculate the structure factors from atomic co-ordinates, it is necessary to know the atomic scattering factors for the atoms involved. For silicon and oxygen, these are listed in available tables. However, reference to the chemical data in table I shows that the nature of the other atoms in a unit cell is varied. A weighted mean of the atomic weights of the elements likely to be in the 'potassium' position corresponded closely to that of potassium, whose f_0 values are given directly in the tables. A similar mean for the 'zirconium' position suggested a quadruply-ionized element of atomic number 36. It was therefore necessary to construct an atomic scattering factor curve appropriate to this average atomic number. The values given in table V have been derived from those of bromine (35) and rubidium (37).

TABLE V. Atomic scattering factor f_0 for 'Zr⁴⁺'.

$(\sin \theta)/\lambda$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	
f_0	...	32.0	31.2	28.4	24.5	21.1	18.7	16.6	14.6	12.8	11.2	9.9

Refinements were made to the atomic parameters given by the model, using trial and error methods, until the best agreement was obtained

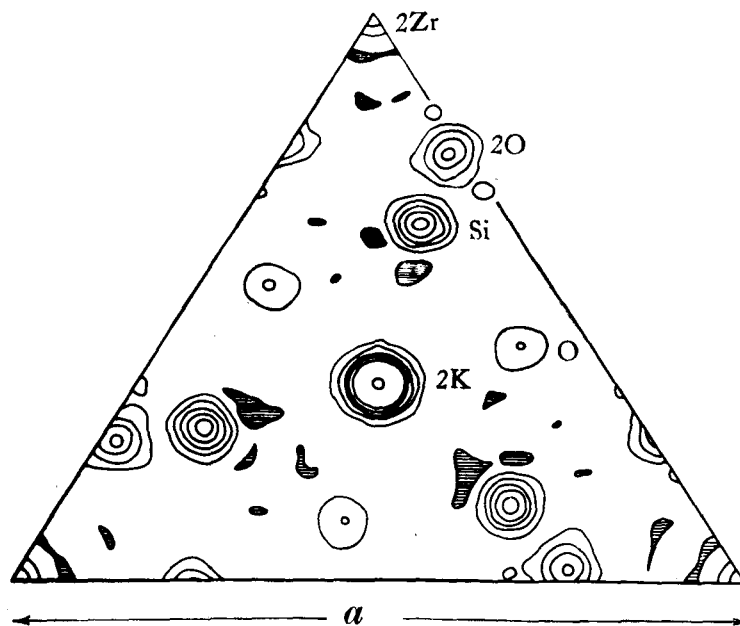


FIG. 3. Projection of electron density along the c -axis of wadeite. The contours are at the arbitrary levels of 0, 1, 2, 3, 4, 5, 10, except at the three zirconium positions where they are at 0, 10, and 20.

between observed and calculated values of the structure factors. The original values of the calculated structure factors had to be multiplied by a factor to reduce their numerical values to the arbitrary scale of the observed structure factors. This factor consists of a constant times the temperature factor. The experimentally determined curve (fig. 2), which includes a small absorption component, corresponds reasonably well to an exponential temperature factor of the form $e^{-B \sin^2 \theta}$, where $B = 0.35$. Final values of F_c are listed in table II.

A two-dimensional Fourier synthesis was carried out using reflections of the form $(hki0)$; the result is shown in fig. 3. All values of F_0 up to $\sin \theta/\lambda = 1$ were used and where these were not observed, owing

to their low intensity, calculated values were substituted. The projection substantially confirms x - and y -co-ordinates listed in table VI, although it suggests $(0.387, 0.256, z)$ and $(0.258, 0.236, z)$ might be more appropriate for the silicon position and the general oxygen position respectively. Adoption of these values does not, however, improve the agreement of F_0 and F_c .

For the second set of reflections investigated $(2h\bar{h}\bar{h}l)$, only 19 significant observed structure factors could be measured out of a total of 108. This is somewhat unsatisfactory and the usefulness of a Fourier projection would be very doubtful. Nevertheless, the agreement obtained, as indicated by $R = (F_c - F_0)/F_c$ in table III, is sufficient to verify the structure already postulated. There is one serious difference between F_0 and F_c for $(6\bar{3}\bar{3}6)$, but this is a relatively weak reflection and thus liable to a large error in measurement. It must be noted that the calculated structure factors for the $(2h\bar{h}\bar{h}l)$ reflections as listed in table III have involved the use of the correlating factor derived experimentally for the $(hki0)$ reflections. This is strictly not justified, since the temperature factor will not be the same in all directions in the wadeite crystal, but the error will not affect the results. The final values for all the atomic co-ordinates are tabulated in table VI.

TABLE VI. Co-ordinates of the atoms of wadeite expressed as fractions of a , a and c .

12O	(0.263 0.236 0.114)	(0.764 0.027 0.114)	(0.973 0.737 0.114)
	(0.737 0.764 0.886)	(0.236 0.973 0.886)	(0.027 0.263 0.886)
	(0.737 0.764 0.664)	(0.236 0.973 0.664)	(0.027 0.263 0.664)
	(0.263 0.236 0.386)	(0.764 0.027 0.386)	(0.973 0.737 0.386)
6O	(0.500 0.100 0.250)	(0.900 0.400 0.250)	(0.600 0.500 0.250)
	(0.500 0.900 0.750)	(0.100 0.600 0.750)	(0.400 0.500 0.750)
6Si	(0.389 0.255 0.250)	(0.745 0.134 0.250)	(0.866 0.611 0.250)
	(0.611 0.745 0.750)	(0.255 0.866 0.750)	(0.134 0.389 0.750)
4K	(0.666 0.333 0.558)	(0.666 0.333 0.942)	— — —
	(0.333 0.666 0.442)	(0.333 0.666 0.058)	— — —
2Zr	(0 0 0)	(0 0 0.500)	

DESCRIPTION OF STRUCTURE.

The structure of wadeite is based on a framework of silica tetrahedra, the potassium and zirconium atoms fitting into the interstices. The fundamental unit of this framework is the $(\text{Si}_3\text{O}_9)^{6-}$ group (fig. 4), two of which combine with 4K^+ and 2Zr^{4+} to form the neutral contents of

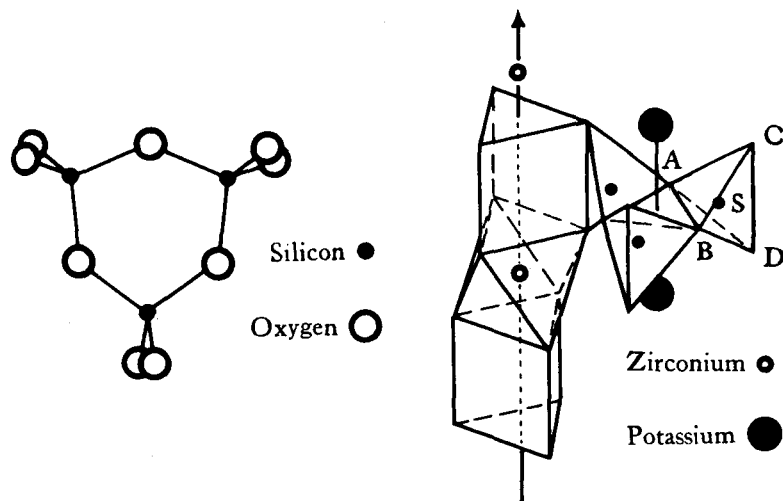


FIG. 4. The $(\text{Si}_3\text{O}_9)^{6-}$ unit, which consists of three silicon-oxygen tetrahedra forming a ring.

FIG. 5. Arrangement of the metal atoms within the silicon-oxygen framework. The oxygen atoms are at the corners of the figure.

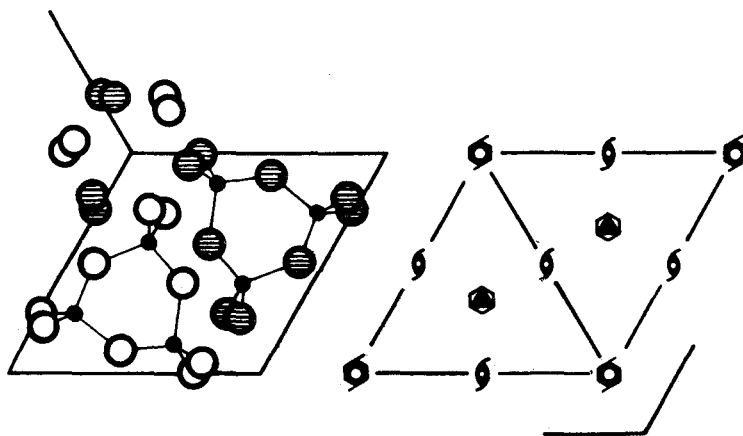


Fig. 6. Grouping of the $(\text{Si}_3\text{O}_9)^{6-}$ units in the unit cell and the symmetry elements of the $P6_3/m$ space group. The shaded groups are separated from the unshaded by a screw component of $c/2$.

the unit cell. The $(\text{Si}_3\text{O}_9)^{6-}$ groups are arranged about the hexad screw axis as illustrated in fig. 5.

The oxygen atoms are grouped in the manner indicated in fig. 5, where an oxygen atom is situated at each corner of the figure. The

zirconium atom is then situated at the centre of the octahedron formed by the six oxygen atoms; i.e. at the positions $(0,0,0)$ and $(0,0,\frac{1}{2})$. Mirror reflection planes intersect the hexad screw axis (6_3) at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, perpendicularly between the octahedra. The $(\text{Si}_3\text{O}_9)^{6-}$ groups lie in these planes with a potassium atom symmetrically above and below the centre of each.

From the co-ordinates listed in table VI, it was possible to calculate the interatomic distances. The values obtained for the O–O distances in the silica tetrahedra (fig. 5) are: $AB = 2.49$, $AC = AD = 2.64$, $BC = BD = 2.53$, $CD = 2.77$ Å. The average of these is 2.60 Å, which is the generally accepted O–O bond distance in these tetrahedra. Although the maximum error in these distances is 0.1 Å., the value of CD is still significantly large.

The Si–O distances obtained are: $SA = 1.60$, $SB = 1.58$, $SC = SD = 1.60$ Å. The accepted value¹ is 1.60 Å. and the close agreement of the measured bond lengths tends to support the large O–O distance quoted for CD . The Zr–O distance is 2.07 Å. Goldschmidt radii for zirconium and oxygen would suggest this value to be about 2.17 Å. The K–K distance was found to be 3.30 Å. as compared with Goldschmidt's distance of about 2.7 Å. Each potassium atom is surrounded by nine oxygen atoms; three at a distance of 2.82, three at 3.06, and three at 3.44 Å. Goldschmidt radii suggest that these figures could be as low as 2.65 Å.

CONCLUSION.

The complete structure of wadeite has been determined by X-ray methods. It has the space group, $P6_3/m$, unit-cell dimensions

$$a \ 6.893 \pm 0.004, \quad c \ 10.172 \pm 0.002 \text{ \AA.},$$

and may be represented ideally by the formula $\text{Zr}_2\text{K}_4\text{Si}_6\text{O}_{18}$.

The fundamental structural unit is the $(\text{Si}_3\text{O}_9)^{6-}$ silicon-oxygen ring. The only previously known silicate mineral to be built up on this unit is benitoite² from San Benito County, California, having the formula $\text{BaTiSi}_3\text{O}_9$ and space group $P\bar{6}c2$ (D_{3h}^2).

There is evidence of some distortion in the individual silica tetrahedra. This distortion causes two-thirds of the oxygen atoms in wadeite to be closer to the positively charged zirconium and potassium ions than

¹ J. V. Smith, Acta Cryst., 1954, vol. 7, p. 479. [M.A. 12-430.]

² W. H. Zacharisen, Zeits. Krist., 1939, vol. 74, p. 139. [M.A. 4-367.]

would be the case for regular tetrahedra, and yet it does not alter the Si-O distances or the average O-O distances in each tetrahedron.

Acknowledgements.—The author is indebted to Professor R. T. Prider who supplied the crystal of wadeite, to Mr. G. B. Robertson whose Geiger-counter equipment was used, to Mr. J. Shearer for helpful advice, and in particular to Professor C. J. B. Clews for his patient and helpful supervision. The work was made possible by a grant from the University Research Grants Committee.
