The crystal structure of dalyite

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With 6 figures

Auszug

Die Kristallstruktur von Dalyit, $K_{1,70}Na_{0,30}ZrSi_6O_{15}$, wurde bestimmt und mittels zweidimensionaler Fourier-Synthesen verfeinert. Es ist ein neuer Schichtsilikat-Typ mit Ringen aus vier, sechs und acht SiO_4-Tetraedern. Die Schichten werden durch ZrO_6-Oktaeder und $(K,Na)O_8$-Polyeder zusammengehalten. Der Si—O-Abstand beträgt 1,54 bis 1,67 Å ($\pm$ 0,01 Å); das Mittel aus zwölf verschiedenen Abständen ist 1,62 Å. Der mittlere Zr—O-Abstand ist 2,06 $\pm$ 0,03 Å, der mittlere K(Na)—O-Abstand 3,02 $\pm$ 0,13 Å.

Abstract

The crystal structure of dalyite, a potassium (sodium) zirconium silicate $K_{1.70}Na_{0.30}ZrSi_6O_{15}$, has been determined and refined by two-dimensional Fourier methods. It is a new type of sheet silicate containing four, six- and eight-membered rings of SiO_4 tetrahedra. The sheets are joined by ZrO_6 octahedra and by $(K,Na)O_8$ polyhedra. The Si—O distances range from 1.54 Å to 1.67 Å ($\pm$ .01 Å) and the average of twelve independent Si—O distances is 1.62 Å. The average Zr—O distance is 2.06 Å ($\pm$ .03 Å), and the average K(Na)—O distance 3.02 Å ($\pm$ .13 Å).

1. Introduction and summary of previous work

Dalyite is a potassium (sodium) zirconium silicate first noticed in sections of rocks from Ascension Island by Professor C. E. TILLEY, and first separated by Dr. S. O. AGRELL. Its chemical composition, unit cell, x-ray powder data and physical properties were published by VAN TASSEL (1952).

The mineral occurs in a medium-grained granite in the trachytic and basaltic tuffs of Green Mountain and Middleton Peak on Ascension Island. It is a rare accessory (about 0.2%) in rocks which are mainly composed of microperthite and quartz, associated in varying propor-

tions with aegirine, strongly pleochroic arfvedsonite and reddish-brown pleochroic aenigmatite. At the time of writing, this is the only locality where the occurrence of dalyite has been reported.

Table 1 lists the physical properties of dalyite and gives details of a microchemical analysis by Dr. M. H. HEY. The data have been summarized from VAN TASSEL's (1952) paper.

Table 1

Chemical composition and physical data of dalyite compiled from VAN TASSEL (1952)

a) Microchemical analysis by Dr. M. H. HEY

			Metals on basis of 15 O		
SiO_2	61.85		Si	5.95	
ZrO_2	21.70		Zr	1.01	
K_2O	14.60		K	1.79	} 2.11
Na_2O	1.75		Na	0.32	
Fe_2O_3	0.37				
H_2O	0.64				
	100.91				

b) Physical data

Colourless, transparent. Lustre, vitreous.
Optical constants: $\alpha = 1.575$; $\beta = 1.590$; $\gamma = 1.601$; $2V_\alpha = 72°$
$\alpha : c = 7°$; axial plane to (100) $= 18°$.

Density 2.84. Hardness $7^1/_2$. Cleavages ($\bar{1}01$) and (010).
Twinning not infrequent with (100) as compositon plane.

c) Unit cell

Triclinic

$a = 7.51 \pm .07$ Å	$b = 7.73 \pm .08$ Å	$c = 7.00 \pm .07$ Å
$\alpha = 106° \pm 1°$	$\beta = 113.5° \pm 1°$	$\gamma = 99.5° \pm 1°$

Unit-cell content $(K/Na)_2ZrSi_6O_{15}$.

The chemical analysis shows that the empirical formula is probably $K_2ZrSi_6O_{15}$ where sodium replaces part of the potassium. There is a possibility that a small amount of Hf replaces Zr (VAN TASSEL, 1952), but this has been neglected in the structure analysis.

The purpose of the structure determination was to discover the nature of the Si_6O_{15} network and to find the relationship between dalyite and wadeite ($K_2ZrSi_3O_9$) to which dalyite is chemically most

closely related. A complete determination of the structure proved possible with two-dimensional x-ray diffraction data, and it was considered that highly accurate bond lengths, anisotropic temperature factors etc. were of too marginal an interest to warrant a full three-dimensional analysis.

2. Materials used

Grains from rocks preserved in Cambridge (Harker slide no. 57219) were selected for the x-ray work. HEY's analysis (VAN TASSEL, 1952) was taken as the basis for the structure determination, the chemical composition being idealized as $K_{1.70}Na_{0.30}ZrSi_6O_{15}$. A regularly-shaped, untwinned crystal about 0.15 mm in all dimensions was chosen to give the best compromise between the conflicting demands for small absorption, small secondary extinction and strong reflection intensity.

3. Cell dimensions and space group

Dalyite is triclinic. Its cell dimensions were redetermined in the present work since VAN TASSEL's (1952) values were only accurate to 1% (cf. Table 1) and would have been one of the greatest sources of error in the interatomic distances.

Precession photographs were used to determine cell angles; axial lengths were found subsequently from oscillation pictures by the method described by WEISZ, COCHRAN and COLE (1948) using extrapolation against $\sin^2\theta$ (FARQUHAR and LIPSON, 1946).

Final values were $\quad a = 7.371 \pm .003 \text{ Å}$ [1]
$$b = 7.730 \pm .003 \text{ Å}$$
$$c = 6.912 \pm .002 \text{ Å}$$
$$\alpha = 106°14' \pm 2' \text{ [2]}$$
$$\beta = 111°27' \pm 2'$$
$$\gamma = 100°0' \pm 2'.$$

To decide on the presence or absence of a centre of symmetry, reflections with $\frac{\sin\theta}{\lambda} < 0.7$ in $hk0, 0kl, h0l$ zones were subjected to the statistical tests of HOWELLS, PHILLIPS and ROGERS (1950). Figure 1 gives the experimental curves. Although the curves follow the centro-symmetric curve at small values of z, they move over towards the

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[1] Errors are limits estimated from experimental graphs of a^*, b^*, c^* against $\sin^2\theta$.

[2] Errors calculated from the reproducibility of several measurements.

non-centrosymmetric one at higher values. It is not, therefore, possible
to make a direct deduction about the presence of a centre.

Reflections in each zone were next subjected to the statistical test
suggested by RAMACHANDRAN and SRINIVASAN (1959). Again using
reflections with $\frac{\sin\theta}{\lambda} < 0.7$, the values of their test ratio N_2/N_1 were
0.67 $(hk0)$, 0.62 $(0kl)$, 0.59 $(h0l)$ as compared with the theoretical
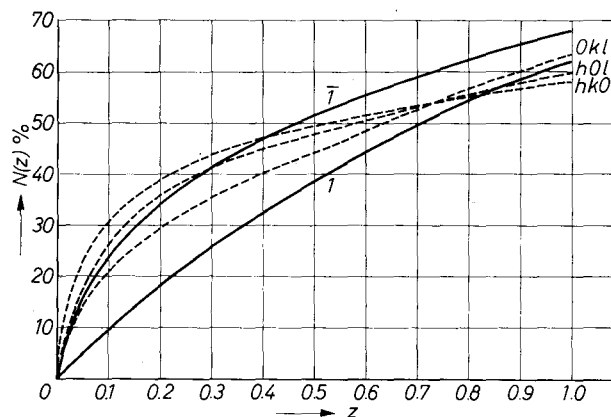

Fig. 1. $N(Z)$ test for $hk0$, $h0l$ and $0kl$ reflections. Experimental curves are dotted,
theortical curves continuous

values of 0.776 for a centrosymmetric structure and 1.96 for a non-
centrosymmetric one. Here then is clear indication of the existence
of a centre. As a further check, tests for piezo- and pyro-electricity
were carried out, but with negative results.

The structure was therefore assumed to be centrosymmetric at
the start of the refinement. Further work confirmed that any depar-
tures from centrosymmetry would be small, and that the space group
is therefore probably $P\bar{1}$.

4. Collection of intensities

X-ray reflections $hk0$, $h0l$, and $0kl$ were recorded on Weissenberg
photographs with filtered $MoK\alpha$ radiation using the multiple-film
technique (ROBERTSON, 1943). Intensities recorded on the film were
measured visually by comparison with an intensity scale made using
the well-shaped $(1\bar{2}0)$ reflection from the crystal. Where α_1, α_2 doublets
were completely resolved, their sum was accepted as peak intensity.
Intensity data were collected in all three projections to values of
$\frac{\sin\theta}{\lambda} = 1.36$ Å^{-1}. The intensity data for each projection, read from

various films, were placed on the same relative scale by comparing the intensities of zones of reflections recorded on more than one film.

Very many high-angle reflections were unobserved despite 200-hour exposures. In fact, there were 94 non-zero $hk0$ reflections, 90 $h0l$ and 118 $0kl$. The range of scaled intensities extended from approximately 1 to 200.

5. Corrections and errors

The intensities were corrected for Lorentz and polarisation effects, and for absorption with programs written for Edsac II by S. DARLOW and M. WELLS. There was a small amount of dispersion caused by Zr with $MoK\alpha$ radiation and this was allowed for by an adjustment of scattering factor (cf. Section 7). No correction was made for the measuring error introduced in the intensities by the increasing re-solution of the α_1, α_2 doublet with $\sin\theta$. Partial allowance was made for secondary extinction by omitting some intense low-angle reflec-tions from the F_o-F_c syntheses during refinement; the reflections so treated are marked with an asterisk in Table 2 where values of F_o's and final F_c's are listed.

6. Deduction of trial structure

Dalyite has one formula unit $(K,Na)_2ZrSi_6O_{15}$ per cell, and it was therefore at once possible to deduce that Zr atoms must lie on centres of symmetry at the cell origin. The heavy-atom method suggested itself as the most promising way of determining the positions of the other atoms. Patterson syntheses were calculated for the projections onto each of the planes (100), (010) and (001). Besides the origin peak, there were eight other large peaks on each map: it was assumed that these peaks were at the ends of vectors between the Zr and the two K/Na and six Si atoms. Since the Zr was at the cell origin, the coordi-nates of the other cations could at once be written down. They were:

Fractional coordinates

Site	x	y	z
1	.2850	.1950	.7000
2	.5000	.6800	.6800
3	.1800	.7400	.3100
4	.1600	.6150	.8450

and the centrosymmetrically-related sites.

Table 2. *Observed and calculated structure factors*
The calculated values are for two formula weights of (K,Na)$_2$ZrSi$_6$O$_{15}$

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$_c$	h k l	F$_o$	F$_c$
1 0 0	57	69	0 5 0	88	96	1̄ 0 2	20	24	6̄ 0 7	81	72	0 6̄ 4	46	-28
3 0 0	24	23	1 5 0	69	63	0 0 2	86	-101	1̄ 0 7	31	25	0 4̄ 4	112	138
4 0 0	73	73	3 5 0	76	78	2 0 2	117*	142	0 0 7	84	74	0 2̄ 4	46	43
6 0 0	90	87	5 5 0	39	37	3 0 2	94	91	1 0 7	52	46	0 1̄ 4	26	-24
7 0 0	27	24	7 5 0	53	56	4 0 2	25	-17	9̄ 0 8	41	39	0 1 4	109	133
10 0 0	54	43	8̄ 6 0	49	48	7 0 2	58	56	3̄ 0 8	61	66	0 2 4	59	56
8̄ 1 0	24	19	7̄ 6 0	33	26	10̄ 0 3	64	56	1 0 8	36	38	0 5 4	39	32
7̄ 1 0	22	22	4̄ 6 0	89	100	9̄ 0 3	37	35	5̄ 0 9	56	44	0 6 4	52	51
6̄ 1 0	62	-66	2̄ 6 0	32	32	8̄ 0 3	34	30	4̄ 0 9	79	66	0 10̄ 5	36	34
5̄ 1 0	56	47	1̄ 6 0	30	-25	6̄ 0 3	42	43	0 0 10	39	31	0 9̄ 5	30	22
4̄ 1 0	93	92	0 6 0	48	41	5̄ 0 3	52	49	0 11̄ 1	55	54	0 8̄ 5	58	55
3̄ 1 0	14	12	2 6 0	58	64	4̄ 0 3	129	160	0 10̄ 1	37	33	0 7̄ 5	44	29
2̄ 1 0	66	-51	3 6 0	61	51	3̄ 0 3	19	-13	0 8̄ 1	45	39	0 5̄ 5	72	80
1 1 0	135	138	4 6 0	34	37	2̄ 0 3	25	18	0 7̄ 1	46	30	0 3̄ 5	13	9
2 1 0	102*	110	5 6 0	26	-27	1̄ 0 3	72	74	0 6̄ 1	58	56	0 2̄ 5	88	101
3 1 0	127*	143	7̄ 7 0	46	45	0 0 3	59	65	0 5̄ 1	21	18	0 1̄ 5	20	18
4 1 0	52	-50	6̄ 7 0	44	39	2 0 3	94	95	0 4̄ 1	18	20	0 1 5	62	67
6 1 0	40	30	5̄ 7 0	35	29	3 0 3	62	60	0 3̄ 1	99*	107	0 2 5	54	58
7 1 0	49	49	4̄ 7 0	26	25	4 0 3	49	42	0 1̄ 1	44	48	0 3 5	46	38
9̄ 2 0	69	68	2̄ 7 0	69	76	6 0 3	77	61	0 1 1	54	59	0 4 5	23	16
8̄ 2 0	72	73	1̄ 7 0	85	89	5̄ 0 4	37	34	0 2 1	120*	137	0 5 5	18	21
7̄ 2 0	71	70	2 7 0	24	26	8̄ 0 4	26	38	0 3 1	63	60	0 9̄ 6	27	18
5̄ 2 0	50	41	3 7 0	50	44	7̄ 0 4	31	27	0 5 1	89	111	0 8̄ 6	51	50
4̄ 2 0	22	15	4 7 0	32	40	6̄ 0 4	74	80	0 8 1	56	50	0 6̄ 6	35	33
2̄ 2 0	101	106	5 7 0	44	55	4̄ 0 4	22	-25	0 9 1	29	29	0 5̄ 6	59	54
1̄ 2 0	196*	203	6̄ 8 0	35	35	3̄ 0 4	94	112	0 10 1	14	4	0 4̄ 6	20	15
0 2 0	74	-66	5̄ 8 0	93	92	2̄ 0 4	109	131	0 11̄ 2	27	24	0 3̄ 6	54	53
2 2 0	117*	122	1̄ 8 0	52	46	1̄ 0 4	78	80	0 9̄ 2	45	42	0 2̄ 6	22	19
3 2 0	110	120	1 8 0	63	63	0 0 4	43	46	0 8̄ 2	60	59	0 1̄ 6	28	24
4 2 0	31	27	5 8 0	37	39	3 0 4	34	31	0 6̄ 2	91	101	0 1 6	15	-14
5 2 0	58	60	4̄ 9 0	62	66	4 0 4	66	57	0 5̄ 2	51	50	0 11̄ 7	51	47
6 2 0	27	26	3̄ 9 0	75	75	5 0 4	40	36	0 3̄ 2	41	40	0 10̄ 7	33	25
6̄ 3 0	99	111	2̄ 9 0	43	40	9̄ 0 5	49	53	0 1 2	10	-6	0 7̄ 7	39	42
5̄ 3 0	71	64	1 9 0	42	36	8̄ 0 5	27	19	0 2 2	81	87	0 6̄ 7	35	33
3̄ 3 0	41	-35	2 9 0	55	50	7̄ 0 5	41	36	0 3 2	28	30	0 4̄ 7	46	42
2̄ 3 0	87	90	3̄ 10 0	38	39	5̄ 0 5	45	42	0 4 2	90	103	0 3̄ 7	55	50
0 3 0	42	36	2̄ 10 0	57	59	4̄ 0 5	57	-52	0 7 2	58	56	0 2̄ 7	22	-17
1 3 0	80	87	0 10 0	40	41	3̄ 0 5	77	83	0 12̄ 3	70	62	0 1̄ 7	42	40
2 3 0	67	55	0 11 0	32	30	2̄ 0 5	85	108	0 9̄ 3	39	33	0 5 7	67	52
3 3 0	40	-36	7̄ 0 1	47	41	1̄ 0 5	57	51	0 7̄ 3	75	75	0 9̄ 8	53	43
4 3 0	77	79	6̄ 0 1	45	40	0 0 5	52	-50	0 6̄ 3	46	39	0 8̄ 8	43	34
5 3 0	40	40	5̄ 0 1	62	61	1 0 5	50	51	0 4̄ 3	44	45	0 6̄ 8	41	33
6 3 0	37	41	3̄ 0 1	45	42	3 0 5	44	38	0 3̄ 3	49	40	0 4̄ 8	21	21
6̄ 4 0	71	73	2̄ 0 1	50	62	5 0 5	56	43	0 2̄ 3	81	80	0 3̄ 8	30	26
5̄ 4 0	32	27	1̄ 0 1	74	88	8̄ 0 6	40	33	0 1̄ 3	114*	121	0 2̄ 8	37	34
4̄ 4 0	41	38	0 0 1	52	48	6̄ 0 6	64	64	0 1 3	27	20	0 1 8	43	31
3̄ 4 0	93	102	1 0 1	137*	149	5̄ 0 6	19	27	0 2 3	45	-48	0 2 8	74	66
2̄ 4 0	54	47	2 0 1	52	-48	4̄ 0 6	55	52	0 3 3	57	65	0 9̄ 9	52	48
0 4 0	22	20	3 0 1	71	63	3̄ 0 6	33	-25	0 4 3	89	98	0 6̄ 9	48	37
1 4 0	83	73	4 0 1	65	59	2̄ 0 6	19	21	0 5 3	27	-29	0 5̄ 9	34	29
2 4 0	48	37	7 0 1	45	47	1̄ 0 6	27	23	0 7 3	61	58	0 3̄ 9	18	24
4 4 0	57	55	9̄ 0 2	45	49	0 0 6	81	77	0 9 3	42	36	0 1̄ 9	27	33
5 4 0	46	43	8̄ 0 2	38	37	1 0 6	30	38	0 10̄ 4	75	74	0 7̄ 10	46	42
7̄ 5 0	56	57	6̄ 0 2	40	-39	2 0 6	63	52	0 9̄ 4	23	13	0 4̄ 10	47	41
5̄ 5 0	57	52	5̄ 0 2	108	126	6 0 6	63	54	0 7̄ 4	76	85	0 1̄ 10	15	18
3̄ 5 0	106	114	4̄ 0 2	82	89	10̄ 0 7	46	42						
1̄ 5 0	59	58	2̄ 0 2	34	-19	7̄ 0 7	88	75						

* reflections omitted during refinement [see text].

It was not possible to determine at this stage which of the cation positions were K/Na and which Si because there was little difference between the four crystallographically-distinct Patterson peaks.

Presumably the K/Na atoms had large thermal motion and hence peak heights that were very little different from those of the silicon atoms.

To discover the K/Na positions, the interbond distances between all the cations were calculated. The cations in site 1 and its centrosymmetrically-realted site are farthest from the other cations (nearest cation neighbour 3.51 Å away): cations in the other sites have neighbours nearer to hand (3.0, 3.0, 3.05 Å away). Clearly the K/Na atoms must lie in site 1, and Si atoms in sites 2,3 and 4.

In order to determine the oxygen positions, Fourier syntheses were obtained with the signs calculated from the known cation coordinates. It was easy to pick out oxygen peaks from the resulting maps. There were 15 oxygens per cell. All were in two-fold general positions except one which lay at the centre of symmetry at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Inspection of cation and anion positions showed that the most reasonable structure was one consisting of sheets of SiO_4 tetrahedra approximately parallel to (010), linked by ZrO_6 octahedra and large K/Na coordination polyhedra.

The sheets are very irregular, but can be described as made up of linked rings containing four, six and eight SiO_4 tetrahedra; alternate tetrahedra pointing roughly up or down. The trial structure proved essentially correct on refinement and will be discussed in detail later (Section 8).

7. Refinement

Refinement was carried out by difference-Fourier syntheses calculated with $hk0$, $h0l$ and $0kl$ reflections. Each projection was refined independently to the limit omitting some reflections (those asterisked in Table 2) because they appeared to be suffering from extinction. When average temperature factors had been once worked out, F_o's were scaled to F_c's using one scale factor.

Scattering factors were calculated assuming that all atoms are half-ionized and that K/Na cations are composite ones of composition 85% K, 15% Na. Scattering-factor curves were constructed by interpolation from those in the literature quoted by Forsyth and Wells (1959), and an expression of the form $f(x) = A \exp(-ax^2) + B \exp(-bx^2) + C$ was fitted to them by the least-squares process they suggested. The constants so found are given in Table 3. The constant C in the expression for the Zr scattering factor was reduced by 2.8 to

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Table 3. *Scattering factor constants calculated for half-ionized atoms*
(After Forsyth and Wells, 1959)

Half-ionized atom.	A	a	B	b	C
O^-	4.322	6.983	3.243	36.48	1.434
Si^{2+}	7.616	2.857	2.252	63.64	2.132
Zr^{2+}	17.835	1.788	12.775	19.73	4.590
$K/Na^{1/2+}$	7.350	0.952	7.603	16.52	1.749

Table 4

a) Atomic coordinates of dalyite

		Fractional coordinates		
		x	y	z
Atoms in special positions:	Zr	0	0	0
	O_1	$^1/_2$	$^1/_2$	$^1/_2$
Atoms in two-fold general positions:	K/Na	.2932	.1887	.7083
	Si_1	.4975	.6817	.6852
	Si_2	.1644	.6226	.8446
	Si_3	.1850	.7389	.3092
	O_2	.0120	.5768	.3029
	O_3	.0814	.8043	.8127
	O_4	.1024	.9131	.2679
	O_5	.2511	.6444	.1058
	O_6	.2810	.2075	.1254
	O_7	.3565	.6017	.7787
	O_8	.3904	.8069	.5495

b) Standard deviations of coordinates

K/Na	$\sigma(x_n)$ =	0.008 Å
Si_{1-3}	$\sigma(x_n)$ =	0.004 Å
O_{2-8}	$\sigma(x_n)$ =	0.012 Å

c) Temperature factors [used in the expression exp $(-B \sin^2 \theta/\lambda^2)$]

Isotropic		Anisotropic					
Atoms	B	Atoms	r	B_r (Å^2)	$\widehat{r\,x}$	$\widehat{r\,y}*$	$\widehat{r}$ normal to x and $y*$
Zr	0.40 Å^2	K/Na	X	3.8	65°	75°	151°
Si_{1-3}	0.22		Y	0.8			
O_{2-8}	0.80		Z	1.2			
		O_1	X	1.8	46°	55°	116°
			Y	0.7			
			Z	0.6			

Fig. 2. x, y and z axis electron-density projections of dalyite. Half the unit cell
is shown in each case. Contours are at arbitrary equal intervals; zero contours
are chained and negative ones dashed. Atomic positions are marked

take account of dispersion (cf. Dauben and Templeton, 1955). The small imaginary component of the dispersion correction for Zr (0.8) was neglected, as were dispersion corrections for all other atoms.

Isotropic temperature factors were chosen for the different classes of atom to minimize the average peak heights at atomic sites on the difference maps. Several atoms showed evidence of anisotropy, but anisotropic temperature factors were only applied to the most anisotropic, which were the K/Na atom and O_1.
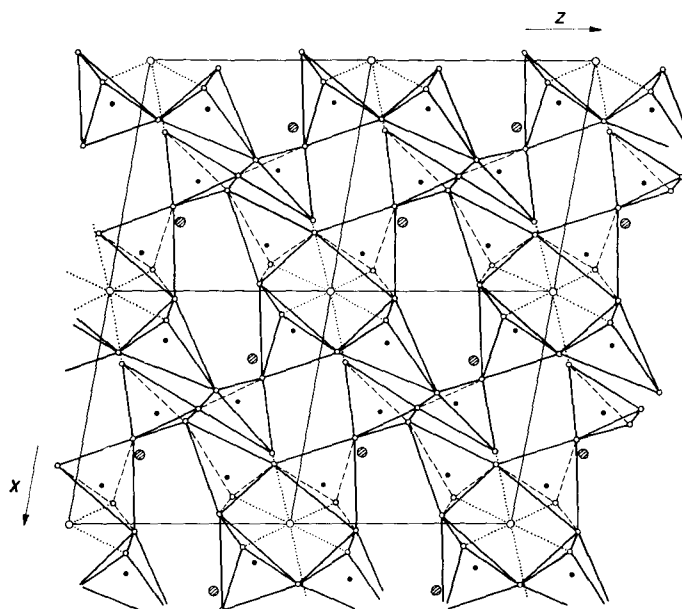
Fig. 3(i). $(Si_2O_5)_n$ framework of dalyite viewed along y axis. (ZrO bonds dotted)

The initial "discrepancy factors", R, were 31.3%, 35.0% and 36.0% for $hk0$, $h0l$ and $0kl$ reflections respectively. At the limit of refinement, the values had fallen to 8.1%, 11.9% and 12.2%, and the final overall R factor was 10.8%.

The final atomic coordinates with their standard deviations are given in Table 4. The standard deviations have been calculated from the final F_o—F_c syntheses with the formula

$$\sigma\,(x_n) = \left\{ \left[\overline{\frac{\partial\,(\varrho_o - \varrho_c)}{\partial x}} \right]^2 \right\}^{1/2} \Big/ C_n$$

(COCHRAN, 1951); it has been assumed that $\sigma(x_n)$ is the same in every direction, and C_n (the curvature at the atomic peak) is estimated from the postulated scattering factor curves modified by temperature factors.
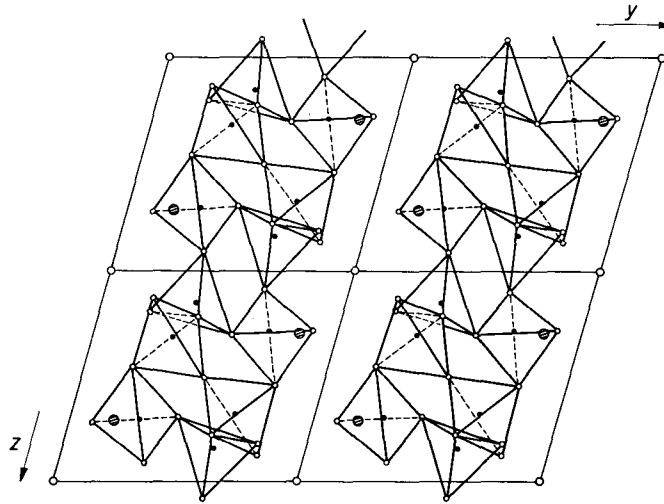
(ii)
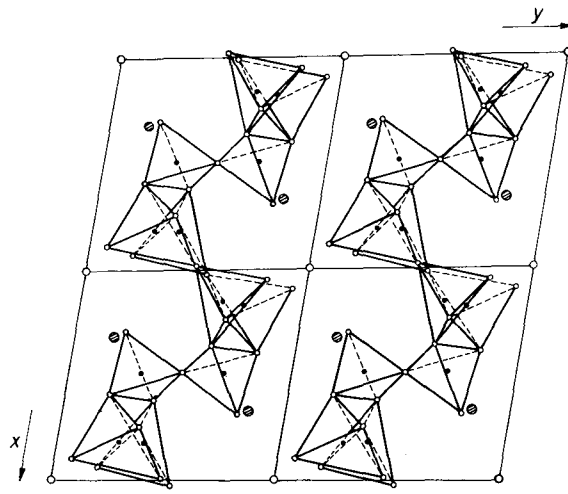
○ Zr   ⊘ K/Na   • Si   ○ O

(iii)

Figs. 3(ii) and (iii). $(Si_2O_5)_n$ framework viewed along x and z axes

The final isotropic temperature factors for each class of atom also appear in Table 4, together with details of the anisotropic temperature factors of atoms K/Na and O_1.

8. Discussion of the structure

Figure 2 shows electron density maps of dalyite calculated with final coordinates and the complete list of F_o's. Figure 3 shows the nature of the SiO_4 tetrahedral linkage. The tetrahedra form corrugated sheets, approximately parallel to (010), which may be considered to be formed by linking distorted β-wollastonite chains (cf. Fig. 4). Successive wollastonite chains have different y coordinates; one chain has Si atoms at $y = 0.62, 0.68$ and 0.74, and the next at $y = 0.38$, 0.32 and 0.26, so that looked at end on [cf. Figs. 3(ii) and 3(iii)], the sheets are two tetrahedra thick.

The $Si—O$ sheets are linked by regular ZrO_6 octahedra and by irregular $(K/Na)O_8$ polyhedra. $Zr—O$ bonds are outlined in Fig. 3(i).

The sheets are of a kind not previously found in silicates. They contain 4-, 6- and 8- membered rings of SiO_4 tetrahedra. Previously known sheet silicates are made up either entirely of 6-membered rings of tetrahedra, or of linked 4- and 8-membered rings[3]. Structures based on sheets of 6-membered rings may have all free tetrahedral vertices pointing the same way as in micas, talc etc., or have more distorted rings linked to give corrugated sheets as in $Li_2Si_2O_5$ (LIEBAU, 1961a), petalite (LIEBAU, 1961c) or sanbornite (DOUGLASS, 1958). Structures based on 4- and 8-membered rings (e.g. apophyllite, TAYLOR and NÁRAY-SZABÓ, 1931; gillespite, PABST, 1943) are formed by linking rings of 4 tetrahedra so that successive rings have their free vertices pointing in opposite directions. Figure 5 shows idealized drawings of the three[3] types of layer silicate now known and includes more detailed diagrams of the $Si—O$ network in some well known examples.

LIEBAU (1962) has classified sheet silicates on the basis of the type of silicate chain from which the sheets can be constituted. He lists the structures as Einer-, Zweier-, Dreier-, Vierereinfachschichten etc. according to the number of tetrahedra in the repeat unit of the

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[3] MAMEDOV and BELOV (1958) have suggested that another type of sheet containing 5- and 8-membered rings of SiO_4 tetrahedra occurs in the calcium silicate okenite, but this has yet to be confirmed by a full structure determination.
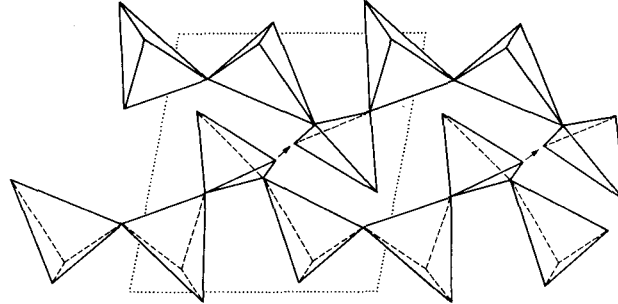
Fig. 4. Distorted β-wollastonite chains. Arrows indicate how successive distorted chains link to form the dalyite (Si_2O_5) sheet
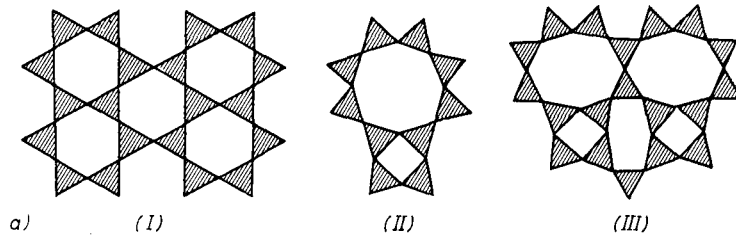

a) (I)   (II)   (III)

Fig. 5A. Three types of layer silicate now known. (i), (ii) and (iii) are idealized mica, apophyllite and dalyite sheets respectively
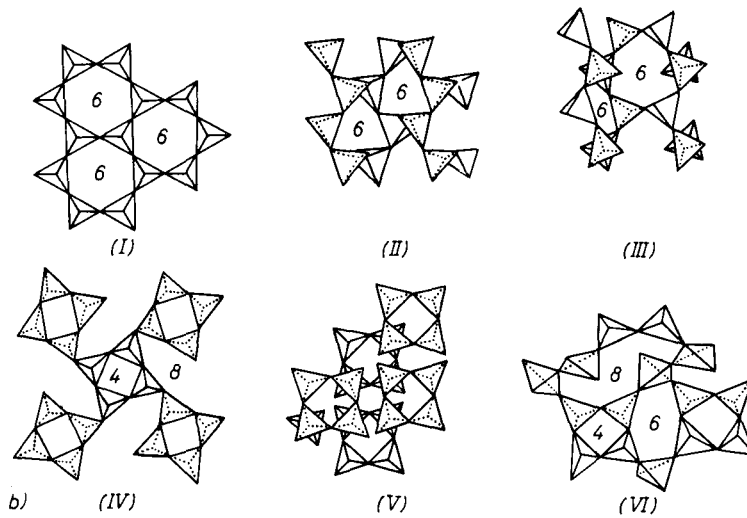

(I)   (II)   (III)

b) (IV)   (V)   (VI)

Fig. 5B. SiO_4 tetrahedral network in (i) mica, (ii) $Li_2Si_2O_5$, (iii) petalite, (iv) apophyllite, (v) gillespite, (vi) dalyite

constituent chain. On this scheme dalyite would be "Dreiereinfach-schichten" type since its sheet structure is made up of wollastonite chains whose repeat length is three tetrahedra.

It is interesting to compare the structure of dalyite with those of other potassium and sodium zirconium silicates. The minerals most closely related chemically to dalyite are wadeite ($K_2ZrSi_3O_9$), cata-pleiite ($NaZrSi_3O_9 \cdot 2H_2O$), lovozerite ($Na_2ZrSi_6O_{15} \cdot 3H_2O \cdot 0.5\ NaOH$) and elpidite ($Na_2ZrSi_6O_{15} \cdot 3H_2O$). In wadeite (Henshaw, 1955) and catapleiite (Brunovskii, 1936), the Si—O radical is a triple Si_3O_9 ring of SiO_4 tetrahedra; the rings being linked by a hexagonal array of Zr octahedra and KO_9 polyhedra in wadeite and by a similar hexagonal array of Zr octahedra and Na decahedra in catapleiite. Elpidite has been supposed (cf. Ilyukhin and Belov, 1960) to contain a two-level

Table 5(i). *Cation—anion bond lengths*

Cation	Type of oxygen	Bond length	σ(bond length) cf. Table 4	Mean cation—anion distance
Zr	O_3	2.028 Å	0.012	2.06 $\pm$ .03 Å
	O_4	2.073		
	O_6	2.090		
K/Na	O_3	(3.494)	0.015	3.02 $\pm$ .13
	O_4	2.825		
	O_6	2.880		
	O_7	3.016		
	O_8	3.150		
	O_2	3.117		
	O_4	2.962		
	O_5	3.001		
	O_8	(3.414)		
	O_7	3.240		
Si_1	O_1	1.622	0.013	1.59 $\pm$ .04
	O_7	1.540		
	O_8	1.644		
	O_6	1.561		
Si_2	O_3	1.664	0.013	1.64 $\pm$ .03
	O_7	1.658		
	O_5	1.626		
	O_2	1.600		
Si_3	O_2	1.604	0.013	1.64 $\pm$ .03
	O_4	1.624		
	O_5	1.672		
	O_8	1.650		

trigonal ring (doubled catapleiite ring), but its structure is not known in detail. Lovozerite contains isolated six-membered Si—O rings linked by an approximately cubic network of Zr octahedra which lie at the corners of a cell 7.31 Å × 7.31 Å × 7.33 Å (Ilyukhin and Belov, 1960). Comparison of the cell dimensions of lovozerite with dalyite led Ilyukhin and Belov to suppose that slight deformation of the (almost) cubic cell to make it triclinic, together with a linkage of the free corners of tetrahedra in one ring with similar corners in another would make a chain of tetrahedra corresponding to the radical Si_6O_{15} and would be a possible model for dalyite. The complete structure determination, however, shows that the Si_6O_{15} linkage in dalyite is not a chain but the corrugated sheet which has been described.

9. Bond lengths

Table 5(i) lists cation-anion bond lengths. The standard deviations of bond lengths within each polyhedron are shown in the last column of the table. All of these are so much greater than the error estimated

Table 5(ii). *O—O distances*

Atoms	Separation	σ(bond length)	
Si_1 tetrahedron			
O_1—O_6	2.612 Å	.020	
O_1—O_7	2.525		*Mean*
O_1—O_8	2.610		$= 2.59 \pm .05$ Å
O_6—O_7	2.558		
O_6—O_8	2.680		
O_7—O_8	2.577		
Si_2 tetrahedron			
O_2—O_3	2.714	.020	
O_2—O_5	2.608		*Mean*
O_2—O_7	2.596		$= 2.67 \pm .08$ Å
O_3—O_5	2.698		
O_3—O_7	2.804		
O_5—O_7	2.603		
Si_3 tetrahedron			
O_2—O_4	2.670	.020	
O_2—O_5	2.658		
O_2—O_8	2.637		*Mean*
O_4—O_5	2.676		$= 2.67 \pm .03$ Å
O_4—O_8	2.728		
O_5—O_8	2.670		

Table 5(iii). *Interatomic bond angles*

Atoms	Angle	
Zr octahedron		
O_3—Zr—O_4	92.3 °	
O_3—Zr—O_6	92.6	
O_4—Zr—O_6	92.5	
Si$_1$ tetrahedron		
O_1—Si$_1$—O_6	110.3 °	
O_1—Si$_1$—O_7	106.0	
O_1—Si$_1$—O_8	106.5	Mean = 109.6
O_6—Si$_1$—O_7	111.1	
O_6—Si$_1$—O_8	115.0	
O_7—Si$_1$—O_8	108.6	
Si$_2$ tetrahedron		
O_2—Si$_2$—O_3	112.5 °	
O_2—Si$_2$—O_5	107.9	
O_2—Si$_2$—O_7	105.7	Mean = 109.4 °
O_3—Si$_2$—O_5	110.2	
O_3—Si$_2$—O_7	115.2	
O_5—Si$_2$—O_7	104.9	
Si$_3$ tetrahedron		
O_2—Si$_3$—O_4	111.6 °	
O_2—Si$_3$—O_5	108.4	
O_2—Si$_3$—O_8	108.3	Mean = 109.5 °
O_4—Si$_3$—O_5	108.5	
O_4—Si$_3$—O_8	112.9	
O_5—Si$_3$—O_8	107.0	
Oxygen coordination angles		
Si$_1$—O_1—Si$_1$	180 °	
Si$_1$—O_7—Si$_2$	145.4 ⎫	
Si$_1$—O_8—Si$_3$	130.2 ⎪	
Si$_2$—O_2—Si$_3$	146.4 ⎬	Mean = 138.6 °
Si$_2$—O_5—Si$_3$	132.6 ⎭	

from $\sigma(x_n)$ as to suggest a real scatter of bond lengths within a poly-hedron.

The average Si—O distance is 1.62 ± .02 Å, which is in good agreement with the value 1.619 Å obtained from SMITH and BAILEY's curve (SMITH and BAILEY, 1963) for a silicate with an O:Si ratio of 5:2.

The average Zr—O distance is 2.06 ± .03 Å, close to the value 2.07 Å, found in the structure of the chemically similar wadeite (HENSHAW, 1955).

K/Na—O distances vary considerably, but the average of 3.02 Å compares with the value 3.11 Å in wadeite where the site is entirely occupied by K. The very high anisotropy exhibited by the K/Na atom is rather large to be caused solely by thermal motion, and it may be that the atom occupies two different sites about 0.25 Å apart with approximately equal probability. For this reason the average K/Na—O bond lengths in Table 5 may not correspond to any real cation-anion links. Only a full three-dimensional analysis could settle the matter.

10. Bond angles

Table 5(iii) gives O—Si—O and Si—O—Si angles. O—Si—O angles within tetrahedra have the spread in values usually found in silicates and do not include any unusual features. Si—O—Si values, however, include one angle of 180° across the oxygen O_1 at the special position $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. LIEBAU (1961d) has reviewed Si—O—Si angles in crystalline silicates and divided them into two types, one type across oxygens near special or accidentally-simple positions having values more than 160°, the other type across oxygens which are not near special positions having values between 129° and 166° with an average angle of about 140°. The angle across O_1 in dalyite is of the first type, and other angles across O_2, O_5, O_7 and O_8 of the second type having an average value of 139°. LIEBAU (1961a, b, c) investigated the structures of $Li_2Si_2O_5$, $\alpha Na_2Si_2O_5$ and petalite which have angles of the first type, and found that although there was marked pseudo-symmetry in each case, the oxygen involved in the bond was in fact slightly displaced from the special position it would have occupied if full symmetry operated. The result of this was to reduce the Si—O—Si angle from 180° to a value close to 160°. LIEBAU (1961d) went on from this to suggest in a later paper that 180° Si—O—Si bonds would not exist in silicates, and to predict that structures such as thortveitite, zunyite, coesite etc. which had previously been found to have 180° Si—O—Si angles would be found on closer inspection to be pseudo-symmetric, the oxygen being displaced from the pseudo-special position to reduce the Si—O—Si angle to about 160°.

CRUICKSHANK, LYNTON and BARCLAY (1962) however, have recently refined thortveitite by least-squares methods with full three-dimensional data and have concluded that it retains the full symmetry (space group $C2/m$) and the 180° Si—O—Si angle of the original structure (ZACHARIASEN, 1930). CRUICKSHANK et al. point out that

the zunyite and coesite determinations are of fairly high quality, and that in these cases too, the $180°$ Si—O—Si angles could only be discounted after very careful refinement.

Figure 6 shows (100), (010) and (001) electron-density projections of the O_1 atom in dalyite. The anisotropy previously referred to (Section 7, Table 4) can be clearly seen. In view of LIEBAU's suggestion (LIEBAU, 1961d), it was thought that the anisotropy might be the result of a wrongly-imposed centre of symmetry, the oxygen actually being displaced from the special position $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The anisotropy of the K/Na atom could also be due to the same thing. Accordingly O_1 was

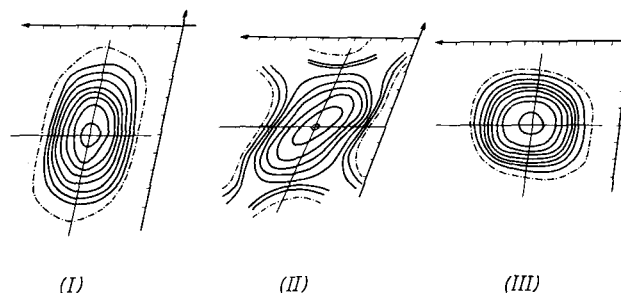*(I)*   *(II)*   *(III)*

Fig. 6. Electron-density projections of oxygen atom O_1 along x, y and z axes respectively. Axial directions divided into 64ths of the cell edges are shown

moved off the special position and refinement was continued on the assumption that the structure was non-centrosymmetric. At the limit of refinement, the R factors on the three projections had been reduced by $0.8°/_0$, $0.6°/_0$ and $0.9°/_0$; O_1 had moved about 0.1 Å from its former site, and the Si_1—O_1—Si_1 angle had dropped to $173°$. The improvement in R factors and in the flatness of the difference maps was so marginal that it was not thought to be significant. Removing the centre of symmetry in any case increased the number of variable parameters from 47 to 62, so that some improvement in R values and difference maps would have been expected. Contours round the O_1 atom on electron-density maps were, however, more nearly circular than those in Fig. 6: — a point in favour of the lower symmetry structure. What does seem clear is that there is definite departure from a strictly straight Si_1—O_1—Si_1 linkage. If the structure is centro-symmetric this takes the form of anisotropic thermal motion of the oxygen; if not, an actual displacement of the oxygen from the special site. Careful refinement with full three-dimensional data would be needed to

discover the correct answer. In lieu of this, the conventional assumption of higher symmetry ($P\bar{1}$ space group) has been made when listing the coordinates, bond lengths and bond angles.

11. Acknowledgements

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