Dalyite, a new potassium zirconium silicate, from Ascension Island, Atlantic.

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EJECTED blocks of plutonic igneous facies have long been known in the trachytic and basaltic tuffs of Green Mountain and Middleton Peak on Ascension Island, and a petrographic account of them has been recorded by Professor R. A. Daly in his memoir on the geology of Ascension Island.[1]

Professor C. E. Tilley while examining thin sections of some of these rocks noticed the presence of the mineral now to be described, and following a preliminary investigation by Dr. S. O. Agrell, who also isolated the first crystal, the author was entrusted with its detailed study.

The mineral occurs as a rare accessory, about 0·2 % of the rock, in medium-grained pinkish-grey alkali-granites mainly composed of microperthite and quartz associated in varying proportions with aegirine and a strongly pleochroic green-brown alkali-amphibole. A rock specimen (B.M. 64685)[2] from Green Mountain kindly provided by the British Museum (Natural History) furnished the first mineral fragments, but most of the material was isolated from rocks preserved at Cambridge[3] (Harker slide collection nos. 57069, 57219).

The mineral is now shown to be a potassium zirconium silicate for which the name *dalyite* is proposed in honour of Reginald Aldworth Daly (1871–), Emeritus Professor of Geology, Harvard University, who

[1] R. A. Daly, The geology of Ascension Island. Proc. Amer. Acad. Arts & Sci., 1925, vol. 60, no. 1, pp. 1–80 (see pp. 63–68). [M.A. 3-385.]

[2] This rock specimen was collected during the cruise of H.M.S. Challenger, 1873–6, and is described by A. F. Renard in the Challenger Report as amphibolic granite. Report on the petrology of Oceanic Islands, 1889, pp. 63–64.

[3] For these and numerous other specimens of ejected blocks on Green Mountain and Middleton Peak the Department of Mineralogy and Petrology at Cambridge is greatly indebted to the Manager of Cable and Wireless Ltd., Ascension Island, who on my inquiry, through the kind offices of the Directorate of Colonial Geological Surveys, arranged for the collection of this material. Grateful acknowledgement is due to Messrs. M. A. Miles, H. W. Benjamin, and G. A. O'Dean, members of the Company's staff, who were responsible for the field work.—C. E. Tilley.

has contributed so much to our knowledge of the geological structure and petrology of Ascension Island.

Rough crushing of the rather friable rock, concentration with suitable heavy liquids, and careful hand-picking under the microscope provided about 100 mg. of pure material.

Dalyite forms colourless, completely transparent, triclinic crystals ranging 0·1–0·5 mm. in size, with short prismatic habit and vitreous lustre. Cleavage directions are observed and twinning is not uncommon. The hardness is about $7\frac{1}{2}$, the mineral just scratching quartz. The principal properties of dalyite are described below under separate headings.

Unit cell.

The unit cell of dalyite was determined from X-ray photographs using copper radiation with a nickel filter. A small crystal $0{\cdot}25 \times 0{\cdot}3 \times 0{\cdot}35$ mm. in size, of which fig. 1A is a true representation, was mounted in a Weissenberg camera of 3 cm. radius and having 2° rotation for 1 mm. traverse. The well-developed prism was set parallel to the rotation axis of the instrument. The equatorial layer was recorded with a normal beam photograph and the first and third layer-lines with equi-inclination photographs. As the reciprocal net constructed from the zero layer-line photograph is non-orthogonal and as adjacent layer-lines do not superpose on it, triclinic symmetry is at once revealed. The cell constants have been chosen in order to give the smallest cell as nearly orthogonal as possible and to satisfy the conventional rule, $c<a<b$, α and β obtuse.[1] From the third layer-line, the oscillation photograph gave c 7·00 Å. The reciprocal cell constants, obtained from Weissenberg photographs, are: for the equatorial layer-line a^* 0·236, b^* 0·219, and γ^* $71\frac{1}{2}°$; for the first layer-line, with beam inclination μ 6° 20′, a^* 0·235, b^* 0·218, and γ^* $72\frac{1}{2}°$; and for the third, with inclination μ 19° 20′, a^* 0·233, b^* 0·218, and γ^* 72°. From these data were deduced the average values a^* 0·235, b^* 0·218, and γ^* 72°. Graphically the following constants were also obtained: c^* 0·259, α^* 68°, and β^* 62°.

The Bravais cell constants, calculated from the preceding data, are a 7·51, b 7·73, c 7·00 Å., α 106°, β $113\frac{1}{2}°$, and γ $99\frac{1}{2}°$. The accuracy for the linear values is $\pm$ 1% and for the angles $\pm 1°$. The calculated volume of this unit cell is 341 Å^3. As the specific gravity determined on the same crystal, by suspension in liquids of known density, is $2{\cdot}84 \pm 0{\cdot}02$, the calculated molecular weight, or a multiple of it, is about 582.

[1] J. D. H. Donnay, Rules for the conventional orientation of crystals. Amer. Min., 1943, vol. 28, pp. 313–328. [M.A. 9–140.]

Morphology.

Twenty-three crystals, all of incomplete crystallographic outline, were measured on the two-circle goniometer. Confirming the triclinic character shown by X-rays, a centre is the only element of symmetry observed. Hence the crystal class is $\bar{1}$ and the space-group $P\bar{1}$. The unit cell

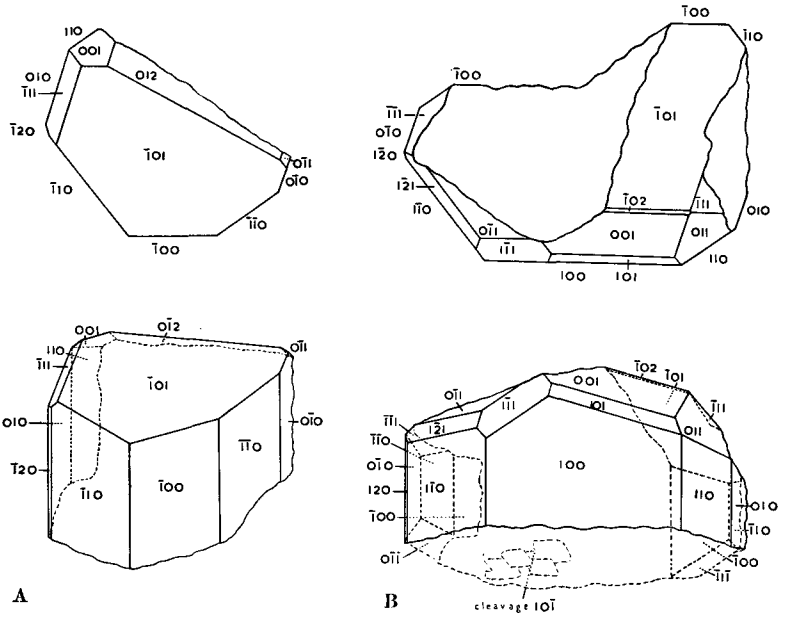

FIG. 1. Top and side views of dalyite crystals in true representation. A, 0·25 × 0·3 × 0·35 mm.; B, 0·25 × 0·45 × 0·5 mm.

deduced from X-ray data served for the assignment of the face indices. Sixteen crystal-forms were identified; they are tabulated below together with the frequency of their observed occurrence:

{100}	{010}	{001}	{$\bar{1}$01}	{110}	{1$\bar{1}$0}	{1$\bar{2}$0}	{$\bar{1}$11}
19	11	6	21	11	13	6	10
{011}	{101}	{$\bar{1}\bar{1}$1}	{1$\bar{2}$1}	{1$\bar{1}$1}	{0$\bar{1}$1}	{$\bar{1}$02}	{0$\bar{1}$2}
2	2	5	4	6	4	2	1

The frequency figures have only a limited value as all the measured crystals were broken fragments. Whenever more or less complete, the crystals show short-prismatic habit. The form {$\bar{1}$01} is most frequent and produces also large faces with excellent reflection. This behaviour suggests another choice for the *z*-axis and the assignment of {001}

indices to the form, but in view of the X-ray data and the conventional rules, the indices tabulated above are assigned in the present study. The forms {1$\bar{1}$0} and {100} are also important; somewhat less so are {010} and {110}, while {1$\bar{2}$0} is narrow. {001} is irregular in behaviour. The forms {$\bar{1}$11}, {0$\bar{1}$1}, {$\bar{1}\bar{1}$1}, {1$\bar{2}$1}, {011}, and {1$\bar{1}$1} usually produce small good faces; {101} and {$\bar{1}$02} are narrow. The form {0$\bar{1}$2} is rather doubtful as it has only once been observed with bad reflection. The good cleavages are {$\bar{1}$01} and {010}, and less distinct {100}.

Two-circle goniometer angles, measured on the two most complete crystals, shown in fig. 1, are given in table I.

TABLE I. Measured two-circle angles of dalyite.

	Crystal A.			Crystal B		
Face.	ρ.	ϕ.	Reflection.	ρ.	ϕ.	Reflection.
(101)	—	—	—	58° 14′	27° 51′	bad
(100)	—	—	—	90 15	17 38	perfect
(001)	31° 00′	46° 01′	bad	30 59	46 25	good
(110)	89 40	51 59	good	89 54	51 55	good
(010)	89 33	90 00	good	89 54	90 00	good
($\bar{1}$02)	—	—	—	17 —	106 —	very bad
($\bar{1}$11)	51 22	118 48	good	50 54	118 45	good
($\bar{1}$20)	90 03	121 11	bad	—	—	—
($\bar{1}$10)	89 43	146 46	good	90 04	147 00	bad
($\bar{1}$01)	31 26	169 12	perfect	31 14	169 35	good
($\bar{1}$00)	89 57	197 20	good	90 04	197 36	good
($\bar{1}\bar{1}$1)	—	—	—	−56 02	170 24	good
($\bar{1}\bar{1}$0)	90 03	232 02	good	90 07	232 25	good
($\bar{1}\bar{1}$1)	—	—	—	46 34	235 45	good
(1$\bar{2}$1)	—	—	—	−55 37	253 26	good
(0$\bar{1}$0)	90 03	269 46	good	90 19	270 17	good
(0$\bar{1}$1)	34 49	306 41	bad	—	—	—
(1$\bar{2}$0)	—	—	—	90 29	301 45	bad
(1$\bar{1}$0)	—	—	—	90 29	327 30	good
(1$\bar{2}$1)	—	—	—	62 14	319 39	good
(1$\bar{1}$1)	—	—	—	55 36	350 47	good
(10$\bar{1}$)	—	—	—	−31 —	355 —	bad (cleavage)
(0$\bar{1}$2)	21 57	319 01	very bad	—	—	—

The better readings, selected among the available data on all the measured crystals, were used for the calculation of the axial angles and ratios:

	Limits.	Number.	Average.
($\bar{1}$00) ($\bar{1}$01)	62° 32′–62° 45′	8	62° 38′
($\bar{1}$10) ($\bar{1}$01)	60 53 –61 06	7	61 01
($\bar{1}$10) ($\bar{1}$00)	50 30 –50 46	5	50 37
(001) ($\bar{1}$01)	53 57 –54 16	4	54 05
(100) (010)	72 30 –72 39	6	72 33

$a:b:c = 0{\cdot}958:1:0{\cdot}899$, α 106° 19′, β 112° 25′, γ 99° 08′.

These goniometric data are in satisfactory agreement with the cell constants obtained from X-rays:

$$a:b:c = 0{\cdot}970:1:0{\cdot}906,\ \alpha\ 106°,\ \beta\ 113\tfrac{1}{2}°,\ \gamma\ 99\tfrac{1}{2}°.$$

Table II summarizes a selection of interfacial angles (mean values), measured on the crystals and calculated from the established parameters.

TABLE II. Measured and calculated interfacial angles of dalyite.

	Meas.	Calc.		Meas.	Calc.
(001) (100)	63° 27′	63° 17′	(001) ($\bar{1}$11)	48° 33′	48° 50′
(001) (010)	68 09	68 01	($\bar{1}$01) ($\bar{1}\bar{1}$1)	42 21	42 17
(100) (110)	37 57	37 57	(001) ($\bar{1}\bar{1}$1)	77 15	77 15
(110) (010)	34 36	34 36	(001) (0$\bar{1}$1)	48 43	48 45
($\bar{1}$10) ($\bar{1}$20)	25 07	25 10	($\bar{1}$01) (1$\bar{2}$1)	90 00	90 03
($\bar{1}$10) (010)	56 53	56 50	(001) (1$\bar{2}$1)	64 50	64 37
($\bar{1}$01) ($\bar{1}\bar{1}$0)	76 18	76 19	($\bar{1}$01) (1$\bar{1}$1)	86 49	86 51
(001) (110)	59 04	59 10	(001) (1$\bar{1}$1)	43 26	43 24
($\bar{1}$01) ($\bar{1}$20)	69 05	69 13	(001) (101)	29 58	30 01
(001) ($\bar{1}$20)	82 42	82 22	($\bar{1}$01) (101)	84 03	84 06
($\bar{1}$01) ($\bar{1}$11)	37 31	37 33	(001) ($\bar{1}$02)	26 38	27 08

Twinning is not rare, as among the 23 crystals isolated for goniometric measurements, four were twinned. They form normal twins with (100) as composition plane. Some of the measured angles (single readings) are compared with the calculated values:

	Meas.	Calc.		Meas.	Calc.
($\bar{1}$01) ($\underline{\bar{1}01}$)	54° 40′	54° 44′	($\bar{1}\bar{1}$1) ($\bar{1}$11)	17° 42′	17° 34′
(001) ($\underline{001}$)	53 04	53 26	($\bar{1}$10) ($\underline{\bar{1}\bar{1}0}$)	78 54	78 46
(010) ($\underline{010}$)	35 03	34 54	(110) ($\underline{110}$)	110 24	110 48

Optical properties.

The refractive indices determined by the immersion method are α 1·575, β 1·590, γ 1·601, all $\pm$0·002. The optic axial angle measured on the universal stage is negative with 2V 72°$\pm$2°. Dispersion is very weak with presumably $v<r$. Using crystals with identified faces the optical orientation was determined on the universal stage: α, acute bisectrix, is nearly parallel to the c-axis ($\alpha:c = 7°$), and the axial plane forms an angle of 18° with (100), which is also the twin plane. Fig. 2 illustrates the crystallographic and optical orientation.

Inclusions are occasionally observed in the crystals of dalyite: (1) isotropic, highly refractive, orange, transparent octahedra of 60–100μ; (2) swarms of very thin needles of rutile (?), and small cavities with crystalline outline of 8–40μ are present, often filled with a bubble. The octahedral mineral, isolated by Dr. S. O. Agrell, has a cell size of

10·4 Å. as determined from X-ray oscillation photographs and is to be regarded as a member of the pyrochlore group.

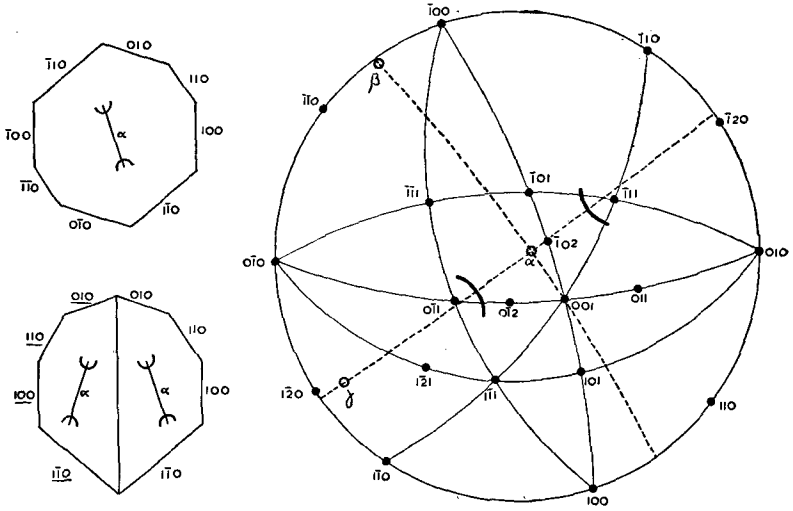

FIG. 2. Stereographic projection of crystal forms and optical orientation, and ideal sections perpendicular to the prism zone in single and twin crystals. $\alpha:c = 7°$.

Chemical composition.

The small amount of available material required special care and the use of micro-methods. Spectrographic investigation, based on arc emission and on visual evaluation of step-sector spectrograms, permitted a semi-quantitative determination. Mixtures of known and similar composition were prepared for comparison and only mineral fragments individually tested and optically free from inclusions, were selected for arcing. Potassium, zirconium, and silicon are the main constituents. Sodium was estimated at about 1% Na_2O. Be, Mn, Sr, Li, Cs, Rb, and F were not detected (limit of sensitivity about 0·001%, except for Cs and F 0·05 %). Other elements were identified, but occur only in negligible amounts.

The evaluation of absolute line intensities permitted the determination of the main constituents, within the stated limits of error, as follows: K_2O 16±3 %, ZrO_2 20±5 %, SiO_2 55±6 %. These constitute almost exclusively the whole mass and molecular ratios based on these figures are K_2O 1·05±0·2, ZrO_2 1±0·25, SiO_2 5·6±0·6. In addition, the neighbouring lines Si 2987–Zr 2985 provide a suitable pair for relative evalua-

tion according to the internal method. In this way the ratio $ZrO_2:SiO_2$ is found to be $1:5{\cdot}5\pm0{\cdot}5$. A compound with the formula $K_2O.ZrO_2.5SiO_2$ has in its simplest expression a molecular weight of 517·7 against 577·8 for $K_2O.ZrO_2.6SiO_2$. As the figure of 582 was determined from X-ray data, the latter formula appears quite probable, hence the unit cell contains one molecule.

The conclusions drawn from the spectrographic data are satisfactorily supported by a microchemical analysis subsequently completed by Dr. M. H. Hey on 22 mg. of the mineral. The interpretation of the analytical results given in table III leads to the formula $K_2ZrSi_6O_{15}$, where sodium replaces a part of the potassium. Zirconium was weighed as ZrO_2 and any hafnium will not alter sensibly the molecular ratio $SiO_2:(Zr,Hf)O_2:K_2O$, as the zirconium content, spectrographically determined on characteristic lines, cannot be less than 15 %. Dr. Hey has preserved the crude ZrO_2 and hopes eventually to have the Hf:Zr ratio determined.

TABLE III. Microchemical analysis of dalyite.

		Mol. ratios.	Oxygens.	Metals.	Metals on a basis of 15O.
SiO_2	61·85	1030	2060	1030	5·95	
ZrO_2	21·70	176	352	176	1·01	
K_2O	14·60	155	155	310	1·79	2·11
Na_2O	1·75	28	28	56	0·32	
Fe_2O_3	0·37	—	—	—	—	
H_2O	0·64	—	—	—	—	
	100·91					

Dalyite is unaffected by warm concentrated nitric acid but is slowly attacked by cold, and readily dissolved by hot hydrofluoric acid. Only when the full heat of a mekker burner is applied does dalyite show a change. Under this treatment very tiny, highly refringent prisms with straight extinction and positive elongation (? zircon) appear along with glass. Dalyite is chemically most nearly related to wadeite,[1] but it is much richer in silica and simpler in composition. Moreover, the crystallographic properties are entirely different.

Powder pattern of dalyite.

For identification purposes an X-ray powder photograph has been taken using copper radiation with nickel filter on a camera of 19 cm. diameter. A print is reproduced in fig. 3. As the pattern is very com-

[1] R. T. Prider. Some minerals from the leucite-rich rocks of the West Kimberley area, Western Australia. Min. Mag., 1939, vol. 25, pp. 373–387.

plex the weaker reflections have been omitted in table IV, which summarizes the measured spacings and the visual intensities.

TABLE IV. X-ray powder data for dalyite.

d.	Int.	*d.*	Int.	*d.*	Int.
6·54	m	2·85	m	1·840	w
5·90	s	2·66	w	1·791	w
4·31	s	2·62	vs	1·675	w
4·20	vs	2·42	m	1·640	w
3·65	w	2·25	w	1·469	w
3·58	vs	2·21	w	1·467	w
3·36	m	2·15	w	1·312	w
3·26	w	2·09	w	1·282	w
3·08	vs	2·07	w	1·211	w

(vs, very strong; s, strong; m, medium; w, weak)

FIG. 3. X-ray powder photograph of dalyite. ($\times\frac{2}{3}$.)

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Summary.—Dalyite ($K_2ZrSi_6O_{15}$), a new mineral, occurs in ejected blocks of alkali-granite from Ascension Island. It forms small colourless triclinic crystals with $a:b:c = 0{\cdot}958:1:0{\cdot}899$, α 106° 19′, β 112° 30′, γ 99° 08′. Absolute parameters: a 7·51, b 7·73, c 7·00 Å., Class $\bar{1}$, space-group $P\bar{1}$. Sixteen forms: {100}, {010}, {001}, {$\bar{1}$01}, {110}, {1$\bar{1}$0}, {1$\bar{2}$0}, {$\bar{1}\bar{1}$1}, {011}, {101}, {$\bar{1}\bar{1}$1}, {1$\bar{2}$1}, {1$\bar{1}$1}, {0$\bar{1}$1}, {$\bar{1}$02}, {0$\bar{1}$2}. Cleavages ($\bar{1}$01) and (010). Normal twinning with (100) as composition plane. Optical constants: α 1·575, β 1·590, γ 1·601, $2V_\alpha$ 72°, $\alpha:c = 7°$, axial plane to (100) = 18°. Unit cell [$K_2ZrSi_6O_{15}$]. Density 2·84. Hardness 7½.