Baddeleyite from Ceylon.

By G. S. Blake, A.R.S.M., B.Sc., F.C.S.
Assistant in the Scientific and Technical Department of the Imperial Institute.

And G. F. Herbert Smith, M.A., D.Sc., F.G.S.
Assistant in the Mineral Department of the British Museum.

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DURING recent years a systematic survey of the mineral resources of Ceylon has been in progress, in connexion with which a large number of specimens have been sent to the Imperial Institute for examination. In 1905 several cases containing coarse gravel from the streams of the gem-district of Balangoda were received. The constituent minerals were mainly zircon, tourmaline, corundum, spinel, ilmenite, together with small quantities of geikielite[1], fergusonite, and other rare-earth minerals. Last summer during the examination of these gravels one of the authors found three black crystals with unusually brilliant faces. The apparently monoclinic form and the general physical characters at once suggested the crystallized native zirconia, baddeleyite, and this conjecture was confirmed by the goniometrical measurements and the chemical analysis.

It is of interest to note that prior to this discovery there is no record of a specimen of this mineral being found in the island since Mr. L. Fletcher[2] first determined, fifteen years ago, not only the crystallographical but also the chemical properties of this species by means of an investigation of a single rough crystal, now exhibited in the Mineral Gallery of the British Museum. This crystal was included among a lot of specimens of heavy minerals which had been collected by Mr. Joseph Baddeley at Rakwana, Ceylon, and brought by him to England. Mr. Fletcher detected the crystal when picking out specimens of the then new mineral, geikielite,

[1] T. Crook and B. M. Jones, 'Geikielite and the ferro-magnesian titanates.' Min. Mag., 1906, vol. xiv, pp. 160–6.

[2] Nature, 1892, vol. xlvi, p. 420. L. Fletcher, 'On baddeleyite (native zirconia), a new mineral, from Rakwana, Ceylon.' Min. Mag., 1893, vol. x, pp. 148–60.

which Mr. Baddeley had courteously offered to the Museum. Crystals of baddeleyite have been found in abundance by Dr. E. Hussak in the magnetite deposits at Jacupiranga, São Paulo, Brazil, and his description[1] of them was published almost simultaneously with Mr. Fletcher's paper.

(a) *Crystallographical Characters.*

Of the three crystals mentioned above, one was broken at both ends and displayed the prism-zone only; it was used for the chemical analysis Each of the remaining crystals possesses faces at one end. One (fig. 1) is a twin of the common type with a (100) as the plane of twinning; of the two individuals, one has the forms $a\{100\}$, $b\{010\}$, $m\{110\}$, $d\{021\}$, $r\{\bar{1}01\}$, $o\{\bar{2}01\}$, and $n\{\bar{1}11\}$, and the other $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $d\{021\}$, and $n\{\bar{1}11\}$. Contiguous faces of the form $d\{021\}$ on the two individuals meet in a re-entrant angle. The crystal measures approximately 5 mm. in length, 8 mm. in width, and 4 mm. in thickness,

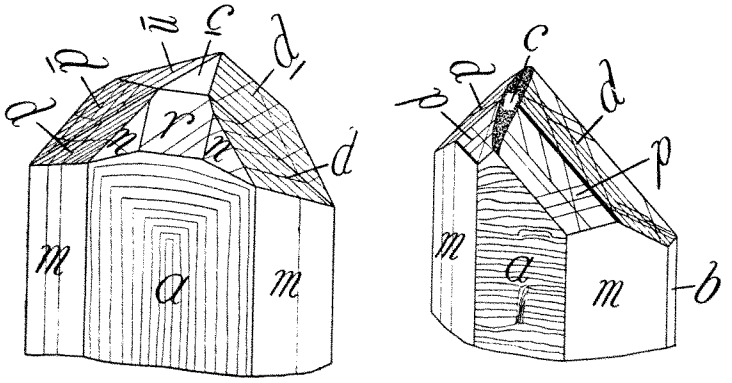

Fig. 1. Fig. 2.

Baddeleyite from Ceylon (twinned and simple crystals).

and it weighs 0·695 gram. The other (fig. 2) is a simple crystal and untwinned. It is remarkable how rare such crystals are; out of some

[1] E. Hussak, 'Über Brazilit.' Neues Jahrb. Min., 1892, vol. ii, pp. 141-5; 'Ueber den Baddeleyit (syn. Brazilit) von der Eisenmine Jacupiranga in São Paulo.' Min. Petr. Mitt. (Tschermak), 1895, vol. xiv, pp. 395-406. The name 'brazilite' was withdrawn by Dr. Hussak.

hundreds of crystals isolated by him, Dr. Hussak[1] found only three which were not twinned, and the crystal described by Mr. Fletcher also is twinned. The simple crystal displays the forms $a\{100\}$, $b\{010\}$, $c\{001\}$, $m\{110\}$, $g\{210\}$, $d\{021\}$, $t\{101\}$, and $p\{221\}$. It measures approximately 9 mm. in length, 7 mm. in width, and 3 mm. in thickness, and weighs 0·775 gram. As shown in the drawing, the top is slightly broken. Both crystals are striated in such a way as to indicate polysynthetic twinning with respect to both a (100) and m (110), a character remarked by Dr. Hussak on the Brazilian crystals and fully described by him. Both are black in colour, and sub-metallic and opaque in appearance. In thin splinters, however, the substance is seen to be transparent and yellowish in colour.

The forms observed, eleven in number, and their characters are as follows:—

$a = \{100\}$ large; striated irregularly: good reflexions.

$b = \{010\}$ small.

$c = \{001\}$ not large; slightly uneven.

$m = \{110\}$ large; striated parallel to the prism-edge: reflexions good.

$g = \{210\}$ large on the simple crystal (at the back as shown in fig. 2), otherwise small; sometimes forms the sides of pittings on a (100): reflexions poor.

$t = \{101\}$ small.

$r = \{\bar{1}01\}$ small: only once observed.

$o = \{\bar{2}01\}$ minute.

$d = \{021\}$ large; striated: reflexions good.

$p = \{221\}$ large; striated: reflexions good.

$n = \{\bar{1}11\}$ not large; striated: reflexions good.

The form $g = \{210\}$ has not been recorded before.

The notation and parameters of Dr. Hussak have been adopted in this paper. Mr. Fletcher selected a slightly different parametral plane; his (hkl) is equivalent to $(h.k.2l)$ of Dr. Hussak.

Both crystals were measured on the three-circle goniometer in the British Museum from the faces of the form $a\{100\}$, which despite the markings on them invariably gave well-defined reflexions, as origin, and the measurements with the corresponding calculated values are given in the following table:—

[1] Min. Pétr. Mitt. (Tschermak), 1894, vol. xiv, p. 399.

TABLE I.

Measurements from a = (100).

Form.		Calculated Values.		Observed Values.			
				Twinned Crystal.		Simple Crystal.	
		Azimuth.	Distance.	Azimuth.	Distance.	Azimuth.	Distance.
c	001	90° 0′*	80° 32′	90° 0′	80° 32′	89° 56′	80° 23′
t	101	,, ,,	55 24½	...	...	,, ,,	55 10
r	10$\bar{1}$	,, ,,	−70 23½	90 0	−70 37		
a	20$\bar{1}$	,, ,,	−47 54	,, ,,	−47 54		
n	11$\bar{1}$	62 56	−72 24	62 57	−72 14		
				62 53	−72 9		
				62 55	−72 2		
d	021	44 23*	83 21	44 17	83 31	44 14	83 18
				44 26	83 27	44 33	83 16
				44 27	83 21		
				44 22	83 13		
p	221	,, ,,	49 41½	...	...	44 14	49 44
						44 33	49 35
b	010	0 0	90 0*	0 0	89 59	0 0	89 53
				,, ,,	89 43		
m	110	...	44 20*	,, ,,	44 27	,, ,,	44 19
				,, ,,	44 14	,, ,,	44 26
				,, ,,	44 12	,, ,,	44 24
				,, ,,	44 24	,, ,,	44 14
g	210	...	26 2	...	...	,, ,,	26 0
							26 3
							26 2

The angles from which the calculations have been made are indicated by asterisks.

The calculated coordinates of the observed forms with respect to the face of symmetry *b* = (010) as origin are tabulated below :—

TABLE II.

Coordinates from b = (010).

$a:b:c = 0{\cdot}9905:1:0{\cdot}5110$; $\beta = 99°\,28'$.

Form.		Azimuth.	Distance.
r	$\bar{1}01$	$-70°\ 23\frac{1}{2}'$	90° 0′
n	$\bar{1}11$	,, ,,	64 18
c	001	80 32	90 0
d	021	,, ,,	44 $46\frac{1}{2}$
t	101	55 $24\frac{1}{2}$	90 0
p	221	39 $30\frac{1}{2}$	56 $58\frac{1}{2}$
a	100	0 0	90 0
g	210	,, ,,	63 58
m	110	,, ,,	45 40
b	010	,, ,,	0 0

The crystals are unusually large, and their faces unusually plane for this mineral; Dr. Hussak, indeed, found crystals measuring as much as 5 mm., but owing to the distortion of the faces they were quite useless for purposes of measurement, and Mr. Fletcher's crystal also gave very ill-defined reflexions. The measured values in the prism-zone agree closely with those recorded by Dr. Hussak; but in the zone of symmetry [*ac*] there is an appreciable difference between the values observed on these crystals and those noted by Dr. Hussak. The following table compares the observed values in the two cases:—

	Hussak.	Smith.
$am = (100):(110)$	$44°\ 17\frac{1}{2}'$	$44°\ 20'$
$ac = (100):(001)$	81 $14\frac{1}{2}$	80 32
$ar = (100):(10\bar{1})$	69 41	70 37
$at = (100):(101)$	55 51	55 $24\frac{1}{2}$

Dr. Hussak found as the limiting values for the angle $ac=(100):(001)$ $80°\ 56\frac{1}{2}'$ and $81°\ 42'$, so that the measurements in the present case lie well outside this range.

On the other hand, the values calculated from the fundamental angles selected in this paper accord in certain cases better with Dr. Hussak's observations than do his own calculated values; thus:—

	Hussak.		Smith.
	Observed.	Calculated.	Calculated.
$an = (100):(11\bar{1})$ . . .	72° 16′	71° 45½′	72° 24′
$ap = (100):(221)$ . . .	49 40½	50 41	49 41½
$ad = (100):(021)$ . . .	83 28	83 51	83 21

There is a noticeable variation in the specific gravity, which is comparable with, though not so great as, that observed in the case of zircon. Mr. Fletcher gives 6·025 as the value for the crystal examined by him, whereas Dr. Hussak obtained 5·5 for the Brazilian crystals. In the case of the present crystals, the specific gravities of the crystal used in the analysis and of the twinned crystal are 5·72 and 5·73 respectively, while for the simple crystal it is as much as 5·82.

(b) *Chemical Examination.*

The crystal which was utilized for the determination of the chemical composition weighed 0·6413 gram, and had a specific gravity of 5·72. It was ground to a powder and fused for several hours with potassium hydrogen sulphate. The resulting mass was dissolved in water, and the silica in the small amount of insoluble residue determined. The hydrochloric acid solution of the bases, freed from potassium sulphate, was treated with ammonium oxalate, and it was found that the thorium and cerium metals were absent. The ammonium oxalate was removed, and sodium thiosulphate was added to the nearly neutral solution. The amount of iron in the filtrate was determined. The precipitate, which consisted presumably of zirconium thiosulphate, was converted into hydroxide and weighed as oxide. The precipitate was re-dissolved and tested for uranium and titanium, but a trace of the latter element only was detected.

The following are the results of the analysis (G. S. B.):—

Zirconia, ZrO_2	98·90
Ferric oxide, Fe_2O_3 } . . .	0·82
Ferrous oxide, FeO }	
Lime, CaO	0·06
Silica, SiO_2	0·19
Loss on ignition.	0·28
	100·25

The following are the characteristic reactions of the principal element in the mineral :—

(*a*) From a solution, ammonium oxalate precipitates the oxalate, which is readily soluble in excess of the reagent, either acid or neutral;

(*b*) Sodium thiosulphate precipitates it from neutral solutions;

(*c*) The neutral sulphate forms an insoluble double salt with potassium sulphate.

These reactions suffice to group the element with thorium, zirconium and titanium. The proof that it is actually zirconium was sought for by the preparation of the fluoride. The oxide obtained from the analysis was dissolved in hydrofluoric acid and the solution slowly evaporated in a covered platinum crucible with the formation of colourless, transparent crystals, which were dried first on filter-paper, and then for two days *in vacuo* over calcium chloride. The crystals have the triclinic symmetry described by Marignac[1], but were not well developed. It was found that 0·3000 gram of this salt yielded 0·1638 gram of the oxide. If the composition be assumed to be $ZrF_4.3H_2O$, the element would have an atomic weight of 91, which is so near that determined for zirconium, viz. 90, as to justify the inference that the oxide contained this element alone of the group given above.

The chemical analysis of the mineral has been further confirmed by a spectroscopic examination, which was undertaken by Mr. A. Fowler at the Royal College of Science, London. The arc-spectrum was photographed with an instrument of high dispersion, and a comparison with the tables of Exner and Haschek in the region of 4367 to 4689 shows all the lines of zirconium recorded by those observers with the exception of one at 4408·54. The only additional strong line in this part is at wave-length 4602·73. The spectrum, however, was found to be identical with that given by a portion of a crystal of common zircon, except that the baddeleyite showed a slight trace of manganese in addition to iron.

[1] Annales chim. phys., 1860, sér. 3, vol. lx, pp. 266–7.