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*On varieties of Zirkelite from Ceylon.*¹

By G. S. BLAKE, A.R.S.M., B.Sc., F.C.S.

With crystallographic notes,

by G. F. HERBERT SMITH, M.A., D.Sc., F.G.S.

Assistant in the Mineral Department of the British Museum.

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THIS paper deals with various specimens received at the Imperial Institute from Ceylon. Some of these specimens were obtained by Dr. A. K. Coomaraswamy at Walaweduwa, in the Bambarabotuwa district of the Sabaragamuwa province, during the course of the Ceylon Mineral Survey. Walaweduwa is a little to the north of the Bambarabotuwa locality where thorianite has been found in considerable abundance. Dr. Coomaraswamy also found specimens in the upper part of the Alupola oya, a stream in the same district. A chemical examination of these specimens showed that titanium dioxide, zirconia, thoria, lime, and iron oxide were the chief constituents. This, taken in conjunction with their

¹ Communicated by permission of the Director of the Imperial Institute. A brief mention of this mineral has already been made, under the name zirkelite, in 'Ceylon: Report on the results of the Mineral Survey in 1904-5,' Colonial Reports, Miscellaneous, No. 37, London, 1906, pp. 29 and 40.

physical characters, indicated that they belonged to the species zirkelite, a species which had been previously found at Jacupiranga, São Paulo, Brazil, and described in this magazine by Dr. E. Hussak and Dr. G. T. Prior.¹

Other specimens of zirkelite were collected at a later date from various consignments of refuse gem-gravel which had been obtained from alluvial deposits in different parts of southern Sabaragamuwa, and sent to the Imperial Institute for examination. The heavy minerals consisted chiefly of zircon, tourmaline, corundum, and spinel; and several rare-earth minerals were also present. The area from which these gravels were obtained includes also the Bambarabotuwa district; but as no definite locality can be assigned to them, it will be convenient to refer to them as being from the 'gem-gravels of southern Sabaragamuwa', in order to distinguish them from the more precisely localized specimens sent by Dr. Coomaraswamy.

Physical Characters.

The specimens received from the Bambarabotuwa district are coarse grains mostly of irregular shape and show very rough surfaces. None of the grains weigh more than about a gram. They are brownish-black in colour, and their specific gravity ranges from 4.72 to 5.22. Those obtained from the 'gem-gravels of southern Sabaragamuwa' are much larger, weighing from 5 to 15 grams. In general appearance there is little to distinguish the latter from the Bambarabotuwa specimens, but their specific gravity is lower, and varies from 4.3 to 4.6. The colour of the streak is chocolate-brown, and is of a slightly darker shade in the uranium-rich than in the thorium-rich varieties. The hardness is $5\frac{1}{2}$ to 6. The fracture is sub-conchoidal, and the lustre is sub-metallic to resinous.

The few small crystals found amongst the material from the Bambarabotuwa district show six-sided prisms terminated by basal planes. Some of them exhibit a slight tendency to cleave parallel to the basal plane. From the 'gem-gravels of southern Sabaragamuwa' crystals of very varied habit and irregular development have been obtained. Some of the larger of these exhibit what may perhaps be regarded as complex twinned

¹ E. Hussak and G. T. Prior, 'Lewisite and zirkelite, two new Brazilian minerals,' *Mineralogical Magazine*, 1895, vol. xi, pp. 80-88. G. T. Prior, 'On the chemical composition of zirkelite,' *Mineralogical Magazine*, 1897, vol. xi, pp. 180-188.

forms : the best of them were submitted to Dr. G. F. Herbert Smith for crystallographic examination (p. 314).

In thin-sections examined under the microscope the material was for the most part opaque, but occasionally showed reddish-brown, translucent specks and small patches.

Chemical Composition.

On heating in the blowpipe flame the mineral decrepitates. The powdered mineral is slowly attacked by hydrochloric acid, and if excess of acid is maintained all but 2 or 3 per cent. passes into solution on the addition of cold water. There is a decided tendency, however, for titanitic acid mixed with zirconium hydroxide to separate if the chlorides become dry. The powdered mineral is very readily decomposed by hydrofluoric acid, and when subsequently converted into sulphate by heating with sulphuric acid, complete solution is effected on the addition of water.

The plan adopted for the analysis of the mineral is based on the following methods :—

- (1) Separation of calcium and magnesium by precipitation of the hydroxides of the other metals with ammonia in the presence of ammonium chloride.
- (2) Precipitation of the rare-earth metals as oxalates by means of ammonium oxalate from an acid solution of the chloride.
- (3) In the filtrate from (2) the separation of zirconium and titanium from iron with sodium thiosulphate.

The details of the methods employed are as follows :—

Solution was generally effected by treating one or two grams of the powdered mineral with hydrofluoric acid and removal of the volatile acid by evaporation with sulphuric acid. On adding cold water a perfect solution was obtained. Hydrochloric acid was added and then ammonia and the precipitate filtered off. This was re-dissolved and the operation repeated. The combined filtrates were evaporated, and lime and magnesia estimated in the usual way.

The hydroxides dissolved in slight excess of hydrochloric acid were then poured into a hot solution of ammonium oxalate and the precipitate of oxalates of thorium, cerium and yttrium groups filtered off after some hours standing. This after ignition was treated with 50 per cent. sulphuric acid, and the sulphates then converted into chlorides.

The thorium was separated from other rare-earth metals by double precipitation with sodium thiosulphate, then re-precipitated with am-

monium oxalate to ensure the complete separation from any zirconium and titanium which may have been carried down with the oxalates first precipitated. The combined filtrates from this separation were treated with bromine water and ammonia. Hydroxides of zirconium, titanium, and iron were thus precipitated, together with ammonium uranate. On the addition of ammonium carbonate all the uranium was obtained in solution, together with a little zirconium, &c. By boiling this solution for a few minutes the zirconium, &c., was precipitated. The uranium in the filtrate was estimated as uranoso-uranic oxide.

The precipitate containing the zirconium, titanium, and iron was dissolved as chloride, and the zirconium and titanium separated with sodium thiosulphate from the iron, which was afterwards precipitated with ammonia.

The titanium and zirconium were finally weighed as oxides. In order to estimate the titanium these oxides were dissolved in hydrofluoric acid and subsequently converted into sulphates as previously described. An aliquot portion of the solution of the sulphates was then titrated colorimetrically in comparison with a standard solution of pure titanium sulphate. Hydrofluoric acid must be completely removed or the results are untrustworthy.

The difference between the percentage of oxides calculated from the results of analysis and the percentage of titanium dioxide obtained colorimetrically is recorded as zirconium dioxide. No alumina nor niobic and tantalic oxides were found by fusion with caustic potash.

The results of analysis show that there are three main varieties of the mineral, in which there are considerable differences in the percentages of thorium and uranium:—

- (1) A variety rich in thoria, with a specific gravity of about 5.1. This contains about 20 per cent. of thorium dioxide and 1 per cent. of uranium oxide (analyses I–III).
- (2) A variety poorer in thoria, with a specific gravity of 4.4. This contains about 8 per cent. of thorium dioxide and 2 to 5 per cent. of uranium oxide (analyses IV and V).
- (3) A variety containing little or no thoria, but as much as 15 per cent. of uranium oxide. Specific gravity 4.4 (analysis VI).

The following table shows the variation in composition of the specimens analysed, I–III being of material from the Bambarabotuwa district and IV–VI of material from the 'gem-gravels of southern Sabaragamuwa'. Under VII Dr. Prior's analysis of zirkelite from Brazil is quoted for comparison.

	I.	II.	III.	IV.	V.	VI.	VII (Prior).
ThO ₂	20.17	20.44	18.78	8.38	8.51	0.28	7.31
U ₃ O ₈	—	1.06	0.65	4.66	2.08	14.81	1.40 ¹
ZrO ₂	—	30.73	32.56	84.19	32.64	35.27	52.89
TiO ₂	—	29.50	30.95	36.26	36.06	34.87	14.95
Ce ₂ O ₃	1.44	2.68	1.40	0.32	0.83	—	2.52
La ₂ O ₃	2.17					—	—
Di ₂ O ₃						—	—
Y ₂ O ₃	0.96	1.08	0.40	—	—	—	0.21
Al ₂ O ₃	—	—	—	—	2.26	—	—
FeO	—	4.07	4.42	4.72	4.65	3.73	7.72
MnO	—	0.03	—	—	—	—	—
CaO	—	6.87	6.78	8.55	9.35	8.18	10.79
MgO	—	2.34	3.04	1.33	1.08	1.96	0.22
PbO	—	0.38	—	—	—	0.44	—
H ₂ O	—	0.46	1.05	1.70	1.74	1.68	1.02
Total	—	99.64	100.03	100.06	99.20	100.67	99.03
Sp. gr.	5.2	5.0-5.1	4.72	4.47	4.32	4.40	4.741

No definite formula can be deduced from these analyses.

Examination for gaseous Constituents.

Only the high thorium variety was examined. A 20-gram sample of the coarsely ground mineral was introduced into a closed tube of Jena glass, and the tube attached to a Töpler pump. After pumping out the air, the sample was heated and the gas collected. It was then re-ground, mixed with powdered acid potassium sulphate, and again heated till decomposed. By this means a further evolution of gas was obtained, and this portion contained most of the helium.

The total volume of gas after freeing it from sulphur dioxide was 134.9 c.c. at 0° C. and 760 mm. pressure, or 6.7 c.o. per gram of the mineral. An analysis showed it to have the following composition:—

	Volume.	Percentage Composition.
Carbon dioxide ...	54.17 c.c.	40.2
Hydrogen	13.74 „	10.2
Nitrogen	47.12 „	34.9
Helium	19.86 „	14.7
	<hr/>	
	134.89 „	100.0

¹ UO₂.

The gas, freed from carbon dioxide, hydrogen, and nitrogen, was examined spectroscopically by Mr. A. Fowler, F.R.S., who stated that the lines of helium were present, but that no argon could be detected. A determination of 15.1 c.c. of the gas gave a density of 3.74 at 0° C. and 760 mm. pressure.

The amount of helium in zirkelite is about one-tenth that found in thorianite, and stands roughly in proportion to the amounts of uranium oxide found in the minerals.

Crystalline Form (G. F. H. S.).

Early in May, 1906, a twin-crystal of zirkelite possessing comparatively brilliant faces was entrusted to the writer by the Director of the Imperial Institute for measurement on the three-circle goniometer in the Mineral Department of the British Museum; three well-developed crystals were afterwards discovered and were also measured on the same instrument. These crystals had been picked out from the 'gem-gravels of southern Sabaragamuwa' (p. 310), and they are identical in specific gravity and streak with the larger water-worn crystals found in the same samples of material (analyses IV-VI, p. 313). It may, therefore, be assumed with some confidence that the crystals here described, like the larger crystals actually analysed, belong to the mineral species zirkelite.

Of the four crystals, two are simple and two are twinned. The symmetry is hexagonal, and six forms in all have been observed:—

- $c(0001)$, varies in relative size; reflections distinct.
- $d(10\bar{1}2)$ } , both small and rare; reflections faint.
- $e(202\bar{3})$ }
- $r(10\bar{1}1)$, large; smoother than s and reflections sometimes distinct; plane of twinning.
- $s(2021)$, large, striated parallel to the axis of the zone [crs]; reflections blurred.
- $m(10\bar{1}0)$, large but not often found; so rough and rounded that definite reflections were rare.

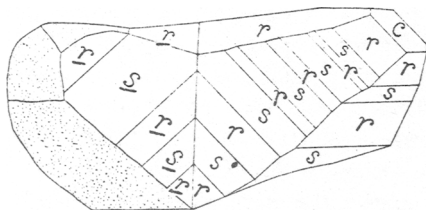
There is considerable oscillation between r and s , as represented in the accompanying text-figure.

Crystal 1 is a hexagonal plate in shape with the forms $crsm$ and about 6 mm. across. It is much worn and no measurable reflections were obtainable except from the basal planes.

Crystal 2 is roughly a hexagonal prism in shape and about 8 mm. in

length. The forms present are *crs*, the last of which is largely developed with some oscillation and gives rise to the prismatic appearance.

Crystal 3 (text-fig.) is a twin, one individual of which is better developed than the other. The whole of the observed forms are present on this crystal. The basal plane is relatively small but gives distinct reflections, and the faces of the form *r* are unusually brilliant. The figure has been drawn directly from the crystal as viewed through the microscope; the stippled parts of the figure indicate the fractured surfaces. The extreme width



Twinned crystal of Zirkelite
from Ceylon.

in the position depicted is about 7 mm. The angle between the faces *cc* of the two individuals is $71^{\circ} 6'$, corresponding to an angle between the axis of twinning and the crystallographic axis of $54^{\circ} 27'$. It will be noticed that the faces in the zone containing the pole of twinning are sensibly smaller in size.

Crystal 4 shows the forms *crsm* and is also a twin, although the angle *cc*, $112^{\circ} 30'$ gives for the angle between the twinning pole and the basal plane a value $56^{\circ} 15'$, which differs considerably from that found for *cr*. The individuals, owing to the large development of the forms *sm*, are prismatic in shape and the basal plane is also prominent. The two individuals are 5 and 4 mm. in length, and 4 and 2 mm. in section respectively.

Measurements from *c*(0001).

Hexagonal; $a : c = 1 : 1.1647$.

Forms.	Calculated Values.	Observed Means.	No.	Limits of Observations.
<i>d</i> (10 $\bar{1}2$)	$33^{\circ} 55'$	$34^{\circ} 10'$	3	$33^{\circ} 15' - 34^{\circ} 45'$
<i>e</i> (20 $\bar{2}3$)	41 53	42 25	3	41 30—43 31
<i>r</i> (10 $\bar{1}1$)	*	53 22	23	52 0—54 30
<i>s</i> (20 $\bar{2}1$)	69 36	69 16	17	68 30—69 55
<i>m</i> (10 $\bar{1}0$)	*	90 0	10	89 0—91 0

The azimuthal angles approximate to 60° , but differed in the extreme limit as much as $1\frac{1}{2}^{\circ}$ from that value. In view of the fact that the blur of light reflected from some of the faces extended over as much as 5° such discrepancy is to be expected.

The crystals are brownish-black, and their lustre is sub-metallic to resinous. Microscopic splinters are yellowish-brown in colour and optically isotropic. In these characters the crystals, though much larger, resemble closely those described by Dr. E. Hussak¹ from Brazil, to which he and Dr. G. T. Prior gave the name zirkelite. The latter are flattened octahedra in form and frequently display spinel-like twins. They were too much striated for goniometrical measurements, but were supposed from their habit and optical characters to belong to the cubic system. The present crystals, on the other hand, have undoubtedly hexagonal or lower symmetry, although minute fragments are isotropic, as seems to be generally the case with crystallized minerals containing rare earths whatever the morphological symmetry. It may be noticed that the value obtained for α above approximates to the angle (100) : (111) in the cubic system ($54^{\circ} 44'$). The Brazilian crystals, which were presented to the British Museum by Dr. Hussak, and are a part of those on which the investigation by him and Dr. Prior was carried out, display apparently cube faces, deeply striated, which have only one pair of opposite coigns truncated by brilliant triangular faces. This development suggests that their morphological symmetry is not strictly cubic, but possibly hexagonal or rhombohedral. Measurements of the angle between the latter faces and the cube faces are very untrustworthy, but approximate to 55° , which is higher than the value obtained for α above, but not so much as to preclude the possibility that the morphological symmetry is the same in both cases and the variations in the angles are merely due to isomorphous changes in the chemical composition.

The large crystals which have been analysed by Mr. G. S. Blake are so water-worn that it is difficult even to conjecture what their morphological symmetry may be.

¹ E. Hussak and G. T. Prior, *Mineralogical Magazine*, 1895, vol. xi, pp. 86-88. Preliminary observations were published by Dr. Hussak in *Tschermak's Min. Petr. Mitt.*, 1895, vol. xiv, pp. 408-410.
