Minerals from Swaziland: Niobates and titanates of the rare earths, chemically allied to Euxenite and Fergusonite; Cassiterite, Monazite, &c. The "Æschynite" from Hitterö.

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THE specimens described in this note were collected by Mr. Sydney Ryan, Managing Director of the Ryan Tin Mines, and were presented by him to the British Museum through Mr. John Ballot, who brought them to England.

They were found in the stanniferous gravels of the Embabaan district in Swaziland, S. Africa. Their probable source is the granite-gneiss which forms the base of the rock-series in that district.[1]

The species represented in Mr. Ryan's collection include euxenite- and fergusonite-like minerals, cassiterite, monazite, scheelite, corundum, magnetite and garnet.

MINERAL CHEMICALLY ALLIED TO EUXENITE.

This mineral was found in loose tabular crystals, which are very rough and worn, and not suitable for accurate measurement. One crystal, in size about 3 × 3 × 1 cm, shows the faces of two prisms, pinacoid (tabular faces) and basal plane. In habit it is very similar to the large crystals from Hitterö, described and figured by Brögger under the name of Æschynite in *Zeitschr. Kryst.* III. (1879), 481, figs. 18 and 19. Measurements with the contact-goniometer gave angles of about 118° and 54° respectively for the two prisms, and an angle of about 90° between base and pinacoid.

In physical characters it is also like the Hitterö mineral. The fracture is sub-conchoidal, with a brilliant vitreous to greasy lustre. The colour is brownish-black; that of the fine powder pale buff. In thin splinters the mineral is translucent, with a yellowish-brown colour, and is isotropic.

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[1] The geology of the district is described by Prof. T. Rupert Jones in the *Geol. Mag.* for March, 1899.

The specific gravity is 4·996, as determined by hydrostatic weighing on a crystal weighing 28 grams.

Two quantitative analyses (I. and II.) were made on 1·2291 gram and 1·2788 gram respectively. The combined result is given under III.

	I.	II.	III.		Molecular Ratios.
Nb_2O_5	36·68	58·17	36·68		·1369
TiO_2	21·89		21·89		·2664
SiO_2	2·12		2·12		·0371
ThO_2		0·61	0·61		·0024
SnO_2	0·29		0·29		·0020
Y_2O_3 Er_2O_3	18·13	17·11	17·11	(molr. weight, 246)	·0696
Ce_2O_3 La_2O_3 Di_2O_3	3·22	4·32	4·32	(molr. weight, 310)	·0140
UO_3	3·16	2·14	2·14		·0074
UO_2		0·49	0·49		·0018
FeO	5·65	5·60	5·63		·0782
CaO	4·19	4·06	4·12		·0736
MnO		0·19	0·19		·0027
MgO	0·22		0·22		·0055
H_2O	3·69		3·69		·2050
			99·50		

Method of Analysis.

In the first analysis the mineral was decomposed by fusion with acid potassium sulphate. The insoluble residue of niobic acid with part of the titanic acid, left on extracting with cold water, was again fused with the sulphate. The insoluble residue left on again extracting with cold water was treated with ammonium sulphide, and then with dilute hydrochloric acid, and afterwards washed, ignited and weighed. In the water extracts the rest of the titanic acid was precipitated by long-continued boiling. The rare earths, together with iron and uranium, were then separated from calcium, &c., by a double precipitation with ammonia. The cerium and yttrium earths were separated from iron and uranium by means of oxalic acid, the iron from uranium by means of ammonium carbonate and sulphide, and the cerium from the yttrium earths by a double precipitation with potassium sulphate. The yttrium earths obtained from the filtrate after the second precipitation with potassium sulphate were slightly coloured by cerium earths, so that the number given in this analysis for the yttria is probably too high. The titanic acid retained in the niobic acid precipitate was determined in the following way. The precipitate was brought into solution in hydrofluoric acid, and potassium fluoride added in order to test for tantalic acid. The solution was then evaporated down with a large excess of sulphuric acid, and the residue gently ignited in order to expel all the hydrofluoric acid. It was then treated with cold water in large excess, and the solution filtered from the slight insoluble residue. The titanic acid in the filtrate was then colorimetrically determined by means of hydrogen peroxide. It amounted to nearly one-half of the total percentage in the mineral.

The silica was determined in a separate portion of the powdered mineral by fusion with soda, extracting with dilute soda solution, acidifying and evaporating to dryness. The silica was estimated as the loss of weight on heating with hydrofluoric and sulphuric acids the insoluble residue thus obtained.

In the second analysis the mineral was decomposed by fuming hydrofluoric acid according to the method of Lawrence Smith (*Original Researches in Mineralogy and Chemistry*, p. 352). Most of the uranium was found in the hydrofluoric acid solution of the metallic acids.

In this analysis the cerium and yttrium earths were separated by only a *single* precipitation with potassium sulphate. The molecular weights were determined in the usual way by converting the oxides into sulphates; that for the cerium earths is only approximate since it is calculated by considering the ignited oxides as sesquioxides. An imperfect separation of the cerium from the lanthanum and didymium oxides, by precipitating with potash and saturating with chlorine, suggested that the latter oxides were present in about double the amount of the former. In stating the result of the analysis, I have preferred to give the approximate molecular weights of the yttrium and cerium earths respectively, rather than ascribe to the individual earths percentage numbers which, with our present means of separation, can have but little value.

The thoria was separated from the cerium earths by precipitation with sodium thiosulphate. After ignition and weighing, the oxide, which was perfectly colourless, was tested by dissolving in dilute sulphuric acid, evaporating the solution to dryness and gently igniting the residue to expel the excess of acid. The residue dissolved in cold water, giving a clear solution in which oxalic acid produced a precipitate insoluble in excess. On adding ammonia until neutral or even slightly alkaline, this precipitate dissolved, yielding a perfectly clear solution, in which the thoria was re-precipitated on addition of excess of concentrated hydrochloric acid. These details are given since some discrepancies appear to have crept into the literature as to the behaviour of thorium with respect to ammonium oxalate.

The numbers obtained in the analyses suggest the formula—

$$2R_2O_3.4RO.6TiO_2.4Nb_2O_5.5H_2O,$$

$$\text{or } R'''_2(TiO_3)_3.2R'''(NbO_3)_3+3R'(TiO_3).R'(NbO_3)_2+5H_2O.$$

In chemical composition the mineral is more closely related to euxenite than to æschynite.

In the habit of the crystals, however, as mentioned above, it is very similar to the "æschynite" from Hitterö described and figured by Brögger.

It seemed advisable therefore to make at least a qualitative examination of material from crystals of the Hitterö mineral in the Museum collection.

The "Æschynite" from Hitterö.

In habit the crystals of this mineral in the British Museum correspond precisely to Brögger's description. They are tabular parallel to *b*{010}, and show the two prisms *n*{130} and *m*{110}, the basal plane *c*{001}, with the dome *x*{021}, and very rarely a pyramid. Measurements made with the contact goniometer varied somewhat in different specimens, owing to the roughness of the faces, but the smaller and more perfect crystals gave values agreeing somewhat closely with those of Brögger. Thus four fairly good crystals gave $nn' = 110°$ (109°32′ of Brögger): one of these showed also the prism *m* and gave $mm' = 52°$ (51°26′ of Brögger); while another showed the dome *x* and gave $xx' = 106°$(106°44′ of Brögger). Other larger crystals, however, with more rounded faces, gave for the prism *nn′* angles varying from 102° to 117°, while for *xx′* two crystals gave an angle as low as 101°. In spite of this there was little reason to doubt that the material in the Museum collection was specifically identical with that described by Brögger.

A qualitative analysis of material from one of the crystals showed that it was similar in composition to the Swaziland mineral, and that chemically it was therefore more closely related to euxenite than to æschynite. Besides niobic and titanic acids, it contained yttrium and cerium earths (the latter in much smaller amount than the former), with iron, uranium and calcium, and little or no zirconium or thorium. The titanic acid appeared to be in larger amount than in the Swaziland mineral. This result showed that in all probability the material from Hitterö *analysed* by Jehn[1] and termed by him *euxenite*, was identical with the crystallised material *measured* by Brögger and referred by him to *æschynite*.

Prof. Brögger in his paper (*loc. cit.*) carefully states that the mineral which from his crystallographic examination he thus refers to æschynite, may possibly be no true æschynite, but another mineral isomorphous with it, and that this can only be decided by an exact chemical analysis.

The results which I had obtained were therefore communicated to Prof. Brögger, and in reply he has very kindly furnished me with the information of that since the publication of his paper, at his request the late Prof. Blomstrand analysed specimens of the "æschynite" from both Hitterö and Arendal, and that these analyses, which have not yet been published, confirm the above result, that these minerals are chemically closely related to euxenite, and not to æschynite.

Prof. Brögger considers that, as shown in his paper, crystallographically this Hitterö mineral has nothing to do with euxenite, but belongs undoubtedly to the æschynite type, and that therefore the Hitterö mineral should receive a new name.

In the present note I have preferred to describe the mineral from Swaziland as a euxenite-like mineral and not under a new name, since, owing to the imperfect state of the crystals, its specific identity with the mineral from Hitterö is not absolutely beyond doubt.

FERGUSONITE ?

The mineral, in the absence of crystals doubtfully referred to fergusonite, was in small rounded lenticular pebbles, and also in rounded fragments intimately intergrown with monazite.

The specific gravity of material of both modes of occurrence was practically the same (5·43 and 5·42). Qualitative analysis in each case showed the presence of water, much niobic acid, iron, uranium and yttrium earths, with very little titanic acid or cerium earths.

CASSITERITE.

The specimen of cassiterite was not from the stanniferous gravels, but showed the mode of occurrence of the mineral in crystals in the matrix, a coarse-grained quartz felspathic rock, probably a vein in the granite-gneiss.

The crystals consisted of long apparently rhombic prisms (up to 2 cm. long and 3-4 mm. broad), suggesting an orthorhombic rather than a

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[1] Jehn, *Inaug. Diss.* Jena, 1871. Analysis quoted by Dana, *Syst. Min.* 1892, p. 744.

tetragonal mineral, and it was only after chemical examination that they were referred to cassiterite.

Measurement of some crystal fragments, made by Mr. L. J. Spencer, showed that the apparently prismatic habit was due to the elongation of the crystals in the direction of the pyramidal edges $[111, \bar{1}11]$. The angle between these faces = 58°—59° (for cassiterite *ss′* = 58°19′). On two crystals, besides these *s* planes, terminal faces *a*{100}, *m*{110}, *e*{101} were identified.

A similar apparently orthorhombic habit in tetragonal minerals has been noted, in the case of rutile by Pirsson[1], and by Miklucho-Maclay[2]; and in the case of tapiolite by Brögger[3] and by Warren.[4] Brögger (loc. cit.) shows that corresponding to columbite and tantalite are the dimorphous tetragonal forms mossite and tapiolite, and that the skogbölite of Finland is identical with tapiolite, the apparently orthorhombic habit being due to twinning about a pyramid, and to the extension of some of the pyramidal faces into a prismatic form, as in the case of this cassiterite from Swaziland.[5]

MONAZITE.

The specimens of monazite consist of rough tabular crystals from the gravels; the predominent pair of faces being *a*{100}.

By means of the contact goniometer the following forms were identified: *a*{100}, *m*{110}, *w*{101}, *c*{001}, $v\{\bar{1}11\}$, *h*{305}.

The specific gravity of one of the larger crystals was 4·62. Qualitative analysis showed the presence of phosphoric acid, and cerium earths with some silica and thoria. The latter was separated from the cerium earths by means of sodium thio-sulphate, and the precipitate was tested in the way described above on p. 98.

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[1] *Am. J. Sci.* XLI. 1891, 249.

[2] *Neues Jahrb. f. Min.* 1885, ii. 89.

[3] *Videnskabsselskabets Skrifter*, 1 *Math.-Natur. Klasse*, 1897, No. 7, Kristiania.

[4] *Am. J. Sci.* 1898, VI. 116.

[5] Since the above description was written, I have received from Prof. Molengraaff a copy of the recently published Annual Report of The State Geologist of the South African Republic for the year 1897, in which he describes and figures, in his account of the occurrence of Tinstone in Swaziland, crystals precisely similar to those described above.