

On Strüverite from the Federated Malay States.

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General remarks.

THE mineral dealt with in this paper was sent for examination to the Imperial Institute by Mr. J. B. Scrivenor, Government Geologist to the Federated Malay States. It occurs on the river Sebantun, about half a mile above Salak North village, Kuala Kangsar district, Perak. The ground on which it was obtained was held on a tin-mining lease, but had to be abandoned owing to the presence of the unknown mineral, which rendered mining unprofitable.

Mr. Scrivenor has ascertained that the locality is occupied by a small alluvial flat, that the mineral in question forms the bulk of the concentrate obtained from the alluvium, and that cassiterite, monazite, topaz, tourmaline, zircon, and iron-pyrites also occur. The mineral was originally supplied to Mr. Scrivenor by Mr. R. L. Corbett, who stated that he had obtained it by magnetic separation with a Wetherill machine, using a current of from 70 to 75 volts and 10 to 14 amperes.

As received at the Imperial Institute, the sample consisted of coarse angular grains, four or five millimetres in diameter. They appeared to consist entirely of a lustrous, black mineral. On looking over the specimen with a lens, however, some grains of a more brownish appearance could be picked out, and these proved to be cassiterite. Occasional particles of quartz were also observed to be intimately associated with the black, lustrous grains.

A preliminary analysis of the specimen indicated that titanium, tantalum, and iron were the essential ingredients. This composition, taken in conjunction with the physical characters of the mineral, led to the conclusion that we were dealing with a specimen of strüverite, as defined by Drs. Prior and Zambonini.¹ The analytical difficulties,

¹ G. T. Prior and F. Zambonini, 'On strüverite and its relation to ilmeno-rutile,' *Mineralogical Magazine*, 1908, vol. xv, pp. 78-89.

however, made the satisfactory chemical proof of this a very tedious piece of work.

Physical characters.

In the mass, the mineral is black and has a somewhat lustrous appearance. The specific gravity, determined on an amount weighing about 13 grams, which had been freed as far as possible from fragments of cassiterite, was found to be 5.80. The streak is not quite black, but has a somewhat greenish tint. This feature suggested the probability that the mineral was not likely to be quite opaque in microscopic splinters.

An optical examination of the fine crushings in this particular case gave interesting results. As far as can be judged from the appearance of the small particles obtained by fine crushing, the mineral seems to be homogeneous. These particles are not opaque, and they show strong pleochroism. Examined with one nicol, most of the thin flakes show a change from brownish-yellow to dull bluish-green on rotating the nicol. These flakes are birefringent, and compensate with a gypsum-plate when the fast vibration-trace of the plate lies along the maximum-absorption vibration-trace of the flake. Occasionally flakes are observed which show only the brownish-yellow colour on rotating the nicol, and these act isotropically. The optical behaviour thus suggests that the mineral is uniaxial, and on this assumption the pleochroism for the thinnest flakes may be defined thus: o = brownish-yellow, e = dull bluish-green. Thicker flakes show a change from brown to black, somewhat resembling that of brown tourmaline, but in the reverse sense, the ordinary ray being less absorbed.

In describing the physical characters of strüverite from Piedmont, Zambonini states that the mineral is opaque even in the thinnest flakes. His description of the mineral powder as 'grey-black', however, may be taken as an indication that the mineral is not quite opaque. In a recently published paper by Hess and Wells,¹ Hess states that the strüverite of South Dakota is opaque; but he describes the powder as having a slightly greenish tinge, from which we may perhaps infer that a closer examination of microscopic flakes would reveal optical characters somewhat resembling those of the Perak specimen.

In this connexion it is interesting to note that the Norwegian ilmenorutile shows a pleochroism closely resembling that of strüverite.

¹ F. L. Hess and R. C. Wells, 'An occurrence of strüverite,' Amer. Journ. Sci., 1911, ser. 4, vol. xxxi, pp. 432-442.

Further, as one would expect, flakes of ilmenorutile are more transparent ; so much so, that flakes showing a good uniaxial figure, of positive sign, can be obtained without difficulty.

Numerous attempts were made to obtain a definite uniaxial figure with the Perak strüverite, but the results were inconclusive, owing to the less transparent nature of the flakes. The optical behaviour of strüverite, however, as outlined above, indicates clearly that it also is positive.¹ In view of Prior's suggestion that ilmenorutile and strüverite are solid solutions of mossite and tapiolite respectively, in rutile, it is interesting to note that these minerals are both optically positive, and that the ordinary ray in each case is less absorbed than the extraordinary. In these respects they resemble rutile.

Chemical analysis (S. J. J.).²

A preliminary analysis of the mineral showed that it is completely soluble in 5 per cent. sulphuric acid after fusion with potassium hydrogen sulphate ; and almost completely soluble in concentrated sulphuric acid after digesting for several days. Titanium, tantalum, and iron appeared to be the chief ingredients ; but tin, niobium, and silica were also present. Calcium, magnesium, aluminium, chromium, uranium, tungsten, vanadium, zirconium, cerium and its allies, and thorium were proved to be absent.

By quantitative analysis the following results were obtained :

TiO ₂	45.74 per cent.
Ta ₂ O ₅	35.96
Nb ₂ O ₅	6.90
FeO	8.27
MnO	trace
SnO ₂	2.67
SiO ₂	0.20
H ₂ O at 105° C. ...	0.08
H ₂ O above 105° C. ...	0.42

100.24

¹ As indicated by compensation with a gypsum-plate, the maximum-absorption vibration-direction is that of the slow ray ; and as indicated by the pleochroism it is also the vibration-direction of the extraordinary ray.

² My thanks are due to Mr. J. Shelton, A.I.C., Assistant in the Scientific and Technical Department of the Imperial Institute, for valuable assistance rendered in connexion with the analysis of strüverite.—S. J. J.

The analysis was made as follows :—The mineral was finely ground and dissolved by heating for several days with hot concentrated sulphuric acid, allowing to cool, and pouring into a large bulk of water. There remained only a slight amount of insoluble residue, which consisted of stannic oxide and silica. A more rapid method of solution is to fuse the mineral with potassium hydrogen sulphate and then to dissolve the melt in 5 per cent. sulphuric acid containing a few drops of perhydrol.

The insoluble residue was reduced in hydrogen, and the tin and silica separated in the usual way.

The sulphuric acid solution was diluted, nearly neutralized with dilute ammonia, and acidulated with hydrochloric acid, and the tin precipitated by passing a current of hydrogen sulphide for some time. The precipitated stannic sulphide contained a small amount of titanium, from which it was freed by treatment with ammonium sulphide and re-precipitation with acid. The matter insoluble in ammonium sulphide was fused with potassium hydrogen sulphate and added to the hydrogen sulphide filtrate.

The stannic sulphide precipitate, together with that obtained from the insoluble residue, was oxidized with nitric acid, ignited, and weighed as stannic oxide. The quantities of stannic oxide found in two determinations by this method were 2.63 and 2.71 per cent. A check determination of the tin made by fusing the mineral with potassium hydrogen sulphate, dissolving in 5 per cent. sulphuric acid, adding a few grams of tartaric acid, and passing hydrogen sulphide, gave 2.68 per cent. of stannic oxide.

The filtrates from the hydrogen sulphide precipitation were nearly neutralized, a considerable excess of sodium thiosulphate added, and the whole boiled for about twenty minutes. The precipitate, which contained all the titanium, tantalum, and niobium, together with traces of iron, was freed from the latter impurity by dissolving in fused potassium hydrogen sulphate and re-precipitation as thiosulphate. The iron was obtained from the filtrates by boiling with excess of ammonia, filtering, and re-precipitating as acetate and finally as hydroxide. The iron was weighed as ferric oxide, the gravimetric determination being checked volumetrically by titration with potassium permanganate.

Several methods were tried for the separation of tantalic and niobic oxides from the titanium dioxide. Amongst these may be mentioned the following :

(a) The fractional crystallization of the acid potassium fluorides (Marignac method). This was found to be unsatisfactory, owing to the

complicating influence of the titanium salt, which interferes with the separation of the tantalic and niobic salts.

(b) Fusion with potassium carbonate at a high temperature was also tried, but although the chief part of the tantalic and niobic oxides was soluble, varying amounts of titanium also passed into solution. The addition of potassium nitrate to the melt seemed to intensify rather than diminish this difficulty.

The following was found to be the most satisfactory method to adopt. The well-washed thiosulphate precipitate was ignited and ground with about its own weight of pure sugar-carbon, transferred to a small porcelain boat, and heated to a high temperature in a Jena-glass tube in a current of chlorine which had passed through carbon tetrachloride. The temperature of the tube, excluding the portion containing the boat, was maintained at about 70° C., and by this means the less volatile tantalum and niobium chlorides were condensed practically free from titanium. The titanium chloride passed over and was caught by a series of wash-bottles containing water; it was found impossible to condense the titanium chloride quite completely by these wash-bottles. By repeating the distillation twice on the more volatile portion, almost complete separation of the tantalum and niobium from the titanium could be effected. The first distillation separated 93 per cent. of the total tantalic and niobic oxides found. The trace of manganese present in the mineral remained in the boat. The chlorides of tantalum and niobium were removed from the tube with the aid of strong hydrochloric acid, precipitated as hydrates, washed, ignited, and weighed.

This method is essentially similar to that adopted by Wells in separating titanium from tantalum and niobium. The use of carbon tetrachloride alone, as suggested by Wells, was found to be less satisfactory than the method we adopted.

A qualitative test for niobium in the above precipitate by the Giles¹ method indicated that this element was present in small quantity. An estimation of the niobium by the Metzger-Taylor² method of reduction with zinc and titration with potassium permanganate gave 6.9 per cent. of niobic oxide. (The factor used was 1 c.c. N/10 KMnO₄ = 0.00708 gram Nb₂O₅.) The tantalum and niobium of another portion of the mixed oxides, which had been separated from the titanium as above, were separated by the Marignac method. By this means the quantity

¹ W. B. Giles, Chem. News, 1907, vol. xcv, p. 37.

² F. J. Metzger and C. E. Taylor, School of Mines Quarterly, New York, 1909, vol. xxx, p. 323.

of niobic oxide found was 7.2 per cent. This result is probably slightly in excess of the quantity actually present, owing to the temperature of the experiment being rather high.

The chlorides which had passed over into the wash-bottles (chiefly titanium chloride) were precipitated by thiosulphate, fused with potassium hydrogen sulphate, the melt dissolved in 5 per cent. sulphuric acid, and the titanium and any tantalum and niobium present estimated gravimetrically as oxide. The titanium was estimated volumetrically by the following process: An aliquot part of the sulphuric acid solution was reduced with zinc and then titrated against N/20 ferric alum solution in an atmosphere of carbon dioxide, using ammonium sulphocyanide as an indicator. The ferric alum solution had been previously standardized against pure titanium sulphate.

The results obtained by the two methods showed that the solution obtained in the wash-bottles contained a small percentage of tantalum and niobium, which varied in amount but did not exceed 2 per cent. In the analysis recorded, this difference amounted to 0.98 per cent., and this quantity was divided proportionately between the niobic and tantalic oxides already found.

A direct estimation of the titanium was made by fusing a fresh portion of the mineral in potassium hydrogen sulphate, and, after removing the stannic oxide, estimating the titanium volumetrically by the process given above. An allowance was made for the niobium already found to be present. The titanium dioxide found in this way amounted to 45.74 per cent. The ferrous iron present was estimated by digesting the finely-ground mineral with 50 per cent. sulphuric acid in a sealed tube at 200° C. for several weeks and titrating with standard potassium permanganate.

The presence of scandium in strüverite.—Professor A. Fowler, F.R.S., kindly undertook to examine the mineral spectroscopically, and found that it yielded the spectrum of scandium. This is of considerable interest, in view of the rarity of that element, and the fact that strüverite has some features in common with 'wiikite'. The latter was found by Sir William Crookes to contain more scandia (1.17 per cent.) than any other mineral, and had tantalic oxide, titanium dioxide, ferrous oxide, and silica as its chief constituents.¹ Since, however, no other mineral examined by him was found to contain as much as 0.01 per cent. of scandium,² there seemed to be little chance of finding this constituent

¹ W. Crookes, Phil. Trans. Roy. Soc. London, 1908, ser. A, vol. ccix, p. 17.

² A specimen of orthite has since been described as containing 0.8-1.0 per

in strüverite, with the comparatively small amount of material available for analysis; and the chemical examination of the mineral for this purpose led only to the indication of a possible trace.

Conclusions.

The mineral strüverite, as defined by Prior and Zambonini (*loc. cit.*), has now been found in three widely separated localities, viz. (1) at Craveggia, in northern Piedmont, Italy; (2) in the Etta mine, Black Hills, South Dakota, U.S.A.; (3) Perak, Malay Peninsula, and it is rather remarkable, in view of the probable nature of the mineral, that the composition, as seen from the analyses given below, should show such slight variations.

	Piedmont (Prior).	South Dakota (Wells).	Perak (Johnstone).
TiO ₂	41.20	47.8	45.74
Ta ₂ O ₅	46.96 ¹	34.8	35.96
Nb ₂ O ₅		6.2	6.90
FeO	11.38	7.3	8.27
MnO	trace	—	trace
CaO	0.51	—	—
MgO	0.17	—	—
SnO ₂	—	1.3	2.67
SiO ₂	—	2.0	0.20
H ₂ O	—	0.4	0.50
	<hr/> 100.22	<hr/> 99.8	<hr/> 100.24
Sp. gr.	5.59	5.25	5.30

There is apparently no reasonable alternative to the view suggested by Prior that strüverite is a homogeneous isomorphous mixture, and that it is to be regarded as consisting essentially of a solid solution of tapiolite in rutile. On this assumption we may regard the ferrous oxide of the Perak specimen as combined with the niobic and tantallic

cent. of scandia; see R. J. Meyer, 'Ueber einen scandiumreichen Orthit aus Finnland und den Vorgang seiner Verwitterung,' *Sitzungsber. Akad. Wiss. Berlin*, 1911, pp. 379-384. Still more recently, a new mineral supposed to consist essentially of scandium silicate, and to contain about 37 per cent. of scandia, has been described; see J. Schetelig, 'Ueber Thortveitit, ein neues Mineral,' *Centralblatt Min.*, 1911, pp. 721-726.

¹ This percentage was divided equally between the niobic and tantallic oxides to accord with a rough indication that these two oxides were present in approximately equal amounts. It seems highly probable, however (see below), that there was a substantial preponderance of tantallic oxide.

oxides to form tapiolite, and treat the mineral as an isomorphous mixture of rutile and tapiolite with small admixtures¹ of cassiterite, silica, and water.

If now we calculate the separate volumes of these constituents,² add these together and divide into the total mass, we get the value 5.33 for the density of the mineral, as against the value 5.30 actually found. Treating the analysis of the South Dakota specimen in the same way, we get the value of 5.17 for the calculated density of the mineral, as against the value 5.25 actually found. The approximation of the calculated to the observed values for the specific gravity may be regarded as sufficiently close, in such a mineral, to be consistent with the solid-solution view.

On the same assumption, a consideration of the analysis of the Piedmont strüverite in relation to its specific gravity leads to an important conclusion. The Piedmont specimen, as the analysis shows, was much purer than those from South Dakota and Perak. The state of combination of the lime and magnesia is uncertain, but the amount is very small. Neglecting these, and recalculating the analysis to 100 in terms of TiO_2 and $Fe(Ta, Nb)_2O_6$, we get:—

TiO_2	41.39	per cent.
$Fe(Ta, Nb)_2O_6$	58.61	„

If now we take the specific gravity of this as being approximately 5.6, and, assuming a specific gravity of 4.2 for the rutile, calculate what the specific gravity of the $Fe(Ta, Nb)_2O_6$ constituent should be, we get the value 7.3, which is approximately the specific gravity of a typical tapiolite, i.e. one containing only a few per cent. of niobic oxide. It appears, therefore, that the $Fe(Ta, Nb)_2O_6$ constituent of the Piedmont specimen must be tapiolite; and if so, it follows that this specimen is really representative of typical strüverite.

In stating the results of his analysis, Prior made it quite clear that he had not adequate quantitative data for stating the exact relative percentages of niobic and tantallic oxides present. These considerations do not seem to have been taken into account by Hess and Wells, who (loc. cit.) have rather hastily concluded that the Piedmont specimen is not a typical strüverite. The evidence detailed above proves their conclusion to be incorrect, if we accept the view, to which they subscribe, that strüverite is an isomorphous mixture.

¹ The stannic oxide in the Perak specimen as analysed is present, in part at least, as free cassiterite; and the silica as quartz granules.

² Assuming the following specific gravities: rutile 4.2, tapiolite 7.35, cassiterite 7.0, quartz 2.65, water 1.