Art. XXXVI.—*An Occurrence of Strüverite;** by Frank L. Hess and Roger C. Wells.

The mineral described in this paper belongs to the tetragonal system, crystallizes like rutile and contains titanium, tantalum, columbium, iron and tin. It is apparently a new mineral and at one time we contemplated giving it a specific name in order to differentiate it from ilmenorutile and suggest its chemical composition, but this was not done for reasons which will be noted. In accordance with modern views, the mineral may probably be regarded as a new member of an isomorphous series of minerals crystallizing like rutile and containing some or all of the metals named.

In 1908 Prior and Zambonini described a mineral from Craveggia, Northern Piedmont, which differs from ilmenorutile in possessing a little more tantalum, in relation to columbium, than had been found in any ilmenorutile up to that time.† After noting its crystallographic similarity to ilmenorutile and the possibility of considering it a solid solution of mossite and tapiolite in rutile, Prior says: "We propose to reserve the name strüverite for those members of the series rich in tantalic acid and to keep the name ilmenorutile for those, like the Norwegian specimens, in which niobic is the prevailing acid." Since the name ilmenorutile is reserved "for those minerals in which niobic is the prevailing acid," a fair inference would lead one to suppose that their mineral carried a preponderance of tantalum oxide, but as analyzed by Prior it showed Ta_2O_5 and Cb_2O_5 only "in about equal amounts,"—23·5 per cent of each,—so that the columbium oxide is in molecular excess as 88:53. It is evident that their definition of strüverite does not fit their mineral, although their mineral suggests the possibility of others having more tantalum. In other words, they named a mineral which was yet to be found.

The mineral described in this paper carries 35·7 per cent Ta_2O_5 and 6·4 per cent Cb_2O_5 and would seem to deserve a new name, but as it has been covered by the definition of strüverite we shall defer to that name in order to avoid overburdening the literature of mineralogy. At the same time we hope that the custom of proposing names for unknown extrapolated members of a mineral series will not become general.

* Published by permission of the Director of the United States Geological Survey.

† On Strüverite and its Relation to Ilmenorutile. Mineralogical Mag., xv, 78-89, 1908.

Occurrence. (F. L. H.)

The mineral is found in considerable abundance as an original constituent of the granite pegmatite dike on which the Etta claim is located, one and a half miles south of Keystone, in the Black Hills of South Dakota. While on a reconnaissance trip for the United States Geological Survey in September, 1908, I visited the claim and collected specimens.

Since the early 1880's the Etta dike has been famous as a storehouse of rare minerals. The claim which is located upon it was first worked for mica, and while being thus operated cassiterite was discovered. Out of the discovery grew the tin excitement of the Black Hills lasting through the late 80's and early 90's. Cassiterite did not prove to be in sufficient quantity to pay for mining, and latterly the dike has been worked for spodumene, which is used as an ore of lithium. The Etta dike is in some ways one of the most remarkable pegmatites known, and although it has been described in geological literature a number of times, some of its features merit attention at this time. It has a roughly oval outline, and is about 150 by 200 feet in horizontal dimensions. Some of its component minerals are gigantic. The crystals of spodumene are probably unequaled in size by any other known occurrence, single crystals reaching 42 feet in length with a cross section of approximately 3 by 6 feet. It is said that 37 tons of spodumene were mined from one crystal. Cassiterite has been found in masses weighing from 50 to 60 pounds each,* and irregular aggregates of columbite weighing 600 pounds.†

In parts of the dike are finer-grained masses predominantly composed of honey-yellow muscovite and white feldspar, both microcline and albite. The microcline shows some crystal faces from one-half inch to several inches across, and is partly flesh-colored. The albite is pure white and occurs in thin plates which reach an inch or more in breadth. The muscovite is in flakes ranging from minute scales to plates three-fourths of an inch across. Through these masses are mixed other minerals in greater or less profusion,—white beryl, small spodumene crystals, cassiterite in small particles, quartz, secondary opal, and strüverite.

Columbite occurs in considerable quantity, in most places as individual crystals ranging from small ones up to those weighing several pounds, with some larger aggregates such as those mentioned above. The crystals are tabular, in many specimens from one-third to one-half longer than wide, though some

* Blake, W. P. Tin: Min. Res. of the United States for 1883-4. Geol. Surv. Washington, 1895, p. 607.

† Personal communication, A. M. Lane, Keystone, S. D.

are nearly square, and the thickness ranges from about one-eighth to two-thirds of the length, Even in most of the very small crystals the tabular form may be distinguished.

Near a point where columbite crystals were especially thickly sprinkled through the dike and where the general texture was comparatively fine-grained, little aggregates of a black, opaque metallic mineral whose luster and color were indistinguishable from columbite but whose crystal form was less distinct, were found rather thickly impregnating the dike for several feet. It was evidently an original mineral in the dike and occurred completely imbedded in microcline, beryl, and muscovite. In the specimens examined none appeared to be entirely surrounded by quartz and none was found in spodumene. From a hasty field examination the mineral was thought to be another form of columbite, but later the surrounding gangue, which in the piece used was mostly microcline, was dissolved with hydrofluoric and sulphuric acids and it was found that the crystals showed no resemblance to the crystal habit of columbite as it occurs in the Etta dike. A slight movement in the dike had crushed most of the crystals so that good specimens for optical measurements were hard to obtain. The separated crystals had been exposed to the action of the acids for about six weeks, and while to the unaided eye they were bright and smooth, W. T. Schaller, to whom they were referred for crystallographic determination, found them to be too badly etched to give a good reflection. He therefore extracted fresh crystals from the matrix and upon these made the crystallographic determinations which are quoted in the next paragraph. The largest crystals collected are about 5^{mm} long by 1·8 to 2^{mm} across the exposed cross sections. The largest aggregate is 16^{mm} across. The powder and streak are nearly black with a slightly greenish tinge. The hardness is 6–6·5 and the specific gravity 5·25. The mineral is opaque in thin section and neither cassiterite nor rutile appears to be enclosed in it, although such a possibility was suggested by the analyses to be described.

Mr. Schaller remarks:

"The small crystals, generally from 1 to 3 millimeters in length and hardly as thick, closely resemble twinned and distorted crystals of rutile, mossite, tapiolite, etc. They are tetragonal, twinned on the *e* (101) face and elongated in the direction of the $(1\bar{1}1)$: (111) intersection edge. The crystals are very poorly adapted for measurement, the faces being rough and reflecting light poorly. The forms present are $a\{100\}$, $e\{101\}$, $s\{111\}$. The habit of the crystals resembles very closely a so-called black rutile described by Headden and

Pirsson.* Their material was probably identical in character with that here described.

In addition to the forms as illustrated by Pirsson, there is often present, on the crystals examined, a narrow face of *e* between a and *a*. The measurements on which the identifications are based follow.

	Measured.	Calculated for rutile.
e	$s = 27°51' - 28°59'$	28°26′
e	$a = 56\ 30 - 57\ 20$	57 13
s	$s' = 55\ 57 - 56\ 50$	56 52
a	$a = 66\ 10 - 66\ 30$	65 34
a	$e = 10\ 30$	8 21″

The mineral does not appear to be radioactive to any considerable degree, but after 15 days' contact of a polished specimen with the sensitive side of a photographic plate, the microcline surrounding the strüverite gave a distinct radiograph, the plate remaining unaffected under the strüverite.

Although it occurs in considerable quantity, the mineral gives little promise of having commercial value as an ore of tantalum, owing to the high titanium content.

Chemical Analysis. (R. C. W.)

The mineral was separated from the gangue almost completely by crushing and panning. The resulting black grains were dried at 100°. Under the microscope there were visible only the black opaque mineral and a few grains of silica.

Suitable tests showed that the essential constituents were titanium, tantalum, columbium, and iron. There were small amounts of tin and silica and a trace of aluminum. Phosphorus, calcium, manganese, molybdenum, rare earths, tungsten, and heavy metals were proved absent. It was concluded that zirconium was also absent because after repeated precipitations of the sulphates of the bases with hydrogen peroxide in the presence of a phosphate no residue finally remained.† With less than one per cent of sulphuric acid present in this last operation, much tantalum and titanium, and to a less extent columbium, are precipitated by the phosphate. But the separation of zirconium is based on the fact that it is almost certainly precipitated in the presence of one per cent of sulphuric acid and possibly in the presence of even more.

The density of the fragments was found by the pycnometer to be 5·25. Since the approximate density of titanium oxide is 4·0, of iron titanate 4·8, of iron columbate 5·9 and of iron tanta-

* Headden, W. P. and Pirsson, L. V. on Black Rutile from the Black Hills. This Jour., 3d ser., vol. xli, 1891, p. 249.

† W. F. Hillebrand, Bull. 305 U. S. Geol. Survey, p. 141.

late 6·9, the mineral evidently contained a heavier constituent than titanium or iron and the presence of tantalum was thus first suggested.

While the analysis of this mineral was in progress the paper by Prior and Zambonini appeared* and other suggestive papers upon the analysis of chemically similar minerals have recently been published. A method for analyzing columbite has been published by E. S. Simpson but is not intended to be used when titanium is present.† W. B. Giles has described the opening up of minerals containing columbium and tantalum.‡ Weiss and Landecker,§ Hauser and Finckh‖ have worked on the separation of these elements.

When it was desired simply to get the mineral into solution, fusion with acid sodium sulphate was employed. The melt was dissolved in 5 or 10 per cent sulphuric acid.

The colorimetric determination of TiO_2 gave 45·8 per cent as an average of several experiments and readings, the series being 47·4, 44·2, 46·4, 45·3, 46·5, 45·3, 43·6, 45·6, and 47·6. All of the precautions mentioned by Merwin¶ with regard to the influence of sodium sulphate, etc., were not considered, but about 5 per cent of sulphuric acid was present in the standard and sample compared.

Since the mineral was not attacked by boiling with dilute sulphuric and hydrofluoric acids, a determination of the state of oxidation of the iron was abandoned. Calculated as ferrous oxide, the amount present was 7·5 per cent.

By reducing the mineral in hydrogen and dissolving in hydrochloric acid 0·6 per cent SnO_2 was obtained. More, however, was obtained by fusing with bisulphate, adding to the solution sodium hydroxide in excess, filtering and adding hydrogen sulphide. This treatment gave 1·09 and 1·14 per cent SnO_2 after correcting for platinum and other impurities. The method of attack recommended by Giles** for determining tin was also tried. He states that by fusing a columbite containing tin at a high temperature with potassium carbonate and digesting in warm citric acid, the tin may be brought into solution as well as other constituents except titanium, zirconium and a little silica. From one gram after three fusions there remained only ·0475 grm. of insoluble matter consisting of ·0351 grm. Fe_2O_3 and a little TiO_2. From the soluble part, however, there was obtained only 0·7 per cent SnO_2 by hydrogen sulphide, which was less than that obtained in the previous way. In a wholly different way as much as 1·7 per cent SnO_2 was

* Loc. cit.
† Chem. News, xcix, 243, 1909.
‡ Chem. News, xcix, 1, 1909.
§ Zs. anorg. Chem. 64, 65.
‖ Ber., 1909, 2270.
¶ This Journal (4), xxviii, 119.
** Chem. News, xcix, 27, 1909.

obtained in one experiment. The mean of all was 1·3 per cent.

A few words may be said upon the results of fusing the mineral with sodium carbonate. It was attempted to make a separation of titanium and other bases from tantalum and columbium by such a fusion and extracting the tantalate and columbate with hot water. After two fusions with sodium carbonate in one experiment, the insoluble portion (*a*) was found to be 83·8 per cent, the soluble portion (*b*) 16·5 per cent. But the separation was incomplete, for, after determining in portion (*a*) 7·8 per cent Fe_2O_3, 42·3 per cent TiO_2 and traces of other constituents, there remained 33·3 per cent unaccounted for, which was probably tantalum and columbium oxides, and in portion (*b*) there was found 4·5 per cent TiO_2. In another experiment one gram was fused with sodium carbonate and very thoroughly extracted with hot water. The residue was re-treated. Three such extractions brought 18 per cent into solution, but of this a third or 6 per cent of the mineral was TiO_2. Hence the columbium and tantalum carried titanium with them into the soluble portions, and it was not possible to extract nearly all the columbium and tantalum by even repeated treatments.

With respect to this sodium carbonate treatment the experiments of Weiss and Landecker demand consideration.* They reasoned that the carrying into solution of titanium by columbium must be due to the formation of a compound of the two which they thought could be decomposed by adding a little niter during the sodium carbonate fusion. A trial of their method was made, but it was found that titanium passes into the soluble part with columbium and tantalum just as it does when no niter is used. In their description the method of freeing titanium from columbium and tantalum by hydrogen sulphide is not clear. In view of these facts the sodium carbonate attack was abandoned.†

Another method of analysis was carried out as follows:

After a bisulphate fusion, silica, tin, and iron were removed by the use of tartaric acid, ammonia, and hydrogen sulphide. The tartaric acid was destroyed by ignition, the total acid earths dissolved by bisulphate and eventually converted into the double fluorides of potassium. These were separated by the method of Marignac. The weight of crude Ta_2O_5 thus obtained was corrected for the TiO_2 present. The total TiO_2 had already been determined. Cb_2O_5 was computed by difference. Two such experiments gave the results below, in which are collected the data for the other constituents so far determined:

* Chem. News, ci, 13, 1910.

† Compare Foote and Langley, this Journal, xxx, 401, 1910.

	1	2
H_2O	0·4	0·4
SiO_2	1·8	1·8
TiO_2	45·8	45·8
SnO_2	1·3	1·3
FeO	7·5	7·5
Ta_2O_5	37·6	30·5
Cb_2O_5 (by difference)	5·6	12·7

Although these results give a fair idea of the composition, it was concluded that a separation of the chlorides by fractional distillation might be a more advantageous method of analysis. The separation of titanium from columbium and tantalum in this way was suggested by a method of separating titanium and iron occasionally employed in steel analysis,* although, of course, the quantities are not exactly comparable.

Experiments were first made on known quantities of TiO_2 and Cb_2O_5 using sugar carbon and dry chlorine to produce the chloride in a hot, hard, glass tube, and it was found that an approximate separation could be made.

A mixture of titanium, columbium and tantalum oxides. obtained from the mineral under examination, and free from other elements, was subjected to treatments with carbon in chlorine.

Taken	0·2248 g.	Found TiO_2	0·1345 g.
		$(Ta,Cb)_2O_5$	0·0789
		Total found	0·2134 g.
		Deficit	·0114 g.

Applying the ratio of Ti to (Ta,Cb) here found to 89·1 per cent of the mineral (the total acid earths) gives TiO_2 56·2, $(Ta,Cb)_2O_5$ 32·9 per cent. This is considerably more TiO_2 than found by the colorimetric method.

Owing to the difficulty of completely converting the oxides into chlorides by the use of carbon, the apparatus was somewhat modified and chloride of sulphur tried instead. It was found possible to convert nearly half of a gram of a mixture consisting of the oxides of titanium, tantalum or columbium into chlorides in two hours. A porcelain boat was used in a long, hard, glass tube. That portion of the tube used for the condensation of the less volatile chlorides was warmed uniformly by a jacket of asbestos containing electrical resistance wire. Sufficient chloride of sulphur was introduced as vapor by merely passing the chlorine through a distilling flask in which sulphur chloride was kept gently warmed. Practically

* Blair, The Chemical Analysis of Iron, 6th ed., p. 74.

no titanium chloride or sulphur chloride condensed in the hard glass tube at a temperature of 70–80°. In fact a considerable number of wash bottles were required to collect all the vapors of titanium chloride, owing to the heat generated by the reactions which occurred with the water of the wash bottles. Unfortunately, however, a little of the columbium and tantalum chlorides passed over with the titanium, a difficulty which no style of condensing chamber seemed to wholly prevent. To decrease this loss as much as possible the condensing tube was inclined slightly so as to force the gases upward. The titanium oxide, after collection, was treated a second time to recover the small fraction of tantalum and columbium which was carried over the first time. By such a repetition *it was possible to separate nearly all the tantalum and columbium from the titanium.* The sublimed columbium and tantalum chlorides are best washed out with concentrated hydrochloric acid and after nearly neutralizing with ammonia precipitated by boiling with sulphur dioxide. The oxides thus precipitated do not run through the filter. A slight residue, partly sulphate, forms in the boat, which is with difficulty converted into chloride. It is possible that the use of carbon tetrachloride vapor might be a better agent for converting the oxides of columbium, tantalum and titanium into chlorides than sulphur monochloride.*

In analyzing the mineral it was found simpler to treat it directly in chlorine than to remove the tin and iron first. In this way three portions resulted,—a slight residue in the boat, a sublimate containing most of the tantalum, columbium and iron, and a dissolved portion containing titanium and tin. The titanium portion was nearly neutralized and precipitated by boiling with sulphur dioxide, leaving tin in solution. After ignition this precipitate was treated again in chlorine to obtain the little columbium and tantalum which escaped the first time. The columbium and tantalum oxides were precipitated together by sulphur dioxide, ignited and weighed.

The tantalum and columbium oxides, finally freed from titanium, were next subjected to the method of Metzger and Taylor for determining columbium in which the columbium sulphate is reduced in a zinc reductor and titrated with $KMnO_4$.† Metzger and Taylor found that on the average 1 grm. $KMnO_4$ was equivalent to 2·232 grm. Cb_2O_5. As in a blank experiment 1 grm. $KMnO_4$ was found eqnivalent to 2·458 grm. Cb_2O_5, the average 2·34 was used in computing the Cb. The results obtained by these methods were:

* A. Demarçay, Compt. rend., civ, 111–13.

† Columbia School Mines Quart., xxx, 323–24, 1909.

Residue	4·4	4·1
TiO_2	48·0	51·2
Ta_2O_5	34·0	33·0
Cb_2O_5	2·6	4·3
FeO	---	6·8

These results were corrected slightly for the residue in the boat. This residue was shown to be 50 per cent SiO_2. The remainder was computed as 90 per cent $(Ta,Cb)_2O_5$ and 10 per cent TiO_2. With these corrections the results become:

SiO_2	2·2	2·0
TiO_2	48·2	51·4
Ta_2O_5	36·6	34·6
Cb_2O_5	2·8	4·5
FeO	---	6·8

An average of the results recorded on p. 436, with the results above gives the final average in the first column below. On microscopic evidence the SiO_2 is considered to be gangue. The second column gives the composition of the anhydrous, gangue free material. The third and fourth columns give the molecular ratios.

H_2O	0·4			
SiO_2	2·0			
TiO_2	47·8	49·1	·613	·622
SnO_2	1·3	1·3	·009	
FeO	7·3	7·5	·104	·104
Ta_2O_5	34·8	35·7	·081	·105
Cb_2O_5	6·2	6·4	·024	
	99·8	100·0		

These results are sufficient to establish the essential composition of the mineral. In view of the fact that the determination of columbium by the Metzger and Taylor method is undoubtedly better than by the first method used, it seems likely that the tantalum content should be a little higher and the columbium content a little lower than here stated, but the higher FeO content, by the first method, 7·5 per cent, probably deserves the greater weight.

The mineral designated "black rutile" by Headden,* which was probably this mineral, was stated by him to consist of TiO_2 90·79 per cent, FeO 8·01, SnO_2 1·35, MnO trace. If the tantalum and columbium oxides determined above are added to the titanium oxide, the result is: Acid earths, 91·2, FeO 7·5, SnO_2 1·3, a striking confirmation of the suspicion, raised by the density, that Headden weighed the tantalum and columbium

* This Journal [3], xli, 249, 1891.

with his titanium. Owing to the unsatisfactory state of the analytical methods applicable to these elements, it seems likely that heretofore small amounts of tantalum or columbium may often have been overlooked in titanium minerals.

The analysis yields no simple formula. Apparently one molecule of FeO is present to one molecule of $(Ta,Cb)_2O_5$, but TiO_2 lies between 6 and 7 molecules. The formula approximates roughly to $Fe(Ta,Cb)_2O_5.6TiO_2$.

Classification of the mineral. (F. L. H. and R. C. W.)

The tetragonal minerals containing titanium, tantalum, columbium and iron evidently form a series with a group at one end to which the name ilmenorutile is given and a group at the other end represented by the mineral described in this paper. Prior and Zambonini's* mineral has a nearly medial composition, but really belongs to the ilmenorutile group. Ilmenorutile, when first described by P. von Eremeyev,† was supposed to be a rutile containing "up to 10 per cent, or more of Fe_2O_3." Brögger,‡ in later analyses under improved conditions, found ilmenorutile to contain from 13·74 to 19·64 per cent of Cb_2O_5, and one specimen showed 0·43 per cent Ta_2O_5. He retains the name ilmenorutile, and it will probably stand for a columbium-iron-rich rutile. Prior§ reviewed Brögger's results and found that the Cb_2O_5 amounted to from 33·02 to 33·50 per cent Cb_2O_5, but found no more Ta_2O_5. In an independent analysis of an ilmenorutile from the Ilmen Mountains, however, he found 21·73 per cent Cb_2O_5 and 14·70 per cent Ta_2O_5 (see table p. 442).

The mineral from Craveggia, Northern Piedmont, is one which was first described by Zambonini‖ as bearing titanium, zirconium, tantalum and columbium, a mistake not unnatural owing to the difficulties of distinguishing in a chemical way between these elements.

After the first publication by Zambonini, further work was done in collaboration with Prior and the mineral was shown to carry¶ no zirconium but to have the composition (mean analysis)** indicated in column I of the table given below, with which are given for comparison an analysis of ilmenorutile (No. II) from the Ilmen Mountains,†† and the mineral from the Black Hills (No. III), the analysis of which has been described.

* Loc. cit.

† Quoted by J. Dana, System of Mineralogy, p. 238.

‡ Brögger, W. C., Die Mineralen der südnorwegischen Granitpegmatitgänge. Pt. 1, Niobate, Tantalate, Titanate and Titanniobate, p. 46.

§ Op. cit. p. 87.

‖ Zambonini, Ferruccio, Strüverite, un nouvo minerale. Rend. R. Accad. Sci. Napoli, 1907, ser. 3, vol. xiii, pp. 35-44.

¶ Op. cit. ** Op. cit. p. 84.

†† Op. cit. p. 87.

	Craveggia. I	Ilmen Mts. II	Black Hills. III
TiO_2	41·20	53·04	49·1
Cb_2O_5	23·48	21·73	6·4
Ta_2O_5	23·48	14·70	35·7
SnO_2	----	----	1·3
FeO	11·38	10·56	7·5
MnO	trace	----	---
CaO	·51	trace	---
MgO	0·17	----	---
	100·22	100·03	100·00
Sp. gr.	5·59	5·14	5·25

Summary.

The occurrence and analysis of a mineral containing titanium, tantalum, iron, columbium and tin is described. Crystallographically it belongs to the rutile group. Chemically it is essentially titanium oxide with iron tantalate and columbate, the tantalate being in excess of the columbate. Tin is an unessential minor constituent. Its formula approximates to $Fe(Ta,Cb)_2O_5.6TiO_2$. It is considered to belong to a group of minerals whose members Prior and Zambonini designated strüverite.