PAPERS READ BEFORE THE CHEMICAL SOCIETY.

VII.—*On the Composition of Natural Tantalates and Niobates.*

By C. RAMMELSBERG, Member of the Academy of Sciences of Berlin.

THE minerals containing *tantalum* and *niobium* occur only in a few localities of the globe, and there only in small quantities. They are principally found in the granitic rocks of Scandinavia, Finland, the Ural (the Ilmen mountains, near Miask), Bavaria (Bodenmais), France (Limoges), the United States (Massachusetts, Connecticut, New Hampshire), and Greenland. Besides those minerals the principal elements of which are formed by tantalum and niobium, many others may exist containing only traces of these rare elements, but it is still very difficult in such cases to detect them; we know, however, that tin-stone (Zinnstein) and wolfram belong to this class.

The history of the mineralogical and chemical investigation of the tantalum minerals, begins in 1801, when Hatchett, in a black mineral from Massachusetts, afterwards named columbite, found a new metallic oxide, "columbium oxide;" and precisely at the same time, Ekeberg, in a similar mineral from Kimit, in Finland, called tantalite, and in another from Ytterby, in Sweden, named yttrötantalite, detected a new oxide, called "tantalum oxide." Some time afterwards Wollaston asserted that columbium oxide and tantalum oxide were identical, and in consequence the name "tantallic acid" was then adopted by chemists.

The chemical properties of the combinations of tantalum were investigated by Berzelius, who used in his experiments only the Finnish and Swedish tantalites, or the acid extracted therefrom. To him we are also indebted for the method of analysing these minerals with bisulphate of potash.

The number of the tantalum minerals was increased by pyrochlore fergusonite, aeschynite, euxenite, polycrase, samarskite and others, and analyses were published by Wöhler, Hartwall, Hermann, Scheerer, N. and A. Nordenskiöld; but the most successful researches in this department of science are the work of Henry Rose.

In the year 1835, Breithaupt asserted that tantalite (columbite) is isomorphous with wolframite; likewise fergusonite with scheelite. Gustav Rose, in 1845, pointed out by special researches, that columbite has really the form and angles of wolframite; and Henry Rose was thereby induced to investigate more especially the minerals and

combinations of tantalum, and to inquire into the cause of the great differences of specific gravity observed by Wollaston, in the tantalic acid of Finnish tantalites on the one hand, and of Bavarian or American columbites on the other.

This was the beginning (in 1840) of the memorable series of researches continued by Henry Rose for twenty years till his death. The discovery of a new element, niobium, was a splendid result of this great, laborious, and, in every sense, difficult investigation, and history will for ever attribute to it an honourable place in science. And although the celebrated founder of Analytical Chemistry failed to discover the right path, nevertheless young chemists, in studying that long series of memoirs on tantalum and niobium, published in *Poggendorff's Annalen*, will be able to trace it out for themselves, and will also understand by what circumstances the guide was diverted from the right way and fell unconsciously into error.

In 1844 H. Rose declared his belief that the metallic acide of the Swedish and Finnish tantalites were one and the same, viz., the true tantalic acid described by Berzelius, but that the tantalites or columbites from Bodenmais and America contained two acids, one much resembling tantalic acid, or perhaps identical with it; the other a new acid, which he named *niobic acid*. These results were deduced from the study of the volatile chlorides formed by heating the acids of those minerals mixed with charcoal in chlorine. By this treatment the acid of the Bodenmais tantalite yielded two different chlorides, one of which was yellow, fusible, and comparatively more volatile; the other, white and infusible. On decomposing the latter with water, and treating the acid thereby separated with carbon and chlorine, both chlorides again appeared; but after several repetitions of the process the acid gave only the white chloride, niobium chloride, which was changed by water into niobic acid.

In 1846 H. Rose, after a long series of researches, became convinced that the second acid of the columbites was not identical with tantalic acid, though very similar to it. He named it *pelopic acid*, and stated that the yellow tantalum chloride was so like pelopic chloride, that a long series of experiments had been necessary to convince him that the two were not identical, pelopic acid having indeed very much the appearance of tantalic acid mixed with niobic acid. Seven years afterwards he became still further convinced of the separate identity of niobic and pelopic acid, but at the same time a very remarkable connexion between the two acids came to light.

When pure niobic acid was mixed with a very large quantity of carbon and slightly heated in chlorine, only the yellow chloride appeared, but the acid separated therefrom gave, when treated in the same manner, both chlorides, the yellow and the white. Hence it fol-

lowed that both were combinations of the same element, and as the yellow (pelopic chloride) contained a larger proportion of chlorine, pelopic acid must be a higher degree of oxidation than niobic acid. A long time elapsed, however, before Rose determined on changing the adopted designation, but in 1852 he resolved to change the name of pelopic acid into niobic acid, and that of the former niobic acid into hyponiobic acid.

The formula of tantalic acid had been taken by Berzelius as Ta_2O_3 ; Rose adopted TaO_2 , and likewise for niobic acid NbO_2 ; for hyponiobic acid Nb_2O_3 .

It is easy to conceive that two chlorides can be formed in the same process; various examples of such formation may indeed be adduced; but Rose never succeeded in changing niobic acid by reducing agents into hyponiobic acid or in oxidising the latter. The change of the one acid into the other could be effected only through the medium of the chlorides; and moreover not directly, for Rose has not shown that the yellow hyponiobic chloride is changed by chlorine into the white niobic chloride.

With regard to the natural combinations, it was thus far established that Swedish and Finnish tantalites and yttrantalite contain tantalic acid, TaO_2 , whereas the columbites from Bavaria, North America, Greenland, and the Ural contain hyponiobic acid, Nb_2O_3 .

Marignac, by a series of very important researches, had found that the fluorides of silicium, zirconium, titanium, and tin, combined with those of mono- or bi-valent elements, are isomorphous, so that the corresponding acids must be regarded as RO_2 , an essential argument for the formula SiO_2 of silicic acid.

It is generally known from former experiments of Berzelius that molybdates and tungstates cannot be changed into fluorides, even by an excess of hydrofluoric acid, only half the oxygen being replaced by fluorine. The combinations thereby generated, viz., fluoxymolybdates and fluoxytungstates, are, according to Marignac, isomorphous with the double-fluorides of the quadrivalent elements above mentioned.

Marignac treated the metallic acid of the Bodenmais columbite, *i.e.*, the hyponiobic acid of H. Rose, with hydrofluoric acid and fluoride of potassium, and found that a fluoxyniobate is formed, which may be converted into a pure fluoride of niobium and potassium by an excess of hydrofluoric acid, but is again decomposed by water. The analytical examination of these salts showed that niobic fluoride must contain 5 atoms of fluorine.

On that occasion Marignac observed an important fact. When the metallic acid of the columbites was dissolved by hydrofluoric acid and fluoride of potassium, the solution gave at first a certain quantity of a sparingly soluble salt, easily recognised as the well known fluoride of

tantalum and potassium; after its separation the oxyfluoride of niobium and potassium was deposited in crystals, easily soluble in water. Another remarkable fact was the isomorphism of the double fluorides of tantalum and of niobium; and on the other hand, that of the fluoxy-tungstate, -molybdate and -niobate of potassium.

The white hyponiobic chloride of H. Rose was recognised by Marignac and by H. Deville as an *oxychloride*; the yellow niobic chloride was found to be free from oxygen; the analyses and the vapour-density gave the formulæ, NbOCl_3 and NbCl_5 .

These new and unexpected results were also confirmed by Blomstrand, who affirmed that all tantalites and columbites contain two acids, and that niobic acid gives a yellow chloride and a white oxychloride. He adopted also as the formulæ of the acids, Ta_2O_5 and Nb_2O_5 .

It may now be seen by what circumstances H. Rose was led into error. At first he had seen quite rightly, that columbites contain two different metallic acids, niobic acid and another (pelopic acid), closely resembling tantalic acid. But he fell into error when he obtained only a yellow chloride from his niobic acid, and believed it to be identical with that produced from the crude acid of the mineral. We now know that the first, formed from the white oxychloride, was pure niobic chloride, whereas the latter was a mixture of the chlorides of tantalum and niobium. Such an error was very excusable, for the two chlorides agree closely in every character, differing only by a few degrees in their melting and boiling points. It is only by studying the fluorides that it is possible to detect the presence of tantalum and niobium. Indeed, it is a strange accident that H. Rose, the discoverer of the volatile oxychlorides of chromium, molybdenum, and tungsten, regarded a similar compound of niobium as a pure chloride—just the same error as Berzelius fell into in taking vanadium oxychloride for chloride—a mistake which remained undetected till Roscoe, in an excellent research, explained this point, and gave to vanadic acid the formula V_2O_5 , corresponding to those of tantalic and niobic acid, thereby explaining the isomorphism of vanadate, phosphate, and arseniate of lead, which I discovered some years ago.

The new facts concerning tantalum and niobium throw great light on the researches of H. Rose, for it is easy to understand that his hyponiobic acid was pure niobic acid, and therefore that all facts, depending thereon, are of full value for science. Such a critical review I have given in *Poggendorff's Annalen*, cxxxvi, 177.

The historical view here given will prove that the true composition and constitution of all minerals containing tantalum and niobium is still unknown, in spite of numerous analyses we possess thereon. It will be necessary to investigate the nature of their metallic acids, to determine whether it is pure tantalic or niobic acid, or a mixture of the two, and then

to separate them by analytical means. Marignac and Blomstrand have published only a few notices relating to the quantities of the two metallic acids in columbites, whereas I myself have undertaken a complete examination of all minerals belonging to that class, as far as their rarity permits.

But besides this point, many other difficulties are met with in such an attempt. Many of the tantalum and niobium minerals contain titanium, zirconium, thorium, and the group of elements designated as yttrium, often associated with cerium and its congeners. All analytical methods hitherto known for separating these rare substances, are incomplete; it was therefore necessary to find new ways, and that was possible only by a special study of the properties and the behaviour of those elements.

In the present paper I shall describe the results of the examination of all the tantaliferous minerals I could procure, viz., tantalite (columbite), yttrotantalite, fergusonite, pyrochlore, euxenite, polycrase, and some others, omitting the details of the analytical processes, and giving only some account of the principal operations.

I. Determination and Separation of the Metallic Acids.—Some of the minerals contain principally tantalum and niobium, associated with small quantities of tin, tungsten, and titanium, *e.g.*, tantalite, tapiolite, yttrotantalite, fergusonite, hjelmite. Another series consists of those which contain niobium (tantalum) and titanium, sometimes associated with traces of tin, tungsten, &c., *e.g.*, pyrochlore, euxenite, polycrase, &c. To a third class belongs woehlerite, which contains niobium, zirconium, and silicium.

The decomposition of these minerals is mostly effected by fusing them with bisulphate of potash. The mass is treated with water, whereby tantalic and niobic acid are left, and the electro-positive elements are dissolved. H. Rose has described very minutely the mode of proceeding, and how to separate tin and tungsten mixed with the insoluble acids, by fusing them with sulphur and carbonate of soda. The purified acids of tantalum and niobium are heated with acid fluoride of potassium (HKF_2), the mass is digested with water and a sufficient quantity of hydrofluoric acid, and the solution is brought to crystallisation. If tantalum be present, a greater or smaller quantity of acicular crystals is soon deposited, consisting of fluoride of tantalum and potassium = K_2TaF_7 .

This salt requires 130—200 parts of water for solution; it may, therefore be easily recognised even in small quantity. It is separated, and the mother-liquor evaporated a little, to separate the rest of the salt. By fractional crystallisation it is not difficult to obtain the whole quantity of tantalum in the form of this double fluoride. It might be dried and weighed, but I found it more accurate to decompose it

with sulphuric acid, and to determine the tantalic acid directly. The mother-liquor must be highly concentrated before the small prisms of the fluoxyniobate, K_2NbOFl_5 , appear. If a direct determination of niobic acid is required, the whole is evaporated with sulphuric acid, and the residue treated with water.

Much more difficult is the separation of niobium (tantalum) and titanium. After fusing with bisulphate of potash and treating with cold water for some time, a great part of the titanic acid is dissolved, but in the way proposed by H. Rose no sufficient separation can be effected. It is, therefore, better to treat the fused mass with water kept in constant ebullition, whereby titanic acid is precipitated almost completely. The acids are heated with $HKFl_2$, and the fluorides, K_2TiFl_6 and K_2NbOFl_5 , are dissolved in water. Being isomorphous, they cannot be separated by crystallisation, notwithstanding that the former requires 60 to 70 parts of water for solution. Marignac proposed to treat the liquid mixed with hydrochloric acid with zinc, excluding the air, till the colour indicates the reduction of titanic acid to titanic sesquioxide, and to determine the oxygen lost by means of a standard solution of permanganate of potash. I have operated in this manner, but I prefer another method, namely, boiling the liquid with a weighed quantity of copper, and weighing the residue after the solution has acquired a green colour. By direct experiments with weighed quantities of K_2TiFl_6 , I had previously determined the quantity of copper necessary for reduction. Both methods are indirect and of no great accuracy, but sufficient for an approximate determination.

II. *Determination of Yttrium, Erbium, Cerium, Lanthanum, and Didymium.*—These elements occur in many minerals of the class, and are occasionally associated with calcium, uranium, and iron. After being fused with bisulphate of potash and treated with water, all these substances are dissolved as sulphates. Oxalic acid precipitates all, except uranium and iron. The oxalates are strongly heated, the oxides redissolved in hydrochloric acid and precipitated by ammonia to separate them from lime, and the precipitate is dissolved in dilute sulphuric acid. We have now to separate the metals of the yttrium and the cerium group.

Mosander had first declared yttrium to be a mixture of three different elements, yttrium, erbium, terbium. The further experiments of Marc Delafontaine seemed to confirm that opinion, but in a very interesting series of researches by Bunsen and Bahr, only two different metals, yttrium and erbium could be obtained from the crude yttria of gadolinite. My own experiments agree with these results.

There is but one known method of separating the yttrium and cerium metals, for which we are indebted to Berzelius. A solution

of their sulphates, mixed and saturated with sulphate of potash, gives, after standing for some time, a crystalline precipitate of double sulphates, which contains the cerium metals and sometimes a part of the yttrium metals. By washing it with a saturated solution of sulphate of potash, the double sulphates of the yttrium metals are dissolved. I cannot here enter into a more special discussion of the precautions necessary for a satisfactory separation. The yttrium metals are precipitated by oxalic acid, heated to strong redness, and weighed. From the quantity of sulphates given by a known weight of them, the proportion of yttria (YO), and erbia (ErO) is easily calculated by the aid of a simple formula given by Bunsen. I need not describe the methods of determining cerium, lanthanum, and didymium, and of separating uranium and iron. Besides these operations, which occur most frequently in analyses of such minerals, there are a few others which are necessary in particular cases, *i.e.*, when *zirconium* or *thorium* occurs in tantalates and niobates. It is well known that these elements exhibit in their reactions the closest resemblance to titanium as well as to the cerium and yttrium metals, so that their detection and separation offer the greatest difficulties. After melting the substance with bisulphate of potash, zirconium sulphate and thorium sulphate are partly dissolved in the acid liquid, and the latter is completely precipitated by oxalic acid, together with the cerium and yttrium metals. The oxalates are changed into oxides by heating to strong redness, and when these oxides are treated with hydrochloric acid, thoracic acid (ThO_2) remains wholly insoluble. It must then be melted with bisulphate, dissolved in water, and heated with hyposulphite of soda, by which means it is precipitated and can be separated from the oxides of cerium, the usual associates of thorium.

Zirconium is often said to occur in our mineral group, but I believe, that in many cases there has been an error. Zirconic acid (ZrO_2) must be searched for in analysis, both in the insoluble part of the metallic acids and in the acid solution. The former are changed into double fluorides of potassium. As those of zirconium are difficultly soluble and form very distinct crystals, the presence of zirconium is easily detected. When the acid solution, containing cerium, yttrium, uranium, iron, &c., is precipitated by an excess of oxalic acid, zirconium oxalate re-dissolves, and may be precipitated by ammonia together with uranium and iron. After heating and reducing by a current of hydrogen, hydrochloric acid dissolves the iron, aqua regia the protoxide of uranium, leaving the zirconia, if there is any present.

I shall now give the results of my own analyses of the tantalum minerals, which enable us to calculate their composition and express their constitution by formulæ. It will, then, be understood what connection exists between their crystalline form and their chemical consti-

tution. In calculating the numbers obtained by experiment, I have adopted the following atomic weights:—

$$\text{Ta}^v = 182; \text{Nb}^v = 94.$$

$$\text{Th}^{iv} = 234; \text{Zr}^{iv} = 90; \text{Ti}^{iv} = 48.$$

$$\text{Er}'' = 112.6; \text{Y}'' = 61.7.$$

$$\text{Di}'' = 96; \text{Ce}'' = \text{La}'' = 92.$$

$$\text{U}'' = 120.$$

Sn, W, Fe, Mn, Ca, Na, &c., are known.

I. *Tantalite and Niobite (Columbite).*

All minerals designated by these names form an isomorphous group of the same composition, their principal constituents being formed by the molecules—

Tantalate of iron..... FeTa_2O_6 , and

Niobate of iron FeNb_2O_6 .

They differ only in the relative proportions of the two, tantalites being richer in the tantalate, niobites containing a predominant quantity of the niobate, so that the best crystallised variety, the niobite of Greenland, contains only some few per cent. of tantalum, and seems to be nearly pure niobate.

A. *Tantalite.*

While Berzelius and H. Rose found in Finnish and Swedish tantalites only one metallic acid, Hermann, in 1857, asserted that the Kimito tantalite contained two, namely, besides tantalic acid, which he designed as “tantalous acid” (*tantalige Säure*), another, to which he gave the name “ilmenige Ilmensäure”; this latter, however, by its properties, specific gravity (5.5), and its reactions with hydrochloric acid and zinc (brown colour), is evidently nothing but niobic acid.

To my own analyses I shall here add the few for which we are indebted to Hermann and Marignac.

I. From Härkäsaari (Tammela) in Finland: sp. gr. = 7.384; powder brownish black.

II. From Rosendal (Kimito) in Finland: sp. gr. = 7.277; powder brownish black.

III. From Kimito; analysed by Hermann.

IV. From Skogböle (Kimito): sp. gr. = 7.272; powder blackish.

V. From Skogböle (ixiolite of A. Nordenskiöld): sp. gr. = 7.232; powder brownish black.

VI. From Sweden, perhaps from Broddbo: sp. gr. = .03; determination of the metallic acids by Marignac.

VII. From Broddbo, near Fahlun: sp. gr. = 6.311.

VIII. From the same locality, but somewhat doubtful, sp. gr. 6.082.

	I.	II.	III.	
			<i>a.</i>	<i>b.</i>
Tantallic acid.....	76·34	70·53	73·07	68·30
Niobic acid.....	7·54	13·14	11·02	9·33
Stannic acid.....	0·70	0·82	0·70	6·94
Titanic acid.....	—	—	—	0·61
Tungstic acid.....	—	—	—	—
Protoxide of iron.....	13·90	14·30	12·40	9·49
Protoxide of manganese.....	1·42	1·20	1·32	5·33
	99·90	99·99	98·51	100·

	IV.	V.	VI.	VII.	VIII.
Tantallic acid	69·97	63·58	65·60	49·64	42·15
Niobic acid.....	12·26	19·24	10·88	29·27	40·21
Stannic acid	2·94	1·70	6·10	2·49	0·18
Titanic acid	trace	—	—		—
Tungstic acid.....	—	—	—	13·77 2·88	—
Protoxide of iron.....	14·83	9·19	17·42		16·00
Protoxide of manganese }		5·97		1·07	
	100·	99·58	100·	98·05	99·61

Calculating these analyses, we find that all tantalites may be included in the formula $m\text{FeTa}_2\text{O}_6 + n\text{FeNb}_2\text{O}_6$,

and in I, $m : n = 6 : 1$

II, „ $= 3 : 1$

III *a*, „ $= 4 : 1$

IV, „ $= 3 : 1$

V, „ $= 2 : 1$

VI, „ $= 4 : 1$

VII, „ $= 1 : 1$

VIII, „ $= 2 : 2$

Tantalites sometimes contain a considerable quantity of *tin*. Weber found in a Kimito tantalite more than 9 per cent. stannic acid; Berzelius in Broddbo tantalite 8 per cent.; in a Finbo tantalite, near 17 per cent., and it must be supposed that FeSnO_3 is a constituent of tantalites, because in stanniferous varieties the atomic ratio of Fe and Ta(Nb) is no longer 1 : 2.

The isomorphism of wolfram and tantalite proves also that FeWO_3 is an isomorphous constituent of tantalites (and likewise FeTa_2O_6 occurs in wolfram).

As *niobite* (columbite) we may designate those varieties which are richer in FeNb_2O_6 . For these minerals, occurring at Bodenmais, in

the United States, and in Greenland, the numbers m and n are, according to the analyses of Blomstrand and Marignac:—

$m : n = 1 : 2.$	Bodenmais.
„ 1 : 3.	Bodenmais, Haddam.
„ 1 : 4.	Bodenmais.
„ 1 : 8.	Bodenmais, Akworth;

while the beautiful crystals from Greenland are nearly pure FeNb_2O_6 .

The crystalline form of tantalites and niobites is the same, but tantalites rarely occur in determinable crystals. They belong to the rhombic system, and are isomorphous with wolframite. The isomorphism of the iron salts of $\text{Ta}(\text{Nb})$, $\text{Sn}(\text{Ti})$, and W , *i.e.*, elements of different atomicity, is connected with analogous constitution, if we suppose—

comparing these salts to nitrates (RN_2O_6), carbonates (RCO_3), and sulphates (RSO_4), derived from the mono- and bi-valent radicals NO_2 , CO , and SO_2 .

The specific gravity of tantalites increases with the quantity of tantalate. The specific gravity of the tantalite of Tammela is 7.38; that of the niobite of Greenland is 5.38; that of tantallic acid is 7.6; that of niobic acid 4.5.

II. *Tapiolite*.

A. Nordenskiöld found tetragonal crystals of a mineral from Sukkula, in Finland, which contains, according to my own analysis:—

Tantallic acid	73.91
Niobic acid	11.22
Stannic acid	0.48
Protoxide of iron	14.47
Protoxide of manganese	0.81
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	100.89

Sp. gr. = 7.496.

It has the composition of a tantalite—

and proves that these compounds are heteromorphous.

III. *Fergusonite* (Yttrotantalite, Tyrite, Bragite).

The numerous older analyses of these minerals could not give a true idea of their composition, because neither the metallic acids nor the oxides of yttrium and erbium had been separated. My own results are as follows :—

1. *Fergusonite* from Greenland. A very rare mineral, crystallised :
sp. gr. = 5.577.

2. Brown yttrotantalite from Ytterby : sp. gr., $a = 5.056$; $b = 4.751$; $c = 4.650$.

3. Yellow yttrotantalite from Ytterby : sp. gr. 4.774.

4. Grey yttrotantalite from Gamle Kararfvet : sp. gr. = 4.306.

5. Tyrite from Helle, near Arendal : sp. gr. = 4.767–4.858.

6. Bragite from the same locality : sp. gr. = 5.267.

All these substances agree in changing their colour to yellow or greenish when heated.

	1.	2.			3.
		<i>a.</i>	<i>b.</i>	<i>c.</i>	
Ta ₂ O ₅	6.30	8.73	9.53	49.85	27.04
Nb ₂ O ₅	44.45	40.16	39.93		28.14
SnO ₂	0.47	0.91	0.23	—	—
WO ₃	0.15		0.21	—	—
YO.....	24.87	38.26	26.25	38.01	24.45
ErO.....	9.81		11.79		8.26
CeO.....	2.00	—	1.79	—	—
La(Di)O....	5.63	—	—	—	—
CaO.....	0.61	3.40	3.04	3.29	4.17
UO.....	2.58	1.98	1.20	2.91	2.13
Fe(Mn)O....	0.74	3.09	0.60		0.72
H ₂ O.....	1.49	4.47	5.20	6.19	5.12
	99.10	101.00	99.77	100.25	100.03
	4.	5.		6.	
		<i>a.</i>	<i>b.</i>		
Ta ₂ O ₅	43.44	—	—	2.04	
Nb ₂ O ₅	14.41	45.82	45.60	43.36	
SnO ₂	—	0.45	0.45	0.83	
WO ₃	—	—	—	—	
YO.....	28.81	18.69	22.31	22.68	
ErO.....	1.73	11.71	13.97	13.95	
CeO.....	0.47	5.70	3.03	3.33	
La(Di)O.....	—	3.56	1.51		
CaO.....	—	2.39	2.05	1.93	
UO.....	1.56	6.21	5.38	8.16	
Fe(Mn)O.....	1.51	1.50	0.82	—	
H ₂ O.....	7.14	4.88	4.88	4.18	
	99.07	100.91	100.	100.46	

On calculating these analyses, we obtain the general result that $R'' : (Ta, Nb)$ is equal to 3 : 2 atoms. All these substances may therefore be expressed by the general formula—

They differ only in the quantities of isomorphous elements, Ta, Nb — Y, Er, Ce, U, Fe, Ca.

Fergusonite is distinguished by its crystalline form (tetragonal and hemihedral), but the same form has been found in yttrotantalite and tyrite.

Water cannot be regarded as a primitive and essential constituent, for the mineral from Greenland, which is least changed of all, contains only a small portion, and the proportion of water in the others is very variable.

IV. *Polycrase and Euxenite.*

These two Norwegian minerals were discovered by Scheerer. Polycrase occurs in rhombic crystals; euxenite is known only massive.

1. Crystallised polycrase from Hitterö: sp. gr. = 5·12.
2. Massive polycrase from Hitterö: sp. gr. = 4·972.
3. Euxenite from Alvö (Arendal): sp. gr. = 4·984 — 5·007.
4. Euxenite from Mörefjär (Arendal): sp. gr. = 4·672.
5. Euxenite from Eydland (Lindesnäs): sp. gr. = 5·058 — 5·103.

	1.	2.	3.	4.	5.
Ta ₂ O ₅	4·00	—	—	—	—
Nb ₂ O ₅	20·35	25·16	35·09	34·59	33·39
TiO ₂	26·59	29·09	21·16	23·49	20·03
YO	23·32	23·62	27·48	16·63	14·60
ErO	7·53	8·84	3·40	9·06	7·30
CeO	2·61	2·94	3·17	2·26	3·50
CaO	—	—	—	—	1·36
UO	7·70	5·62	4·78	8·55	12·12
FeO	2·72	0·45	1·38	3·49	3·25
K ₂ O	—	—	—	—	0·82
H ₂ O	4·02	3·00	2·63	3·47	2·40
	<hr/> 98·84	<hr/> 98·72	<hr/> 99·09	<hr/> 101·54	<hr/> 98·77

Both minerals contain isomorphous niobates and titanates of normal composition. They differ only in the proportion of these constituents—

Like fergusonite, &c., they give very different amounts of water:

but the water is, in my opinion, not a primitive and essential constituent of these minerals.

V. *Woehlerite*.

A yellow or reddish mineral from the zircon-syenite of Brevig, in Norway, where it was detected by Scheerer. It fuses before the blowpipe, and is decomposed by hydrochloric acid, the insoluble part being a mixture of silicic and niobic acids, while zirconic acid, lime, and soda are dissolved. Repeating the former analyses of Scheerer and Hermann, I have obtained—

Niobic acid.....	14.41
Silicic acid.....	28.43
Zirconic acid.....	19.63
Lime.....	26.18
Protoxide of iron.....	2.50
Soda.....	7.78
	<hr/>
	98.93

Hence follow the atomic ratios—

By changing 2Na into R'' , the ratio of $\text{R}'' : (\text{Nb}, \text{Si}, \text{Zr})$ is $1 : 1, 1$. I therefore propose the simple formulæ—

The crystals of woehlerite are rhombic, the primitive vertical prism being of $90^\circ 16'$, according to the observations of Des Cloizeaux.

VI. *Pyrochlore*.

Pyrochlore was found in the zircon-syenite of Fredriksvärn and Brevig, in the southern part of Norway. Then it was detected near Miask, in the Ural mountains, and more recently in the Kaiserstuhl, a small group of doleritic mountains between the Rhine and Freiburg, in Baden. It is mostly crystallised; the crystals are regular octahedrons.

The history of the chemical investigation of pyrochlore is very remarkable, on account of the great differences in the analyses, not only of different investigators, but also of the same chemists who have endeavoured to determine the elements of this interesting mineral.

Woehler at first declared the pyrochlore from Fredriksvärn to be a titanate of calcium, cerium, uranium, and iron, but seven years after he found a considerable amount of tantalic acid. On examining the pyrochlore of Miask, Woehler obtained the same elements, moreover sodium, fluorine, and thorium, but no uranium, while the pyrochlore of Brevig, much resembling that of Fredriksvärn, gave also thorium, but could not be completely investigated.

The pyrochlore of Miask was analysed by Hermann in the years 1844, 1850, and 1869, but the three analyses published by him differ considerably. They gave, *i.e.*—

	1.	2.	3.
Thoric acid	0	0	8·88 per cent.
Zirconic acid	5·57	0	0 „
Oxides of Ce, La	5·32	15·23	6·20 „

It is evident that these analyses left many doubts on the true composition of pyrochlore. I therefore endeavoured in my own analyses to separate the constituents by the best methods, and to verify the results by investigating the single substances.

The metallic acids of pyrochlore are niobic, titanio, and thoric acid. I never found zirconic acid. Thorium occurs solely in the pyrochlore of Miask and Brevig; titanium in all varieties except the pyrochlore of Kaiserstuhl.

1. Pyrochlore from Miask: sp. gr. 4·35 — 4·37. Mean of four analyses.

2. Pyrochlore from Brevig: sp. gr. = 4·22.

3. Pyrochlore from Fredriksvärn: sp. gr. = 4·228.

4. Pyrochlore from Kaiserstuhl: sp. gr. = 4·563; analysed by Prof. Knop of Carlsruhe, and communicated to the author.

	1.	2.	3.	4.
Nb ₂ O ₅	53·19	58·27	47·13	58·62
TiO ₂	10·47	5·38	13·52	—
ThO ₂	7·56	4·96	—	—
CeO*	7·00	5·50	7·30	9·56†
CaO	14·21	10·93	15·94	15·15
MgO	0·22	—	0·19	—
FeO	1·84	5·53	10·03	2·09
UO	—			
Na	3·71	3·94	3·12	8·60‡
Fl	(3·06)§	3·75	2·90	(5·98)
H ₂ O	—	1·53	1·39	—
	101·26	99·79	101·52	100·

* Including La, Di. † I found in that variety 62·46 Nb₂O₅ 6·69, CeO 3·00 (La, Di)O.

‡ 5·28 Na, and 3·32 K.

§ Woehler found 3·43 per cent.

If R'' designs Ce, Ca, U, Fe, the following formulæ may be deduced from the analyses:—

Miask. Brevig. (1. 2.)	Fredriksvärn. (3.)	Kaiserstuhl. (4.)
$\left\{ \begin{array}{l} m \text{ RNb}_2\text{O}_6 \\ n \text{ R(Ti,Th)}\text{O}_3 \\ o \text{ NaFl} \end{array} \right\}$	$\left\{ \begin{array}{l} \text{R}_2\text{Nb}_2\text{O}_7 \\ \text{RTiO}_3 \\ \text{NaFl} \end{array} \right\}$	$\left\{ \begin{array}{l} 3\text{R}_2\text{Nb}_2\text{O}_7 \\ 5(\text{Na,K})\text{Fl} \end{array} \right\}$
1. $m = 5$ $n = 4$ $o = 4$.		
2. $m = 5$ $n = 2$ $o = 4$.		

While the molecules RNb_2O_6 and $\text{RR}^{\text{iv}}\text{O}_3$ must be considered as isomorphous, according to the experiments on the foregoing niobates, we find in the two varieties 3 and 4, a basic niobate. Now it is shown by Marignac, that the double fluorides $\text{R}''\text{R}^{\text{iv}}\text{Fl}_6$ are isomorphous with $\text{R}''\text{WO}_2\text{Fl}_4$ and $\text{R}''\text{NbOF}_5$; it may therefore be supposed that the corresponding oxyalts $\text{R}''\text{R}^{\text{iv}}\text{O}_3$ and $\text{R}''\text{Nb}_2\text{O}_7$ may also be capable of assuming the same form.

There are still two minerals, containing tantalum or niobium, which I have not myself had the opportunity of analysing, namely, samarskite and aeschynite. Aeschynite has, however, been the object of researches by Marignac, who has pointed out that it is a mixture of niobates, titanates, and thorates of Ce, La, Ca, and Fe, leading to the formulæ—

On comparing the composition of the natural tantalates and niobates as far as possible with their crystalline forms, it will soon be understood that there are several interesting series of isomorphous and heteromorphous bodies.

A. Isomorphous Groups of the Rhombic System.

	Ratio of the axes.	
	<i>a.</i>	<i>c.</i>
Tantalite, Niobite	0·82	: 0·82
Wolfram	0·83	: 0·87
Tantalie acid.....	0·83	: 0·82
Wolframic acid	0·83	: 0·87
Titanic acid (Brookite)	0·84	: 0·94
Polycrase (Euxenite)	0·94	: 0·91
Aeschynite	0·49	: 0·67
Woehlerite	0·99	: 0·75
Broncite (MgSiO_3)	1·03	: 1·18

B. Isomorphous Groups of the Quadratic System.

	<i>e.</i>
Tapiolite	0.64
Titanic acid (Rutile)	0.64
Zircon ((Zr,Si)O ₂)	0.64
Tin ore (SnO ₂).....	0.67
Zirconic acid	1.00
Thoric acid	0.16
Xenotime (Y ₃ P ₂ O ₈).....	0.62
Fergusonite	1.50
Scheelite (CaWO ₄)	1.53
Scheelbleierz (PbWO ₄)	1.57
Gelbbleierz (PbMoO ₄).....	1.58

We must therefore assume—

1. The molecules RTa₂O₆, RWO₄, RTiO₃ are isomorphous with the anhydrides Ta₂O₅, WO₃, TiO₂.

2. All these molecules are dimorphous. The regular form of pyrochlore is certainly also connected with the forms of its component minerals. We know that KFl and NaFl, like CaTiO₃ (perowskite) are regular, and that the same crystalline form is to be found in BaN₂O₆, SrN₂O₆, PbN₂O₆, which are analogous to RNb₂O₆.

The tantalates and niobates hitherto found in minerals are RNb₂O₆, R₂Nb₂O₇, R₃Nb₂O₈, corresponding to the phosphates and arsenates.