

## CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

### No. 6. On the chemical composition of blomstrandine and euxenite.

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**Abstract:** Complete analyses of two samples of blomstrandine and two samples of euxenite were carried out by chemical methods and by emission and fluorescent x-ray spectroscopy. Pure mineral samples were prepared by repeated treatment with heavy liquids and by magnetic separation. The major constituents were determined by chemical methods; niobium, tantalum, and titanium being separated and determined by precipitation with the organic reagent N-benzoyl-N-phenylhydroxylamine. Minor and trace elements were determined by emission spectroscopy and rare earths by fluorescent x-ray spectroscopy.

#### **Introduction.**

The analysis of minerals and ores containing niobium, tantalum, and titanium is regarded as one of the more difficult types of analysis. The analytical separation of these elements is particularly difficult, and earlier separation methods have in many cases proved to be inadequate.

In a previous paper (1), the authors described a procedure for separation and gravimetric determination of niobium, tantalum, and titanium by precipitation with N-benzoyl-N-phenylhydroxylamine. Procedure was applied, and satisfactory results were obtained in the

analysis of solutions containing known amounts of niobium, tantalum, and titanium.

It was also found of interest to test the applicability of the reagent and the procedure in the analysis of complex niobium-, tantalum- and titanium-bearing substances, and for this purpose the minerals blomstrandine and euxenite were selected. These minerals, classified as titanoniobates, contain as essential constituents niobium, titanium, and tantalum, as well as rare (usually yttria) earths. In addition a series of minor and trace constituents are present.

New data on the chemical composition of blomstrandine and euxenite obtained by improved analytical methods were believed to be of interest also to the mineralogists, and it was therefore decided to carry out complete analysis of representative samples of the minerals.

### **Selection and origin of samples.**

From the collection at the Mineralogical Museum, University of Oslo the following samples were selected for analysis:

Blomstrandine from Kåbuland, Iveland; blomstrandine from Rasvåg, Hitterøy; euxenite from Kalstadgangen, Kragerø; euxenite from Eitland, Farsund.

### **Mineral separation.**

The samples contained blomstrandine and euxenite intimately mixed with other minerals, and extensive separations were necessary to obtain uncontaminated materials.

Each sample was initially divided into two portions, of which one was taken for analysis, while the other was reserved for microscopical examination and reference.

The samples selected for chemical analysis were broken into small pieces and crushed in a steel mortar to pass a 90 mesh sieve. The finest fraction (including dust) was removed by suspension in water. A hand magnet was applied to remove fragments of the mortar and the main part of strongly magnetic minerals. Blomstrandine and euxenite were then separated from the other minerals by repeated treatment with heavy liquids (tetrabrommethane; density 3.0 and thallium malonate-thallium formate; density 4.0) and by use of Franz isodynamic, mag-

netic separator. The separations were followed by x-ray and microscopical examination, and in the final products the only mineral contaminations detected by these methods were: Xenotime in the sample of blomstrandine from Kåbuland, and xenotime and anatase in the sample of blomstrandine from Rasvåg. The amounts of these minerals are negligible as seen for example by the determination of phosphorus, see Table 1.

### Qualitative analysis.

The 4 mineral samples were analysed by emission and fluorescent x-ray spectroscopy, and the following elements were detected: Nb, Ta, Ti, U, Th, Y, Yb, Er, Dy, Gd, Lu, Tm, Pb, Sn, Fe, Al, Mg, Ca, Ba, Sr, Cr, Mn, Si, Zr, Sc, traces of Co, Cu, Ni, K and Na. Nonmetallic constituents present were phosphorus and water.

The following elements were sought for, but could *not* be detected by the methods employed:

La, Ce, Pr, Nd, Sm, Eu, Tb, Ho, Sb, Be, Bi, Ge, Au, Hf, W, In, Mo, platinum metals, Ag, Tl and V.

Small amounts of La, Ce and Eu were later detected in all rare earth fractions by emission spectroscopy, see Table 1.

### Quantitative analysis.

The complete analysis of the minerals were accomplished by chemical methods and by emission and fluorescent x-ray spectroscopy. The main constituents were determined chemically, trace elements by emission spectroscopy, and the rare earths by fluorescent x-ray spectroscopy.

In Table 1 the results are given for the four minerals analyzed.

The purity of some of the weighed oxides of niobium, tantalum and titanium was controlled by emission spectroscopy. The weighed oxides of niobium contained about 1 % of tantalum pentoxide, while their content of titanium dioxide varied from 0.1 % up to about 1%. The oxides of tantalum contained some per cent of niobium pentoxide and from about 0.1 % up to about 1 % of titanium dioxide. Finally, the oxides of titanium contained about 0.01 % of the pentoxide of niobium and about 0.01 % of the pentoxide of tantalum.

Table 1. Analytical Data (in per cent) of Blomstrandine and Euxenite.

Constituent	Method of determination	Blomstrandine		Euxenite	
		Kåbuland	Rasvåg	Eitland	Kalstad-gangen
Nb <sub>2</sub> O <sub>5</sub> .....	Chem.	17.72	14.26	23.19	23.49
Ta <sub>2</sub> O <sub>5</sub> .....	»	4.29	2.59	0.49	2.55
TiO <sub>2</sub> .....	»	31.71	35.20	25.45	25.64
SiO <sub>2</sub> .....	»	0.28	0.24	0.51	0.47
ZrO <sub>2</sub> .....	Em. spectr.	< 0.01 <sup>2</sup>	< 0.01 <sup>2</sup>	< 0.01 <sup>2</sup>	< 0.01 <sup>2</sup>
SnO <sub>2</sub> .....	Chem.	0.05 <sup>3</sup>	0.07 <sup>3</sup>	0.20 <sup>3</sup>	0.12 <sup>3</sup>
UO <sub>2</sub> .....	»	4.32	1.27	7.80	7.95
UO <sub>3</sub> .....	»	0.08	2.40	4.32	nil
ThO <sub>2</sub> .....	»	5.80	5.78	2.85	2.40
Σ rare earths <sup>1</sup> .....	»	24.90	27.71	22.70	25.77
Sc <sub>2</sub> O <sub>3</sub> .....	Em. spectr.	< 0.005	< 0.005	0.06	0.03
PbO .....	Chem.	0.05	0.03	0.36	0.12
Al <sub>2</sub> O <sub>3</sub> .....	Em. spectr.	0.60	0.60	0.07	0.07
FeO .....	Chem.	0.34	0.53	0.83	0.40
Fe <sub>2</sub> O <sub>3</sub> .....	»	3.33	3.96	3.89	4.66
MnO .....	»	0.20	0.21	0.46	0.18
MgO .....	Em. spectr.	0.06	0.10	0.05	0.08
CaO .....	»	1.7	1.0	2.4	2.8
BaO .....	»	< 0.001 <sup>4</sup>	< 0.001 <sup>4</sup>	< 0.001 <sup>4</sup>	< 0.001 <sup>4</sup>
SrO .....	»	< 0.001	< 0.001	< 0.001	< 0.001
Cr <sub>2</sub> O <sub>3</sub> .....	»	< 0.001	< 0.001	< 0.001	< 0.001
CoO .....	»	< 0.001	< 0.001	< 0.001	< 0.001
NiO .....	»	< 0.001	< 0.001	< 0.001	< 0.001
CuO .....	»	< 0.001	< 0.001	< 0.001	< 0.001
K <sub>2</sub> O .....	»	Not detected	Not detected	Not detected	Not detected
Na <sub>2</sub> O .....	»	< 0.1 <sup>2</sup>	< 0.1 <sup>9</sup>	< 0.1 <sup>2</sup>	< 0.1 <sup>2</sup>
P <sub>2</sub> O <sub>5</sub> .....	Chem.	0.11	0.04	n. d. <sup>5</sup>	n. d. <sup>5</sup>
H <sub>2</sub> O+110° C .....	»	3.99	3.53	3.63	3.26
Total .....		99.53	99.52	99.26	99.99
Density .....	Pycnometr.	4.838	4.786	4.826	4.797

<sup>2</sup> Not included in total.

<sup>3</sup> The stannic oxide is contaminated with barium.

<sup>4</sup> The actual content of barium is probably higher.

<sup>5</sup> n. d. = not determined. (The microscopical examination of these samples showed that Xenotime was absent.)

Table 1, (Cont.)

Constituent	Method of determination	Blomstrandine		Euxenite	
		Kåbuland	Rasvåg	Eitland	Kalstadgangen
<sup>1</sup> Separate rare earths:	Fluorescent X-ray spectr.	(The content of the separate rare earths are given in per cent of the rare earth fractions)			
Pr <sub>2</sub> O <sub>3</sub> .....	»	not detected	0.30	not detected	not detected
Nd <sub>2</sub> O <sub>3</sub> .....	»	3.80	3.65	3.00	2.30
Sm <sub>2</sub> O <sub>3</sub> .....	»	5.40	3.65	2.45	3.80
Gd <sub>2</sub> O <sub>3</sub> .....	»	6.80	4.60	3.90	5.80
Tb <sub>2</sub> O <sub>3</sub> .....	»	1.50	1.25	1.05	1.60
Dy <sub>2</sub> O <sub>3</sub> .....	»	8.65	9.10	8.00	10.80
Ho <sub>2</sub> O <sub>3</sub> .....	»	1.65	1.90	2.10	2.25
Er <sub>2</sub> O <sub>3</sub> .....	»	6.20	7.60	9.30	8.25
Tm <sub>2</sub> O <sub>3</sub> .....	»	not detected <sup>6</sup>	not detected <sup>6</sup>	not detected <sup>6</sup>	not detected <sup>6</sup>
Yb <sub>2</sub> O <sub>3</sub> .....	»	9.30	12.00	15.00	14.50
Lu <sub>2</sub> O <sub>3</sub> .....	»	0.95	1.30	1.90	1.40
Y <sub>2</sub> O <sub>3</sub> .....	»	51.00	55.75	52.00	51.00
La <sub>2</sub> O <sub>3</sub> .....	»	< 1.0	< 1.0	< 1.0	< 1.0
Ce <sub>2</sub> O <sub>3</sub> .....	»	< 1.0	< 1.0	< 1.0	< 1.0
Eu <sub>2</sub> O <sub>3</sub> .....	Em. spectr.	≅ 0.1	≅ 0.1	≅ 0.1	≅ 0.1

<sup>6</sup> Thulium was detected by emission spectroscopy.

### Analytical methods.

The methods applied in the chemical analyses will be outlined shortly.

The mineral samples were pulverized in an agate mortar, dried at 105°–110° C and stored in a desiccator. About 0.5 g were weighed out and fused with potassium pyrosulphate. The melt was dissolved in a mixture of sulphuric and tartaric acid (30–40 ml of 25 % tartaric acid solution containing 2 ml of concentrated sulphuric acid). Without filtering the solution, hydrogen sulphide was introduced. The precipitated sulphides together with hydrated silica and small amounts of titanium and earth acids were collected on a medium-textured filter paper, (the filtrate being reserved for later determinations), and the precipitate was dried, charred and ignited at about 600° C. The residue

was decomposed by fusion with a small amount of potassium pyrosulphate and the melt was dissolved as described above. The undissolved material was filtered, ignited at low temperature in a previously weighed platinum crucible and weighed as the sum of lead sulphate and the dioxides of tin and silicon. The filtrate was added to the main filtrate. Silica was determined in the usual way by evaporation with hydrofluoric and sulphuric acid. Lead was then dissolved by treating the residue with ammonium acetate solution. Hydrous stannic oxide was filtered off and determined gravimetrically as stannic oxide. Lead was finally precipitated and weighed as lead chromate. To the combined filtrates were added 2.5 g of ethylenediamine tetra-acetic acid, disodium salt, and sulphuric acid until the solution was about 0.2 N with regard to this acid. Niobium, tantalum and titanium were then precipitated (The addition of macerated filter paper before precipitation is recommended.) with a 10 % solution in ethanol of N-benzoyl-N-phenylhydroxylamine, the reagent being added in an amount 8–10 times the amount of metals present. The beaker with the precipitate was left on the boiling water bath for 45–60 min. The precipitate was collected on a loose-textured filter paper and ignited at about 600° C. The oxides were decomposed again with potassium pyrosulphate, the melt was dissolved as before in a mixture of sulphuric and tartaric acid, and niobium, tantalum and titanium were reprecipitated with N-benzoyl-N-phenylhydroxylamine under the conditions given above. The precipitate was treated as described above and finally ignited at about 900° C.

Niobium, tantalum and titanium were then separated and determined with N-benzoyl-N-phenylhydroxylamine according to the detailed procedure given by the authors in a previous publication<sup>1</sup>. The filtrate after the final precipitation of titanium may contain small amounts of coprecipitated constituents, and should therefore be reserved for the determination of the remaining elements.

The combined filtrates after the precipitation of niobium, tantalum and titanium were evaporated on the hot plate, and organic matter was destructed with fuming nitric acid. The further determinations were carried out according to the conventional procedures given in the textbooks by SCHÖELLER and POWELL(2) and by HILLEBRAND, LUNDELL, BRIGHT and HOFFMANN(3). A double group precipitation with ammonia solution separated iron, aluminium, thorium, uranium,

rare earths etc. from alkaline metals, earth alkaline metals and manganese which were determined separately. The hydroxides were dissolved in hydrochloric acid. Thorium and rare earths were precipitated together with oxalic acid, and thorium was separated from the rare earths by a double precipitation with hexamethylenetetramine. The filtrate after the precipitation with oxalic acid was treated with fuming nitric acid to destruct organic matter. Iron was precipitated with cupferron and determined gravimetrically as ferric oxide. Uranium (VI) was reduced to uranium (IV), precipitated with cupferron and finally weighed as  $U_3O_8$ . The following constituents were determined separately by conventional methods: quadrivalent uranium, manganese, phosphorus, ferrous iron and water ( $H_2O^+$ ). The density of the minerals was determined pycnometrically.

*Advantages of decomposition by HF.* In the present investigation the minerals were decomposed by fusion with potassium pyrosulphate. By this procedure and by the subsequent additions of sulphuric acid considerable amounts of sulphates were introduced, and the precipitates of niobium, tantalum and titanium were contaminated with sulphates which were difficult to remove completely by washing.

In order to avoid the high concentrations of sulphate, hydrofluoric acid was tried as decomposing agent for the mineral samples and also for the oxides of the earth acids and titanium. This method of attack was found to offer advantages. The coprecipitation of sulphates was considerably lowered, and in addition a quantitative separation of insoluble rare earth and alkaline earth fluorides from the soluble fluorides of earth acids and titanium was obtained. At the same time quadrivalent uranium was separated from sexivalent uranium. It was also possible to replace the initial double precipitation of niobium, tantalum and titanium (in the presence of ethylenediamine tetra-acetic acid, disodium salt and tartaric acid) by a single precipitation.

The analytical data obtained with the two decomposition methods compared favourably, but the method of attack by hydrofluoric acid seems to offer advantages in the analysis of minerals soluble in this acid. The application of hydrofluoric acid as decomposing agent necessitates a separate determination of silica. Silica, tin and lead are conveniently determined by a separate decomposition with potassium pyrosulphate.

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