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Columbium in Khibinsk and Lovozersk Minerals (Titanium
and Zirconium Silicates)

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COLUMBIUM IN KhibINSK AND LOVOZERSK MINERALS (TITANIUM AND ZIRCONIUM
SILICATES)

Columbium and tantalum -- elements of the fifth periodic group -- were discovered in the first years of the 19th century but their valuable properties (high melting point, capacity to form superhard alloys, ductility, and acid resistance) were appraised only recently.

Until recently, the sources of columbium and tantalum production were columbite and tantalite (isomorphous mixtures of metacolumbates and metatantalates of iron and manganese), the deposits of which are of commercial importance in Australia and the United States. Both columbite and tantalite occur on the territory of the Soviet Union in the Transbaykal, Ural, and Central Asia. In 1934, the expedition of O. A. Vorob'yeva discovered foyaites and lujaurites which were permeated with crystallites of loparite -- a rare earth titanium columbate. Along with loparite, columbium was also discovered in fersmanite -- a mineral of the titanium silicate type which is widely distributed on the Kola Peninsula. This brought up the problem of verifying the columbium content in all titanium silicates. The technology of the extraction of columbium and tantalum from loparite ore and also their analytical determination are still in the development stage. The successful completion of these is faced with many difficulties; the fundamental difficulty is that loparite can be decomposed only with hydrofluoric acid or by fusion with $K_2S_2O_7$. This circumstance prompted the suggestion to seek other minerals which could serve as the ore for the production of columbium and tantalum.

The possibility of discovering columbium and tantalum in minerals of the Khibinsk and Lovozersk tundras was dealt with by

A. Ye. Fersman in the paper "Rare elements of alkaline massifs" [1]; he proposed that geochemical laboratories include in their investigations the distribution of columbium and tantalum.

This work was included in the 1935 work project of the geochemical laboratory of the Kola Base imeni S. M. Kirov.

Of the nineteen minerals containing titanium and zirconium, which I examined, only four did not contain columbium and tantalum. Up to then, "earth acids" were not determined in analyses and were erroneously reported as titanium oxide. This error is easily explained by the chemical similarity among columbium, tantalum, and titanium. The determination of the earth acids is quite difficult because of the capacity of each of the three elements to interfere with and obscure the reactions of each other [2]. Thus for example, one could expect, on the basis of the characteristics of the individual elements, that treatment of the persulfate melt of columbium and tantalum pentoxides and titanium oxide with cold water would leach out all the titanium, leaving columbium and tantalum in the residue; however, some titanium always remains in the residue with the columbium and tantalum, while some columbium and tantalum go into solution, depending on the presence of a larger or smaller amount of titanium. The presence of zirconium increases the solvent effect of titanium on the earth acids [3]. In extracting a pyrosulfate melt of titanium, zirconium, columbium, and tantalum with an acid solution of tannin, the columbium and tantalum should, because of their properties, coagulate, while the sulfates of titanium and zirconium should go into solution. But in practice, we get a precipitate of columbium and tantalum adulterated with titanium and zirconium and a solution containing columbium and tantalum in addition to titanium. This

loss of individuality in the presence of titanium and zirconium and also the extreme ease with which the salts of columbium and tantalum hydrolyze make the detection of earth acids in the minerals very difficult and critical.

The works by Schoeller and Powell (The Analyst 1920-1935) formed the basis for the development of a method of analysis of minerals containing earth acids. The determination of Cb and Ta was carried out by two methods: (1) boiling tartaric acid complexes with nitric or hydrochloric acid (tartaric acid hydrolysis) and (2) combination pyrosulfate tannin method + hydrolysis of the tartaric acid solution. These two methods cannot be called the quantitative separation of all the columbium and tantalum from the titanium; it is more correct to call these fractional separation. The final value of $\sum (Cb, Ta) 2O_5$ is obtained after 3-4 treatments. The second method is preferred; tartaric acid hydrolysis is considered suitable for small quantities of titanium and large amounts of columbium. If the amount of titanium is 15-20 times greater than that of columbium, the metacolumbic acid may not precipitate during the hydrolysis. Thus, in determining columbium in ramsayite, no precipitate was formed when the tartaric acid complexes were boiled with HNO_3 and it was erroneously assumed that the ramsayite did not contain columbium, but when the same material was analyzed by the pyrosulfate tannin method, a rather definite value (1.63 percent) of $\sum (Cb, Ta) 2O_5$ was obtained. The pyrosulfate tannin method is based on the capacity of tannin to exert a solvent action on the titanium sulfates and to precipitate columbium and tantalum during the extraction of the

bisulfate melt with 1 percent tannin solution and 5 percent sulfuric acid. This reaction was utilized by Schoeller in qualitative analysis but it also forms the basis for the development of the quantitative separation of the earth acids [3].

A second treatment of the filtrate with tannin makes it possible to separate practically all the earth acids, avoiding the more extended and laborious and less accurate methods such as the oxalate-salicylic [4] or the hydrolysis of the tartaric acid complexes. The minerals were decomposed with hydrofluoric acid. A greater portion of the minerals (mosandrite group) belongs to the rare earth calcium titanosilicates and, by decomposing a sample with hydrofluoric acid, it is possible to separate rapidly and almost completely the insoluble fluorides of the rare earth and alkali earth metals from the soluble fluorides of the earth acids -- titanium, iron, aluminum, and alkali. The filtrate was evaporated with sulfuric acid to white fumes, which indicated the complete removal of hydrofluoric acid. The liquid mixture was cooled and dissolved in tartaric acid. Then, after the iron was removed with ammonium sulfide, the titanium, zirconium, columbium, and tantalum remaining in the filtrate were precipitated with cupferron. Then the precipitate was ignited (carefully), fused with $K_2S_2O_7$, and the cold melt treated with a 1 percent solution of tannin and 5 percent sulfuric acid. (In analyzing pink-colored sphene, eudialyte, and catapleiite, the sulfuric acid was replaced with hydrochloric acid, as suggested in the paper by V. S. Bykova in this collection.) The separating mixture had a dark-red color, indicating a large amount of entrapped titanium; it was boiled and allowed to settle on a water bath for 2-3 hours. The precipitate was filtered the next

day and washed with a two-fold diluted reagent. The precipitate was ignited and, after fusing with $K_2S_2O_7$, it was purified of the adulterating titanium oxide by hydrolyzing the tartaric acid complexes with nitric or hydrochloric acid. The filtrates were combined and treated with cupferron or tannin to extract the remaining fraction of the earth acids. The value of $\sum (Cb, Ta) 2O_5$, after the second and third precipitation, was close to the original value of the earth acids. (At present, a more rapid and accurate method of determining columbium in compositions similar to loparite ore has been developed. It is probably applicable to titanium-columbium minerals (see paper by V. S. Bykova in this collection of papers)). In some minerals, the columbium and tantalum were separated by the Schoeller and Powell method.

This method is based on the difference between the hydrolytic dissociation of oxalo-tantallic acid and oxalo-columbic acid in the presence of tannin in a weakly acid solution.

The mixture of Cb and Ta pentoxides was fused with $K_2S_2O_7$, the melt was dissolved in a saturated solution of $(NH_4)_2C_2O_4$, the solution was brought to a boil, a 2 percent solution of tannin was added, and the boiling solution was neutralized with 0.5 N ammonia. At first, a grey-yellow precipitate (the product of adsorption by the tannin) of oxalo-tantallic acid was formed. Upon further neutralization with ammonia, orange-red complexes of oxalo-columbic acid were precipitated. Neutralization with ammonia must be discontinued at the moment of formation of the orange precipitate of columbic acid and NH_4Cl added and the solution

boiled to coagulate the precipitate. The orange precipitate is filtered, ignited, and treated repeatedly until it loses its orange tinge and, upon ignition, remains white while hot. The ignited hot tantalum pentoxide does not have a yellow tinge unlike the columbium pentoxide and titanium dioxide.

It is obvious from the above mentioned that the detection of columbium and tantalum is not simple and that the analysis is prolonged.

All the results of the analyses are summarized in a table at the end of this paper, in which the values of titanium oxide are also listed. The data indicate that, during the weathering of the mineral, there is an accumulation of Cb_2O_5 concurrent with an accumulation of TiO_2 . In some minerals, the Ta was separated from the Cb; the results indicate that tantalum accompanies columbium everywhere, but in very small amounts which do not exceed tenths of a percent. In minerals of one series, which are similar in chemical composition, the content of earth acids is characteristic. Loparite is at the beginning of the table.

1. Loparite, which does not belong to the titanium silicates, is listed as the first mineral because it was the first to be used in determining Cb and Ta in Khibinsk minerals.

Below are the results obtained by me in the analysis of loparite from the Nivchurt Hill in the Lovozersk Tundras (collection by V. I. Gerasimovskiy in 1934):

SiO ₂	0.27 percent
TiO ₂	39.24
ThO ₂	0.67
Cb ₂ O ₅	10.82 Ta ₂ O ₅ /TiO ₂ = 3.42
Ta ₂ O ₅	0.66
Ce ₂ O ₃	16.29
(La, Di) ₂ O ₃	15.55
Y ₂ O ₃	10.46
Fe ₂ O ₃	0.06
Al ₂ O ₃	0.06
CaO	5.26
SrO	0.62
Na ₂ O	9.06
K ₂ O	0.75
Ignition loss	--
	<hr/> 99.77 percent

Loparite -- a mineral containing rare earths, columbium, tantalum, and titanium -- was first described by W. Ramsay in his paper in 1889 [5] as a new mineral resembling perovskite; he designated it as mineral Number 1, without any definite nomenclature. In 1921-1922, the expedition of I. G. Kuznetsov discovered loparite crystals on the contacts of Mannepakhk, where material was also collected for its crystallographic and chemical investigation. It was given the name loparite by I. G. Kuznetsov.

The first chemical analysis of loparite was made by Yu. N. Knipovich. His results were published in a paper by Kuznetsov [6].

Columbium and tantalum were not indicated but they were accepted as titanium dioxide and were thus omitted. In 1930, Gertner [7] observed the columbium and tantalum lines in loparite by means of a spectroscope; in 1933, in the geochemical laboratory of the Kola Base of the Academy of Sciences, columbium and tantalum were determined chemically by V. S. Eykova in loparite from the Mannepakhk Hill in the Khibinsk area and in 1934 and 1935 I made complete analyses of loparite from the Kukisvumchorr Hill (Khibinsk area) and Ninchurt Hill (Lovozerk tundra).

2. Fersmanite is a fluoro-columbo-titano-silicate of calcium and alkali. (Paper by I. D. Starynkevich-Borneman in Collection of Papers dedicated to V. I. Vernadskiy.

The mineral is of the monoclinic system. On the basis of its chemical composition, it was compared by A. N. Labuntsov [8] with the molengraaffite from the lujaurites of the Transvaal, but it differs sharply from it by its physical and optical properties. There is no indication of earth acids in the analysis of molengraaffite [9]. This apparently explains the impossibility of identifying these two mineral types.

The color of the crystals is dark-brown, fracture is uneven, hardness is 5.5, specific gravity is 3.30-3.44. Fersmanite was first discovered optically (—) in 1922 by one of the details of the Khibinsk Geological-Mineralogical Expedition of academician A. E. Fersman. It was named in honor of A. E. Fersman and classified as a new mineral type much later (in 1929), when its properties were investigated and described by A. N. Labuntsov.

The columbium and tantalum lines were first determined by V. V. Shcherbina in 1932 [10]; in 1934, in the laboratory of the Kola Base, M. Ye. Vladimirova determined \sum (Cb, Ta) $2O_5$ in the amount of 15.36 percent. In 1935, V. S. Bykova accomplished the separation of columbium and tantalum -- Cb_2O_5 15.00 percent and Ta_2O_5 0.36 percent.

Below are the results of the complete chemical analysis of fersmanite from the valley of the Vuonnemiok River (analysts M. E. Vladimirova and V. S. Bykova):

SiO_2	23.36 percent
TiO_2	21.72
Cb_2O_5	15.00
Ta_2O_5	0.36
Fe_2O_3	0.52
CaO	25.88
SrO	0.32 (CbTa) $2O_5/TiO_2$ -- 1.4
FeO	-
MnO	0.26
MgO	0.12
Na_2O	7.62
K_2O	0.62
H_2O	1.80
F	<u>4.56</u>
	102.14
$F_2 \sim O$	- 1.92
	<hr/>
	100.22 percent

It can be seen that the value of Cb_2O_5 is higher than in loparite. It is possible that it will be increased still further because hydrolysis of tartaric acid complexes with nitric acid was utilized in the analysis of the fersmanite. Only one sample was analyzed. It would be of interest to analyze fersmanite from the deposit of the Yukspor Hill, which was discovered in 1934.

3. Ramsayite is a new mineral, discovered in 1921-1922 by the expedition of A. E. Fersman. It was named in honor of the Finnish geologist W. Ramsay who was the first to investigate the Khibinsk area; it was investigated and described by Ye. Ye. Kostyleva in 1925 [11] and by V. I. Gerasimovskiy in 1935 [12].

Ramsayite -- ramsayite talus of the Angvundaschorr cirque. Analysis was performed by S. M. Kurbatov.

SiO_2	34.07 percent
TiO_2	47.00
Al_2O_3	- In analyzing ramsayite from the deposit of the Sengilchorr cirque, I determined columbium + tantalum as a total of 1.63 percent.
FeO	1.71
MnO	-
CaO	0.09 There are no indications of the earth acids in the given analysis; in all probability, they were omitted.

MgO	-
K ₂ O	0.12
Na ₂ O	16.88
T. R.	-
Ignition loss	-
	<hr/>
	99.87 percent

Ramsayite is a titano-silicate of sodium. The color of the crystals resembles that of dark-brown sphene, its hardness is somewhat higher than 6, and its specific gravity is 3.437. It is decomposed only with hydrofluoric acid. It is of the rhombic system and, according to data by Ye. Ye. Kostyleva and V. I. Gerasimovskiy, it has a great similarity to the mineral lorenzenite which was discovered in Greenland and described by Flink.

Analysis of lorenzenite from Narsarsuk Greenland [3].

SiO ₂	34.26 percent
TiO ₂	35.15
ZrO ₂	11.92
Na ₂ O	17.12 Lorenzenite differs from ramsayite chemically by its greater content of ZrO ₂ .
K ₂ O	0.37
FeO	-
CaO	-
H ₂ O	0.77
	<hr/>
	99.59 percent

There was no indication of the presence of earth acids. It is possible that they were also reported together with TiO_2 and thus were omitted. The presence of ZrO_2 in ramsayite was established by V. S. Bykova, but in an insignificant amount [12].

Ramsayite is one of the most frequently found minerals in both the Khibinsk and Lovozersk tundras.

I made an investigation of ramsayite from the Sengischorr cirque of the Lovozersk tundra (collection of Ye. Ye. Kostyleva in 1923). The total of Cb and Ta pentoxides, as determined, was 1.63 percent.

4. Sphene is a titano-silicate of calcium. It is known from 1787 [13]. Recently, it became commercially important as an ore for the production of titanium oxide.

A large zone containing apatite-sphene rock was discovered on the Kola Peninsula, in the locality of the Yukspor and Kuknevumchorr Hills in the Khibinsk tundra.

Columbium was found in three samples of sphene; tantalum was present in an insignificant amount. The first sample was taken from Yukspor Hill (collection by N. N. Gutkova). The crystals have a honey-yellow color and are surrounded with large formations of loparite. The $\sum (Cb, Ta) 2O_5$ is 1.8 percent. The second sample was taken from the Gakman Ravine (collection by N. N. Gutkova in 1930). The sphene is golden, without any formations of loparite grains. The $\sum (Cb, Ta) 2O_5$ is 1.01 percent. The third sample was taken from the Lopara Valley; it was a pink-colored sphene (collection by Ye. Ye. Kostylava in 1934, Number 321).

in the Kola Base Museum) with (Cb, Ta) $2O_5$ being equal to 0.88 percent.

The possibility of discovering Cb and Ta in sphenes was pointed out by E. M. Bonshtedt [13] with reference to roentgen-chemical determinations by Khevishi. These determinations showed very small amounts of Cb and Ta in eight sphenes -- from 0.002 to 0.06 percent Cb_2O_5 and from 0.001 to 0.12 percent Ta_2O_5 . According to Gol'dshmit, CaTi was partially replaced with NaCb in the compound $CaTiSiO_5$ [14].

The results of analyses by F. Zambonini, which are given in the Doelter Handbook, do not indicate the presence of earth acids in sphenes.

Below are the results of the analysis of Khibinsk sphenes. The sphenes were from Yukspor Hill and had a golden color. The analysis, the results of which were printed in the paper "Titanite" by E. M. Bonshtedt, was performed by N. I. Vlodavets.

SiO_2	30.51 percent
TiO_2	39.40 ¹
ZrO_2	0.15
Al_2O_3	0.46
Fe_2O_3	0.36
(T.R.) $2O_3$	0.34
FeO	0.21
MnO	0.16
CaO	25.37
SrO	0.75
BaO	-

1. Cb_2O_5 0.97 percent and Ta_2O_5 0.04 percent

MgO	-
Na ₂ O	1.37
K ₂ O	0.05
F	0.04
Cl	-
Ignition loss	0.30
V ₂ O ₅	0.11
<hr/>	
	99.58 percent
F ₂ ~ 0	-0.02
<hr/>	
	99.56 percent

In the paper "Lamprophyllite of the Khibinsk Tundra" [9] by E. M. Bonshtedt, there is a table with analytical data of minerals having much in common with regard to both the mineralogy and chemical composition. These include astrophyllite, lamprophyllite, and murmanite. There was no indication of the presence of earth acids in these minerals, but in similar minerals (loweite and wohlerite), the content of earth acids amounts to 4.20 percent and 15.85 percent. In addition, the analytical data for astrophyllite from Colorado (analysts, L. G. Eakins and G. A. Konig), as given in the Doelter Handbook, show Ta₂O₅ from 0.34 to 0.80 percent.

In the sample of astrophyllite from Yukspor Hill, which I analyzed, the (Cb, Ta) ₂O₅ was 0.78 percent.

5. Astrophyllite is a titano-silicate of iron and alkali and contains fluorine and chlorine.

It has a golden-bronze color; on the basis of its cleavage, it resembles mica. Its hardness is 3 and specific gravity 3.28. The mineral is of the rhombic system. It occurs frequently in the Khibinsk and Lovozersk tundras. It differs from astrophyllite of other deposits by its considerably smaller content of zirconium. There was no previous indication of the presence of earth acids in Khibinsk astrophyllite. The following analysis was performed by N.

I. Vlodayets:

SiO ₂	34.78 percent
TiO ₂	11.08
(Cb, Ta) ₂ O ₅	0.78 ¹
ZrO ₂	0.57
Al ₂ O ₃	0.60
Fe ₂ O ₃	2.76
FeO	26.71
MnO	6.65
CaO	1.61
SrO	0.05
BaO	0.15
MgO	1.54
Na ₂ O	3.00
K ₂ O	5.90
F	0.86
Cl	0.35
-110°	
H ₂ O +110°	0.11
H ₂ O	2.98
	100.48 percent
	- 0.44
	100.04 percent

6. Lamprophyllite is one of the minerals recently discovered in the Khibinsk and Lovozersk tundras. It was first mentioned by W. Ramsay in his paper in 1890 [5]; he referred to it as a loweite-like secondary mineral of Luyavrurt.

A detailed description of lamprophyllite is given in the paper "Lamprophyllite from the Khibinsk and Lovozersk Tundras" by E. M. Bonshtedt [9].

Lamprophyllite is a fluoro-titano-silicate of strontium and alkali; in external appearance, it resembles astrophyllite closely; the shape of the crystals is monoclinic, the color golden-brown, the hardness between 2 and 3, and the specific gravity 3.35-3.53. Earth acids were not detected despite the thorough and repeated analysis of lamprophyllite (from the deposit of Poachvumchorr Hill). The results of the analysis performed by I. D. Borneman-Starynkevich are given below.

SiO ₂	30.40 percent
TiO ₂	27.48
ZrO ₂	-
Fe ₂ O ₃	3.87
FeO	1.97
MnO	2.33
CaO	1.41
SrO	14.58
BaO	1.25
MgO	0.25
Na ₂ O	12.35
K ₂ O	2.31

H ₂ O	0.60
F	1.82
Cl	-
	<hr/>
	100.62 percent
$\text{-F}_2 \sim \text{O}$	<hr/>
	0.77
	<hr/>
	99.85 percent

7. Murmanite (15, 16, 17) is a widely distributed mineral ^(one part of) in the Lovozersk tundra, [REDACTED] where it occurs. It is a hydrous titanosilicate of sodium. It is of the monoclinic system and separates in the form of lilac-colored plates; upon disintegration, it acquires a violet color. Murmanite disintegrates easily, losing silica and alkali, absorbing water, and increasing the titanium content in the earth acids. It is decomposed completely by acids; under the action of sulfuric acid, it forms a pink solution, which indicates the presence of manganese in the peroxide state.

The first information about murmanite was furnished by W. Ramsay [5] who gave its approximate chemical composition; he called it a new mineral and designated it as Number 3. A more detailed description of murmanite and its chemical analysis are given in the paper by N. I. Gutkova. It is also mentioned in the paper "Minerals from the southeastern section of Luyavrurt" by V. I. Gerasimovskiy. I performed three analyses, the results of which are given in the following table.

Oxides	Samples			Remarks
	No 1 (%)	No 2 (%)	No 3 (%)	
SiO ₂	31.24	30.93	24.52	1. Lovozersk tundra, Sengischorr cirque, 1930 collection by Ye. Ye. Kostyleva.
TiO ₂	30.40	29.51	31.36	
ZrO ₂	1.62	1.40	1.18	
Ob ₂ O ₅	6.56	7.71	10.00	2. Lovozersk tundra, southeastern section of Luyavrurt, Punkaruayv Hill, 1933 (fresh) col- lection by V. I. Gerasimovskiy.
Ta ₂ O ₅	0.56	0.50	0.56	
Fe ₂ O ₃	2.96	3.34	3.04	
Al ₂ O ₃	-	-	0.24	
MnO	2.38	2.42	2.26	
MgO	0.64	0.27	0.38	
CaO	3.16	2.74	3.76	
SrO	traces	traces	traces	
Na ₂ O	8.64	7.44	2.34	
K ₂ O	0.62	0.56	0.70	
F	-	0.19	-	3. Same deposit as No 2 Sample was disinte- grated.
H ₂ O -110°	6.13	6.06	10.69	
+110°	5.37	6.46	9.35	
H ₂ O 2				
	100.28	99.53	100.38	

Murmanite from Sengischorr and from Punkaruayv Hill was analyzed in 1933 and in 1934. Columbium and tantalum were not detected. The earth acids were determined by hydrolysis of the tartaric acid complexes with nitric acid and the resulting precipitate was reported as zirconium. The tannin reaction could not be used for lack of reagent.

The analysis was repeated in 1935 in the laboratory of the Kola Base; the results were as follows: content of Cb+Ta ranged from 6.57 percent to 7.7 percent, while in the disintegrated sample, it amounted to as high as 10.50 percent. In this manner, the accumulation of columbium during weathering occurs along with that of titanium. The titanium content in this, as well as in other Khibinsk titano-silicates, was comparatively small: 0.56-0.50 percent.

I analyzed the following minerals of the mosandrite group:

8 -- lovchorrite,

9 -- rinkolite,

10 -- vudyavrite, and

11 -- calcium rinkite. These are titano-silicates of rare earths and calcium and contain alkali, fluorine, and strontium. They were discovered in the Khibinsk tundra, in the 20's, by members of the expedition under the leadership of A. E. Fersman. A similar description is given in the paper "Lovchorrite and similar minerals" by I. D. Starynkevich-Borneman [18]. This paper gives the complete chemical analysis of the indicated minerals and corrections to be applied to the determinations of TiO_2 made necessary by the presence of earth acids in these minerals. The results of the analyses of the minerals of the mosandrite group are given in the following table.

ANALYSES OF MINERALS OF THE MOSANDRITE GROUP

(IN %)

[See next page for Table Headings]

Oxides	A	B	C	D	E
SiO ₂	28.38	23.43	29.44	34.15	30.71
TiO ₂ + (Cb, Ta) 2O ₅	12.86 ¹	16.51 ²	11.00 ³	12.81 ⁴	5.33
ZrO ₂	-	0.05	0.16	0.19	7.43
ThO ₂	0.94	0.90	0.46	0.37	0.34
CeO ₂	-	-	-	-	6.34
Ce ₂ O ₃	7.99	9.79	7.02	-	10.45
(La, Di) 2O ₃	6.68	12.08	7.69	4.70	-
Y ₂ O ₃	1.26	1.87	1.80	0.44	3.52
Al ₂ O ₃	0.34	0.41	1.52	0.83	-
Fe ₂ O ₃	0.14	0.14	0.06	0.22	0.56
MnO	0.39	0.16	0.12	0.26	0.45
CaO	24.14	5.12	26.38	36.23	22.53
SrO	3.38	1.22	1.62	0.73	-
MgO	0.35	0.19	-	0.13	0.63
U ₃ O ₈	0.02	-	-	-	-
K ₂ O	0.15	0.24	0.42	0.69	0.38
Na ₂ O	8.31	1.35	6.52	5.14	2.44
F ₂	5.80	0.19	5.98	5.50	2.06
H ₂ O	0.70	26.10	1.78	0.40	7.70
	101.83	99.75	101.97	102.79	100.87
F ₂ ~ O	- 2.44	-0.08	- 2.52		0.86
	99.39	99.67	99.45	100.47	100.01

1. Cb₂O₅ + Ta₂O₅ = 2.18%

2. (Cb, Ta)₂O₅ = 3.78%

3. Cb₂O₅ + Ta₂O₅ = 2.57%

4. Cb₂O₅ = 3.83%

Ta₂O₅ = 0.04%

- A -- Lovchorrite. Yunkspor Plateau. 1933. Analyzed by Burova
 B -- Vudyavrite. Yunkspor. 1933. Analyzed by Burova
 C -- Rinkolite. Takhtarvumchorr. 1934. Analyzed by Burova
 D -- Calcium rinkite. Yunkspor. 1934. Analyzed by I. V. Stepanova.
 E -- Mosandrite. Loven, Greenland. 1890. Analyzed by Burova

Earth acids were determined in all minerals of this series, in amounts from 2.10 to 4.64 percent. Tantalum was determined only in calcium rinkite; its content was very insignificant -- 0.04 percent.

In lovchorrite samples taken from different slopes of Yunkspor Hill mine, the content of earth acids did not vary but was equal to 2.16 percent.

Lovchorrite is a mineral of amber-yellow color; in external appearance, it resembles solidified glue. It was first determined in the amorphous state [19]; recently, its cryptocrystalline structure was established by P. N. Chirvinskiy [20]. Its hardness is about 5, it is melted easily by a blowpipe, and it dissolves easily in acids. Rinkolite is similar to lovchorrite; its crystalline structure is quite obvious [19], it has a glass-like lustre, and its crystals have a star-like or arrow-like shape. It contains 2.57 percent earth acids and 8.43 percent TiO_2 . The ratio $\sum (Cb, Ta) \frac{2O_5}{TiO_2}$ is equal to 3.3.

Lovchorrite is surrounded by a peculiar crust which is called vudyavrite (from the location, Lake Vud'yavr).

This entirely amorphous mineral [18] is the end product of the disintegration of lovchorrite.

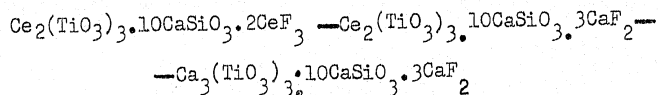
The processes which take place in vudyavrite are the isomorphous substitution of calcium with rare earths, lixiviation of the silica, fluorine, and alkali, and also accumulation of Cb+Ta along with that of titanium (the sum of $(Cb, Ta) 2O_5$ increasing from 2.16 percent to 3.78 percent).

In 1933, L. B. Antonov found in the Lopara cirque of Yukspor Hill a mineral which outwardly resembled talc; it was ivory black in color, amorphous, and of 1.2 specific gravity. It could not be classified as vudyavrite; it is probably some modification of lovchorrite. It contained 4.64 percent earth acids and 17.10 percent TiO_2 . The ratio of $\sum(Cb, Ta) 2O_5 / TiO_2$ was equal to 3.6

Calcium rinkite was found in 1933 by M. S. Afanas'yev on the plateau of Yukspor Hill.

Outwardly it resembles yuksporite. It has a similar fibrous structure and is grey-white. Its specific gravity is 3.10. It contains 3.83 percent Cb_2O_5 , 0.04 percent Ta_2O_5 , and 8.43 percent TiO_2 .

The ratio of earth acids to TiO_2 is equal to 2.3. In chemical composition it resembles closely the lovchorrite group. It was classified by I. D. Starynkevich-Borneman [18] as the last member of the isomorphous lovchorrite-rinkite series without the rare earths.



12. Neptunite is a titano-silicate containing iron, manganese, and alkali; up to 1922, only two deposits of neptunite were known--in Greenland and in California [21]. In 1922, neptunite was discovered in the southern depression of Mannepakhk (which was called the neptunite depression by the expedition of academician A. E. Fersman) and in the western contact zone of Mannepakhk in the Khibinsk tundra. It was also discovered in the Lovozersk tundra--in the upper reaches of the Tavaioka River, in the Angvundasyok and in the southern cirque Alluayv.

The hardness of neptunite is greater than 5. The color of the mineral is dark red. The specific gravity is 3.2. Chemical analysis, as determined by S. M. Kurbatov, does not indicate the presence of earth acids.

I, too, could not detect any earth acids when I checked the material from the neptunite depression.

The same negative result with respect to \sum (Cb, Ta) was obtained in the investigation of

13 -- enigmatite and

14 -- titanomagnetite from Africanda

Oxides	Neptunite depression, northwestern section of Khibinsk tundra. Analyst S. M. Kurbatova (in percent)	Greenland Analyst Flink
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SiO ₂	52.68	51.53
TiO ₂	18.21	18.13
FeO	5.16	10.91
MnO	9.95	4.97
MgO	0.12	0.49
CaO	0.43	-
K ₂ O	4.94	9.26
	100.65	100.17

15. Yuksporite. This is also a fluoro-titano-silicate of calcium [22]. It was first discovered in 1922-1923 in the talus of the Gakman Ravine and the Yuksporlak Pass by the expeditions of academician A. E. Fersman.

In 1929, B. A. Berezin discovered the original deposit of yuksporite in the upper reaches of the Lopara River and, in 1930, N. N. Gutkova came across several other deposits of yuksporite in the Gakman Ravine.

Yuksporite is a mineral of light-pink to yellow-red color. Its structure is flaky-fibrous. Its hardness is about 5 and its specific gravity 3.06. It dissolves easily in acids. It contains 4.30 percent Cb₂O₅; Ta₂O₅ was not detected by the reaction of oxalate-oxalic complexes with tannin.

Analysis of yuksporite was performed by M. I. Stepanova.

SiO ₂	39.32 percent
TiO ₂	11.09
(Cb, Ta) ₂ O ₅	4.30 ¹
Fe ₂ O ₃	0.32
Al ₂ O ₃	0.31
MgO	0.18
MnO	0.09
CaO	19.30
SrO+BaO	6.20
K ₂ O	7.32
Na ₂ O	6.02
F	3.38
Cl	0.80
H ₂ O	2.71
	<hr/>
	101.34
--F ₂ ~O	1.42
--Cl ₂ ~O	<hr/> 0.18
1. \sum (Cb, Ta) ₂ O ₅	99.74 percent

was determined by the author

I completed my work of checking the content of earth acids in Khibinsk and Lovozersk minerals with an analysis of certain zirconium silicates which are very widely distributed on the Kola Peninsula, i.e., minerals of the eudyalite-eucolite series [23]. This series includes eudyalite, eucolite, and an intermediate member of the series, mesodialyte.

These are zirconium silicates of calcium and alkali. There is noted a continuity of properties of the members of this series. Eudyalite is optically positive; mesodialite shows + and ---; eucolite is optically (---) the index of refraction increases from eudyalite to eucolite. Such an increase is also noted in the case of the specific gravity; the specific gravity of eudyalites is 2.76 and of eucolites, 2.95.

According to investigations by Ye. Ye. Kostyleva, minerals of the eudyalite-euolite series consist of an isomorphous mixture of two metasilicates: $\text{Ca}(\text{Mn}, \text{Fe}, \text{Mg})\text{SiO}_3$ and $\text{Na}_2(\text{H}_2, \text{K}_2)\text{SiO}_3$. The continuity of the properties of the members of the eudyalite-euolite group is explained by this very isomorphism.

The eudyalite from the Lovozersk tundra is of commercial importance as a raw material for the production of zirconium oxide. The possibility of finding earth acids in the eudyalite was pointed out by Doelter [24] who cited the analyses of eudyalite and euolite from deposits of Narsarsuk, Barkevik, and Arkansas; some of these minerals contained 0.34 to 3.52 percent columbium and others, from 0.39 to 2.35 percent Ta_2O_5 .

In the paper "Results of analysis of certain minerals of the Khibinsk laccolite of the Kola Peninsula" by G. P. Chernik [25], there is given an analysis of eudyalite from Lovchorr; traces of (Cb+Ta) were determined in a very large sample of this mineral.

An examination of the results of analyses in the paper by Ye. Ye. Kostyleva shows no indication of earth acids, but the total

results in all cases are less than 100 by about 1 percent. Apparently, this shortage accounts for the undetermined Cb+Ta. In determining zirconium with phospho-sodium salt and titanium colorimetrically, the columbium and tantalum remain in solution because the phospho-sodium salt with hydrogen peroxide do not precipitate the columbium and tantalum while in the colorimetric determination of titanium, the columbium and tantalum do not form colored compounds and, in the presence of H_2O_2 in an acid solution, are not precipitated.

I analyzed two samples of eudyalite from Vud'yavchorr Hill in the Khibinsk tundra and from the Lovozersk tundra (from the collection by Ye. Ye. Kostyleva). In the first sample, the \sum (Cb, Ta) $2O_5$ was 0.68 percent and in the second, 0.60 percent.

Analyses of eucolites showed twice as large a content of earth acids; also, the tantalum amounted to hundredths of one percent. Such a small content of tantalum was also determined in the case of eudyalites.

In 1932, I analyzed a pink and brown sample of eucolite from the valley of the Tul'ya River. At that time, columbium and tantalum were not determined. TiO_2 was determined gravimetrically (by precipitating with cupferron). Therefore, since in correcting the results of the analysis for the Cb_2O_5 content, the values of the earth acids were calculated from the value of the TiO_2 , the total percentage remained the same as before. In analyzing eudyalite, the content of earth acids was added to the total because the ZrO_2 was determined with the phospho-sodium salt and TiO_2 .

was determined colorimetrically, i.e., Cb and Ta remained in solution and were not weighed with any other precipitate.

Considering the statement by Ye. Ye. Kostyleva regarding the connection between the eudyalite-eucolite series and catapleite, I analyzed a sample of catapleite from Kukisvumchorr Hill (from the collection by E. M. Bonshtedt). The analysis showed 0.42 percent earth acids.

Catapleite is a hydrous zircono-silicate of alkali. In the Khibinsk tundra, it was discovered in the central section in 1930 and 1931 by details under the leadership of E. M. Bonshtedt and Ye. V. Tsinkerling. Its crystals have the shape of plates and vary in color from dark-chocolate to practically colorless. Its hardness is 5-6 and its specific gravity is 2.38.

In her paper "Catapleite of the Khibinsk Tundra", Ye. Ye. Kostyleva points out that the formation of catapleite must have proceeded by way of a simple rearrangement or recrystallization of the constituents, without the formation of side products of the disintegration of eudyalites. ZrF_4 , upon decomposition with water, reacted with eudyalite and enriched it with ZrO_2 and H_2O .

There was no indication of the enrichment of catapleite with earth acids. The value of $\sum(Cb, Ta) 2O_5$ was almost twice less than in eudyalites; the same was true for the TiO_2 content. In other words, here as well as in other minerals, we can see a connection between columbium and titanium but not with zirconium.

The results of the analysis of catapleite from the valley of the Tul'ya River (as reported by the analyst V. S. Bykova) are

given below. Here the ZrO_2+TiO_2 were determined with cupferron and TiO_2 was determined colorimetrically, i.e., the earth acids were determined together with the ZrO_2 and, hence, the total percentage was not changed by the determination of columbium oxide.

Having checked the content of columbium and tantalum in various Khibinsk and Lovozersk minerals, we come to the conclusion that columbium is, together with titanium and partly with zirconium, a usual element in the Khibinsk area. Tantalum occupies a secondary place with regard to columbium, being only its accessory mineral. The amount of columbium in the minerals reaches up to 15 percent (fersmanite), but it is more frequently of the order of 2 percent (lovchorrite) and less. The ratio of earth acids to titanium varies from 1.35 in fersmanite to 3 in minerals of the lovchorrite group and in murmanite, 14.6 in astrophyllite, and close to 30 in sphene and ramsayite. In zirconium minerals, eudyalite, and catapleiite, it is equal to 0.7 and in eucolite it is 0.2. Upon the disintegration of the minerals (lovchorrite, vudyavrite, and murmanite), the accumulation of columbium proceeds along with that of titanium. Tantalum remains in its original proportion. Some minerals, such as sphene, lovchorrite, and eudyalite, are finding application in industry; the discovery of earth acids in these minerals may even increase their importance. They contain from 7.12 to 10.56 percent earth acids (e. g., murmanite) and are very widely distributed in the Lovozersk tundra.

ANALYSIS OF EUDYALITE, EUCOLITE, AND CATAPLEITE
 [See next page for Table Headings]

Oxides	A	B	C	D
SiO ₂	30.09	48.03	48.44	44.77
TiO ₂	0.39	0.23	0.24	0.28
ZrO ₂	12.82	10.48	11.84	29.43
Cb ₂ O ₅	0.54	1.53	1.62	0.42
Ta ₂ O ₅	0.06 ¹	0.06	0.04 ²	
Fe ₂ O ₃	0.60	0.86	0.63	1.02
TR	2.12	2.92	2.62	
FeO	1.79	4.56	3.15	
MnO	2.31	3.03	3.11	0.03
CaO	8.96	11.31	9.16	3.72
SrO	-	0.40	1.38	-
MgO	traces	traces	traces	0.26
Na ₂ O	15.55	11.38	12.53	10.29
K ₂ O	0.62	0.90	0.51	1.02
Cl	0.74	1.26	1.11	-
S	traces	0.08	0.07	-
H ₂ O	3.06	2.52	2.98	9.56
Sum	99.65	99.55	99.43	100.80
-O ~ Cl ₂ -	0.15	-0.26	-0.25	
	99.50	99.29	99.18	

1. (Cb, Ta) ₂O₅ was determined by the author in 1935.

2. (Cb, Ta) ₂O₅ was determined by the author in 1935.

- A -- Eudyalite, Lovozersk tundra. Analyst N. I. Vlodavets in percent.
 B -- Eucclite, Khibinsk tundra, valley of Tul'ya River, brown color.
 Analyst T. A. Burova in percent.
 C -- Eucclite, Khibinsk tundra, valley of the Tul'ya River, pink
 color. Analyst T. A. Burova in percent
 D -- Catapleite, original deposit, Tul'ya River. Analyst V. S.
 Bykova in percent

Columbium in Khibinsk and Lovozersk Minerals

Titanium Silicates

Mineral and deposit	Percent		Ratio of (Cb,Ta)	
	Cb_2O_5	Ta_2O_5	TiO_2	$2O_5$ to TiO_2
Loparite-Lovozersk tundra, Ninchurt Hill. Collection by V. I. Gerasimovskiy, 1934.	10.00	0.66	39.72	3.42
Fersmanite-valley of Vuonemyok River. Analyzed by M. E. Vladimirova in 1934 and by V. S. Bykova in 1935.	15.00	0.36	21.72	1.35
Sphene-Yukspor Hill. Collection by N. N. Gutkova. Sample with formations of loparite.	1.81		38.53	21.3
Sphene (golden)-Gakman Ravine. Collection by N. N. Gutkova, 1930. Sample No 83 (Kola Base Museum).	1.01		38.39	37.
Sphene (pink)-Lopara Valley. Collection by Ye. Ye. Kostyleva, 1934 (No 521, Kola Base Museum).	0.88		38.53	43.

Ramsayite-Lovozerk tundra.				
Sengischorr cirque. 1923	1.63	45.37	27.3	
collection				
Astrophyllite-Yukspor Hill.				
Sample by Mikhalev,				
Lovchorritevy Mine	0.78	11.08	14.6	
Lamprophyllite-Poachvunchorr				
Hill. Collection by Gutkova				
(sample from the Kola Base				
Museum).		not found		
Murmanite-Lovozerk tundra,				
Puankruayv Hill southwest				
of Luyavrurt Hill. Collection				
by V. I. Gerasimovskiy, 1933				
(sample disintegrated).	10.00	0.56	31.36	3.00
Murmanite-same deposit. Fresh				
sample	7.71	0.50	29.51	3.6
Murmanite-Lovozerk tundra.				
Sengischorr cirque. Col-				
lection by Ye. Ye. Kostyleva,				
1930.	6.56	0.56	30.40	4.2
Yuksporite-Yukspor Hill	4.30	not	11.09	2.5
		found		
Vudyavrite-Lopara cirque.				
Samples by L. B. Antonova				
(white modification)	4.64	17.10	3.6	
Vudyavrite-Vud'yavchorr Hill	3.78	12.73	3.3	

Lovchorrite-Yukspor Hill.

Height 715 m. No 5.

Section 5th vein. Samples

by Mikhalev, Lovchorritovyy

Mine	2.18	10.68	4.9
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Lovchorrite-Vud'yavchorr Hill

Samples by Mikhalev 2.16

Rinkolite-Takhtarvumchorr Hill.

Lower vein. Collections by

Ozhinskiy.	2.57	8.43	3.3
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Calcium rinkite-Yukspor Plateau

Samples by Afanas'yev.	3.83	0.04	8.94	2.3
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[1]	[2]	[3]	[4]	[5]	[6]
Zirconium Silicates					Ratio of (Cb, Ta)
Mineral and Deposit	Cb_2O_5	Ta_2O_5	TiO_2	ZrO_2	$2O_5$ to TiO_2

Eucolite--valley of Tul'ya

River.

Collection by N. N. Gutkova,

1932 (pink sample).	1.62	0.04	0.24	11.84	0.2
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Eucolite (brown) - same de-

posit	1.53	0.06	0.23	10.48	0.2
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Eudyalite-Vud'yavchorr Hill 0.68

Eudyalite-Lovozerk tundra.

Collection by Ye. Ye. Kostyleva,

1930.	0.54	0.06	0.39	12.82	0.7
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[1]	[2]	[3]	[4]	[5]	[6]
Catapleiite-Kukisvumchorr Hill. Collection by E. M. Bonshtedt, No 104 (sample from Kola Base Museum).	0.42	0.28	29.43	0.7	

The check-up on a whole series of minerals and the detection of earth acids in these minerals made it possible to define more accurately and introduce substantial corrections in their chemical formulae.

Further work is necessary to simplify the procedures of determining Cb and Ta and also of separating them from TiO_2 . The lack of accurate and rapid methods made the work difficult and prolonged; each analysis became a separate investigation.

I wish to extend my gratitude to I. D. Starynkevich-Borneman for the assistance and guidance in this work.

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