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NEW DATA ON KOMAROVITE SERIES MINERALS

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The complex (electron microprobe, X-ray diffraction, IR-spectroscopy etc.) research was accomplished for representative collection of samples of komarovite series minerals, occurred in pseudomorphs after vuonnemite from Lovozero and Khibiny alkaline massifs (Kola Peninsula), representations about their cation composition are much extended. New and earlier published materials on these minerals are critically considered and generalized. In light of their strongly pronounced zeolite-like structure, the schemes of isomorphism and decationization are discussed. Ideal general formula for komarovite series members: $(Na,M)_{6-x}Ca(Nb,Ti)_6[Si_4O_{12}](O,OH)_{14}(F,OH)_2{\cdot}nH_2O$ where M = Ca, Sr, Ba, K, Pb, REE, Th etc. In this series, it is propesed to distinguish two mineral species: **komarovite** (decationized, corresponds to original komarovite, with x > 3) and **natrokomarovite** (cation-saturated, with x < 3). Within the limits of the modern nomenclature the latter term is represented more correct than earlier used for this mineral name «Na-komarovite». Komarovite and natrokomarovite strongly differ in chemical composition but are close on X-ray powder diagrams and IR-spectra. In chemical relation, oxosilicates of the komarovite series occupies an intermediate position between oxides of the pyrochlore group and silicates of the labuntsovite group. That causes a place of natrokomarovite in general scheme of evolution of niobium mineralization in differentiates of alkaline complexes: it appears as an intermediate product at fluctuations of the activity of silica in pegmatitic-hydrothermal systems. Komarovite is a typical transformational mineral species formed by solid-state transformation (decationization, ion exchange, additional hydration) of natrokomarovite under late hydrothermal and probably in hypergene conditions.
3 tables, 2 figures, and 18 references

Komarovite series minerals occur in derivatives of agpaitic rocks from three high-alkali massifs: Lovozero and Khibiny at Kola Peninsula, and Ilimaussaq in South Greenland. Proper komarovite, hydrous niobosilicate of calcium and manganese, was characterized as a new mineral from Lovozero (Portnov *et al.*, 1971). Two years earlier E.I. Semenov (1969) has described a «white Nb-silicate» from Ilimaussaq, its proximity to komarovite was shown later (Krivokoneva *et al.*, 1979). This mineral differed from specimen from Lovozero by high content of sodium (Na >> Ca) was not voted by the IMA Commission on New Minerals and Mineral Names. Nevertheless it has come in a number of mineralogical handbooks (Gaines *et al.*, 1997; Mandarino, 1999) with the name «Na-komarovite» proposed by G.K. Krivokoneva with co-authors (1979). Insufficiently studied mineral from Khibiny described as M53 (Khomyakov, 1990) is very close to «Na-komarovite».

Already at the analysis of the first X-ray powder patterns the relationship of Greenland «white Nb-silicate» with pyrochlore has discovered, and the homological relations of these minerals were continued (Semenov, 1969). G.K. Krivokoneva with co-authors considered komarovite as a «silificated pyrochlore»: in opinion of these researchers, its crystal structure consists of oxide (pyrochlore) and silicate modules (Krivokoneva *et al.*, 1979). Fine-grained structure of aggregates, significant variations of the chemical composition, and presence of other mineral admixtures strongly complicate the study of komarovite and its high-sodic analogue. Because of that, until recently their major characteristics, not only crystal structure and correct formulae, but even the symmetry and unit cell parameters remained debatable.

The find of «Na-komarovite» single crystals in Ilimaussaq has allowed to T. Balic'-Zunic' with co-authors (2002) to solve its crystal structure, appearing unique. The assumptions of E.I. Semenov (1969) and G.K. Krivokoneva with co-authors (1979) have basically proved to be true: the pyrochlore type blocks connected by Si, O-groups underlie in a basis of komarovite structural type. The mineral is orthorhombic, space group *Cmmm*, unit cell parameters: a = 7.310, b = 24.588, c = 7.402 Å (Balic'-Zunic' *et al.*, 2002). We shall note, M. Dano obtained the same dimensions of the orthorhombic unit cell (a = 7.411, b = 24.612, c = 7.318 Å) for Greenland «white Nb-silicate» from the X-ray powder data (Semenov, 1969). Pyrochlore layers (blocks) are oriented in such a manner that axes a and c in komarovite are parallel directions <110> in pyrochlore; unit cell parameters

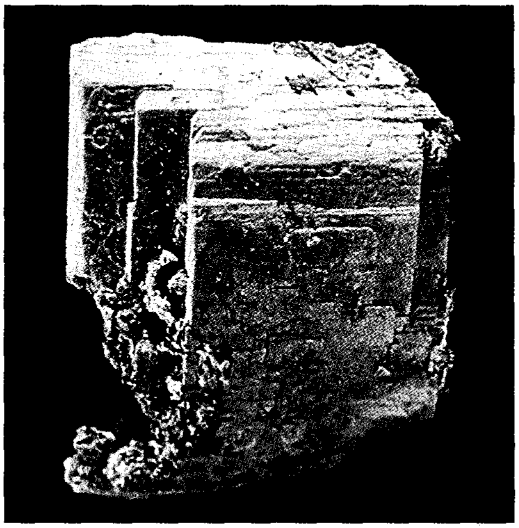

FIG. 1. Komarovite pseudomorph after cluster of vuonnemite crystals (specimen 2.5 x 2 cm) from the Komarovitovoe pegmatite, Kukisvumchorr Mt., Khibiny massif. A.S. Podlesnyi collection. Photo: N.A. Pekova

a and *c* of komarovite (7.3 – 7.4 Å) represent half of diagonals of pyrochlore cubic unit cell (~10.4 Å). Pyrochlore block is formed by (Nb,Ti)-octahedra and eight-vertex polyhedra of large cations (Na, Ca, etc.). F sites in crystal structures of pyrochlore and komarovite are analogous except that in the latter molecules of H_2O on the block surface replace the F atoms. In the crystal structure of komarovite the pyrochlore fragments are «interlaid» with isolated four-membered Si, O-rings, $[Si_4O_{12}]$ (of labuntsovite type), lying in the plane parallel (001). Between these rings and pyrochlore blocks, there are channels parallel [100], inside which additional Na atoms (in ten-vertex polyhedra) and H_2O molecules are localized (Balic'-Zunic' *et al.*, 2002). Thus, the structural type of komarovite has turned out to be the striking representative of the plesiotype family of oxysalts (Makovicky, 1997) with pyrochlore oxide modulus. The ideal formula for studied crystal is $Na_6CaNb_6Si_4O_{26}F_2 \cdot 4H_2O$, and general crystallochemical formula for minerals of komarovite type was proposed as $(Na,K)Na_{5+x-y}Ca_{1-2x+y}REE_xTi_yNb_{6-y}Si_4O_{26}F_2 \cdot 4H_2O$ (Balic'-Zunic' *et al.*, 2002). X-ray powder diagram of komarovite-like minerals is absolutely individual and allows making the undoubtful diagnostics of them. Thus, belonging of komarovite from Lovozero and A.P. Khomyakov's phase M53 to structural type of Greenland mineral is not raise doubts.

T. Balic'-Zunic' with co-authors (2002) has proposed to unite the minerals from Lovozero and Ilimaussaq under the general name *komarovite*, in spite of sufficient difference in their chemical composition. On the contrary, we are represented expedient to consider low-sodium and high-sodium phases as two different mineral species, the members of the solid solution series. Thus the original name **komarovite** should be kept for a low-sodium mineral, which was given by A.M. Portnov with co-authors (1971), and high-sodium mineral we propose to name as **natrokomarovite** (especially as the name «Na-komarovite» did not accept by the IMA CNMMN). The data obtained within the present work on samples from Lovozero and Khibiny allow essentially extending conception about cation composition and isomorphism in the komarovite series. Using both published and new materials, we have tried to show dependence of chemical composition of these minerals from formation conditions, and also the place of komarovite series members in general scheme of niobium mineralization evolution in derivatives of agpaitic complexes.

Occurrences

In Ilimaussaq, natrokomarovite («white Nb-silicate») was first found in hydrothermalites of naujaites from North Slope of Mt. Nakalaq, in pseudomorphs after epistolite plates, reached 5 x 3 x 1 sm in size, an also as independent segregations among analcime. It forms white fine-grained aggregates and usually occurs in close intergrowths with neptunite (Semenov, 1969). The second finding of natrokomarovite in Ilimaussaq provided a material for crystal structure study was made in albitite at Kvanefjeld plateau. Here it forms yellowish transparent crystals up to 0.4 x 0.04 x 0.02 mm in size, flattened on {010} and elongated on [100]. These crystals form segregations (probably pseudomorphs after vuonnemite) in aegirine-albite rock with neptunite, epistolite, analcime, tugtupite etc. (Balic'-Zunic' *et al.*, 2002).

In Lovozero massif, komarovite was found only in core of hydrothermally altered pegmatite № 61 (according to E.I. Semenov's numeration) at North Slope of Mt. Karnasurt where it occurs in significant amounts. It is included in polycomponent pseudomorphs after large (up to 10 cm in size) tabular crystals of vuonnemite. These pale-pink pseudomorphs usually located among natrolite are composed by fine-grained aggregates of komarovite, labuntsovite group minerals (mainly it is the members of organovaite and kuzmenkoite series), and strontiopyrochlore. Albite, microcline, aegirine, yofortierite, mangan-neptunite, leifite, epididymite, lorenzenite, catapleiite, elpidite, nontronite, oxides of Mn etc. are associated with them. Here there are perfectly shaped lamellae-pseudomorphs up to 3 x 2.5 cm in size, consist mainly of komarovite. Their shape does not give up doubts that vuonnemite was the protomineral (Portnov *et al.*, 1971; Pekov, 2000; Azarova *et al.*, 2002).

In Khibiny, both natrokomarovite and komarovite are determined. They are found in several hydrothermally altered pegmatites uncovered by underground minings of Kirovskii mine at Mt. Kukisvumchorr. For the first time natrokomarovite («phase M53») was found here as pale-pink rectangular lamellae up to 5 x 3 x 1 cm in size with strong vitreous lustre in selvages of natrolite veinlets (Khomyakov, 1990). The similar pseudomorphs with lilac to pink colour, reached to 16 cm across and to 4 cm thick were determined by us in axial natrolite zone of the «Belovitovoye» pegmatite. The largest their intergrowth consisting of five crystals of replaced vuonnemite has the sizes 25 x 12 cm. The main components of pseudomorphs are natrokomarovite and apatite forming fine-grained aggregates. Komarovite (the product of alteration of natrokomarovite), nenadkevichite and X-ray amorphous hydrous oxide of Nb and Ti, close to gerasimovskite, are present in subordinate amounts. Microcline, aegirine, lamprophyllite, gaidonnayite, belovite-(La), belovite-(Ce), neotocite, ancylite-(Ce), sulfides etc. are associated with these pseudomorphs. We have found proper komarovite in hydrothermal parageneses yet of two pegmatites, one of them was named «Komarovitovoye». Here pink, cream, brown-grey and dark-grey pseudomorphs (Fig. 1) after well-shaped tabular crystals of vuonnemite up to 7 cm in diameter grow on the wall of large cavity. They consist of fine-grained aggregates of komarovite, nenadkevichite, pyrochlore, and apatite; in association with them there are natrolite, calcite, fluorite, aegirine, magnesio-arfvedsonite, murmanite, lamprophyllite, eudialyte, lorenzenite, catapleiite, tsepinite-Na, tainiolite, sphalerite etc. In cavities of closely located small pegmatite, komarovite containing significant amounts of lead and titanium form pink fine-grained pseudomorphs after well-shaped crystals of vuonnemite associated with natrolite.

Table 1. X-ray powder data of komarovite series minerals

1		*2*		*3*		*4*		
I	*d, Å*	*I*	*d, Å*	*I*	*d, Å*	*I*	*d, Å*	*hkl*
90	12.364	73	12.3	100	12.36	100	12.15	020
75	7.034	25	7.00	14	7.00	8	6.97	110
75	6.359	30	6.30	25	6.35	4	6.37	021
20	6.170	10	6.15	12	6.17	19	6.04	040
90	5.464	30	5.43	13	5.45	8	5.41	130
5	5.104							111
30	4.739	15	4.75	10	4.73			041
75	3.278	20	3.26	6	3.28	37	3.204	112
100	3.174	100	3.170	24	3.16	5	3.175	042
100	3.149	40	3.128	10	3.13	5	3.106	240
5	3.079							080
25	3.066			8	3.063	8	3.057	132
10	2.895							241
20	2.841	17	2.840	8	2.840	5	2.810	081
75	2.749	25	2.748	11	2.751			062
75	2.732	25	2.718			4	2.715	260
60	2.604	20	2.589	4	2.592	4	2.586	202
5	2.563							261
5	2.547							222
10	2.461	3	2.456			3	2.429	0.10.0
5	2.408			4	2.389			172
5	2.354							280
5	2.337							330
5	2.197							262
5	2.139							1.11.0
10	2.115	7	2.110			2	2.068	063
5	2.097							351
5	2.052							0.12.0
5	2.042							2.10.0
5	2.019			3	2.010			223
30	1.986	17	1.983					282
5	1.977							332
30	1.852	9	1.850			2	1.842	004
30	1.829	8	1.825			2	1.816	400
5	1.810							420
75	1.788	45	1.783	5	1.786	8	1.781	2.10.2

Note:
1 — natrokomarovite, Ilimaussaq: Guinier camera, analyst M. Dano (Semenov, 1969); 2 — komarovite, Lovozero: diffractometer, analyst G.K. Krivokoneva (Portnov et al., 1971); 3-4 our data (diffractometer DRON UM-1, Cu Ka radiation, Ni filter, analyst V.G. Shlykov): 3 — komarovite, Lovozero; 4 — PbTi-variety of komarovite, Khibiny.
hkl indices are given on (Balic'-Zunic' *et al.*, 2002).

X-ray and IR-spectroscopic data

Pseudomorphs after vuonnemite containing komarovite series minerals from Lovozero and Khibiny were studied in present work by

Table 2. Wavenumbers (cm^{-1}) of absorption bands in the IR-spectra of komarovite and natrokomarovite

Komarovite, Lovozero	*Natrokomarovite, Khibiny*	*Band assignment*
3380	3400	ν(O-H)
3240 sh	3265 sh	
1795 w		δ(H_3O)
1720 w		
1637	Recovered by bands of admixed phases	δ(H_2O)
	1593	Admixture of organic matter?
	1420 w	
	1353 w	
1136	1130 sh	ν(Si-O-Si)
1099	1090 sh	
1020 sh	1020 sh	ν(Si-O)
992		
939	940	
842	810	Mixed vibrations of (Nb,Ti)Si-framework
750	840	
658	650	ν(Nb,Ti-O)
585	580 sh	
543	540 sh	
	520	
439	445	δ(O-Si-O)
390 sh	385	

Note:
ν — stretching vibrations; ; δ — bending vibrations; sh — shoulder; w — weak line

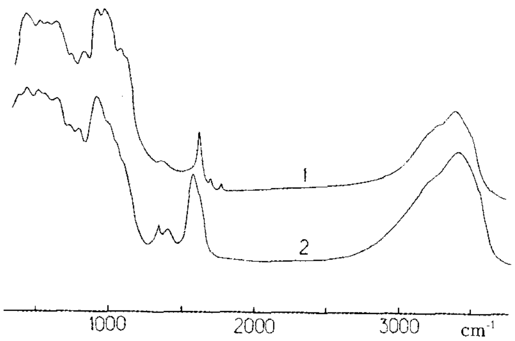

FIG. 2. The IR spectra of komarovite from Lovozero (1) and natrokomarovite from Khibiny

electron microprobe analysis method, X-ray powder diffraction, IR-spectroscopy, optic and electron microscopy.

X-ray powder diffraction is a most effective method for precise determination of mineral belonging to komarovite series, including mixtures. As already was mentioned, these minerals have absolutely individual X-ray powder diagram (Table 1). As a main diagnostic feature it is possible to propose the pair of intensive reflections in small angle ($d > 3$ Å) region, with interplanar distances ~12.3 and ~5.45 Å. Other intensive reflections obtained in the X-ray powder diagrams of komarovite series members (regions ~7.0, 6.30 – 6.36, 3.12 – 3.17 Å) can overlap with strong reflexes of the labuntsovite group minerals which often compose pseudomorphs after vuonnemite together with komarovites (Azarova *et al.*, 2002; Chukanov *et al.*, 2003). Komarovite series members do not practically differ among each other on X-ray diagrams, the reason of that is discussed below.

The IR-spectroscopy as well as X-ray diffraction can be used as reliable method of identification of komarovite series members. The IR-spectra of these minerals (Fig. 2, Table 2) were obtained by spectrophotometer Specord 75 IR for powder samples pressed in KBr; the frequencies of bands were measured with accuracy ±1 cm^{-1} (standards: polystyrene and gaseous ammonia). The spectra of komarovite and natrokomarovite are close among each other. In contrast to majority of other cyclosilicates, these minerals are characterized by high coefficients of extinction in the range of wavenumbers 500 – 660 cm^{-1}, that is caused by the absorption of IR-radiation by pyrochlore-like blocks. The main difference of the IR-spectrum of natrokomarovite from Khibiny (№ 8 in Table 3) from the spectrum of komarovite from Lovozero is an absence of the strong band with maximum at 992 cm^{-1} in the first one that results in decrease of medium-weighted frequency of Si-O-stretching vibrations. More often this frequency decrease is caused by the reduction of degree of condensation of silica-oxide tetrahedra in the mineral structure (Chukanov, 1995). Moreover, the band of mixed vibrations of komarovite framework at 842 cm^{-1} is shifted up to 810 cm^{-1} in case of natrokomarovite. The frequencies of other bands on komarovite and natrokomarovite spectra are close, but differ in the intensities, that means similarity of structural motif, but also different character of spatial allocation of charge in frameworks of these minerals.

Komarovite and natrokomarovite both contain large amount of weakly connected water

Table 3. Chemical composition of komarovite series minerals

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
wt %									
Na_2O	12.26	13.71	0.85	0.84	0.67	0.76	12.2	6.32	0.15
K_2O	0.15		0.30	0.85	0.67	0.74	1.6	0.36	0.21
CaO	3.36	5.30	4.70	3.95	3.22	3.39	4.8	7.95	7.65
SrO				4.31	4.22	4.35	0.4	2.68	0.38
BaO				1.10	1.09	1.01	0.6	5.75	3.61
PbO				n.d.	n.d.	n.d.		bdl	12.03
MnO			5.00	0.30	0.69	0.11	0.1	0.83	1.09
REE_2O_3	1.68*	0.46		n.d.	n.d.	n.d.		bdl	bdl
Fe_2O_3	0.18**	0.48	1.50	0.24	1.04	0.49	0.1	0.13	0.71
Al_2O_3		1.38	1.00	1.20	1.83	1.33	0.2	0.14	bdl
SiO_2	17.50	16.46	23.50	15.68	15.93	16.71	18.7	15.01	15.54
ThO_2				n.d.	n.d.	n.d.		4.02	bdl
TiO_2	3.34	5.27	2.50	2.79	3.64	3.44	6.8	9.95	14.90
Nb_2O_5	53.98	50.23	47.00	47.32	50.72	52.94	46.1	33.39	26.91
Ta_2O_5				n.d.	n.d.	n.d.	0.4	bdl	bdl
H_2O	n.d.	4.64	12.00	n.d.	n.d.	n.d.	6.0	n.d.	n.d.
F	3.03	2.50	1.21	n.d.	n.d.	n.d.	2.0	n.d.	2.57
$-O=F_2$	-1.28	-1.05	-0.51				-0.8		-1.08
Total	94.20	99.38	99.05	78.58	83.72	85.27	99.2	86.53	84.67
Formula calculated on Si+Al=4									
Na	5.43	5.88	0.27	0.38	0.29	0.32	5.00	3.23	0.07
K	0.04		0.06	0.25	0.19	0.21	0.43	0.12	0.07
Ca	0.82	1.26	0.82	0.99	0.76	0.79	1.09	2.24	2.11
Sr				0.58	0.54	0.55	0.05	0.41	0.06
Ba				0.10	0.09	0.09	0.05	0.59	0.36
Pb									0.83
Mn			0.69	0.06	0.13	0.02	0.02	0.19	0.24
Fe	0.03	0.08	0.18	0.04	0.17	0.08	0.02	0.03	0.14
REE	0.14	0.04							
Al		0.36	0.19	0.33	0.48	0.34	0.05	0.04	
Si	4.00	3.64	3.81	3.67	3.52	3.66	3.95	3.96	4.00
Th								0.24	
Ti	0.57	0.88	0.30	0.49	0.61	0.57	1.08	1.97	2.88
Nb	5.58	5.02	3.44	5.01	5.07	5.24	4.40	3.98	3.13
Ta							0.02		
F	2.19	1.75	0.62				1.34		2.09
H_2O		3.42	6.49				4.23		
Σoct.	6.18	5.98	3.92	5.54	5.85	5.89	5.52	5.98	6.15
Σe.f.c.	6.43	7.18	1.84	2.36	2.00	1.98	6.64	7.02	3.74

Note:
1-2, 7-8 — natrokomarovite; 3-6, 9 — komarovite.
1 — Kvanefjeld, Ilimaussaq; 2 — Nakalaq, Ilimaussaq; 3-6 — Karnasurt, Lovozero; 7-9 — Kukisvumchorr, Khibiny.
References: 1 — Balic-Zunic *et al.*, 2002; 2 — Semenov, 1969; 3 — Portnov *et al.*, 1971; 7 — Khomyakov, 1990; 4,5,6,8,9 — our electron microprobe data (analysts N.N. Korotaeva and A.N. Nekrasov).
Σoct. — sum of octahedral cations: Nb+Ta+Ti+Fe; Σe.f.c. — sum of extra-framework cations: Na+K+Ca+Sr+Ba+Pb+Mn+REE+Th.
* — La_2O_3 0.57, Ce_2O_3 1.11 wt %; ** — recalculated from 0.16 FeO; n.d. — not detected; bdl — below detection limits

molecules, giving in the IR-spectra the strong wide bands at 3380 – 3400 cm^{-1}. Komarovite from Lovozero apparently contains also small amount of hydronium ions $(H_3O)^+$, about than it is possible to judge on presence of weak bands at 1795 and 1720 cm^{-1} in its IR-spectrum. In the range 1350 – 1593 cm^{-1} of the spectrum of natrokomarovite from Khibiny there are bands, which by their positions and intensities ratios, probably, are caused by mechanical admixture of organic matter.

Chemical composition

The study of samples from Lovozero and Khibiny by means of optic and electron microscopy has shown the mineral individuals of komarovite series as a rule are flattened and have submicrometer size. Usually the pseudomorphs after vuonnemite are heterogeneous, and grains of other minerals in them are comparable in size with particles of komarovite. That strongly complicates the obtaining of correct chemical data of our minerals, including electron microprobe method. During present work, more then twenty samples of pseudomorphs after vuonnemite from Lovozero and Khibiny, in which previously X-ray and IR-spectroscopic methods have obtained the significant contents of komarovite-like phases, were studied by microprobe instruments Camebax-MBX equipped by energy-dispersive spectrometer LINK AN 10000 and Camebax SX 50 (WDS method). Only some from more than fifty analyses were carried out from homogeneous (or nearly homogeneous) minerals of the komarovite series. The typical chemical compositions are presented in Table 3; the formulae, according to crystal structural data, were calculated on $(Si+Al)=4$, the same method was used for calculation of earlier published analyses. The sum of octahedral cations (Nb, Ta,Ti,Fe) for correct analyses are close to 6 (the limits of fluctuations are from 5.5 to 6.2, Table 2). Only in the first chemical analysis of komarovite (№ 3 in Table 3), carried out by wet chemical method (Portnov *et al.*, 1971), the significant greater amount of strontium than in all other analyses and abnormally high contents of manganese and iron are observed. It is impossible to exclude that the sample was polluted, for example, by fine fibres of yofortierite, $(Mn,Fe)_5Si_8O_{20}(OH)_2 \cdot 8-9H_2O$, which is closely associated with komarovite.

Table 3 shows that both samples from Ilimaussaq are characterized by high content of sodium and contain admixtures of rare-earth elements, whereas some appreciable amounts of potassium, strontium, barium, and manganese are absent in them. The samples from Kola Peninsula usually contain much potassium, strontium, barium, and manganese, and in some cases also lead and thorium. In Lovozero only komarovite with $Na_2O < 1$ wt % was detected, and in Khibiny there are natrokomarovite (both typical high-sodian with 12.2% Na_2O and with slightly decreased content of sodium: 6.3% Na_2O) and komarovite (0.15% Na_2O). In all studied samples from Khibiny there is not enough aluminium. They are strongly enriched by titanium and depleted by niobium in comparison with samples from Lovozero and Ilimaussaq.

Discussion

Komarovite series minerals have complicated and variable chemical composition, especially in large cation part. As it is shown in the Table 3, they contain: Na_2O 0.1 – 13.7 wt%; K_2O 0.1 – 1.6%; CaO 3.2 – 8.0%; SrO 0.0 – 4.4%; BaO 0.0 – 5.8%; PbO 0 – 12%; REE_2O_3 0.0 – 1.7%; ThO_2 0 – 4%. At so wide isomorphism, their X-ray powder diagrams vary a little (Table 1). It is connected to that komarovite series minerals have pronounced zeolite-like structures and can be considered as niobosilicate analogues of zeolites with mixed framework formed by vertex-connected Si-tetrahedra and (Nb,Ti)-octahedra. That explains many peculiarities of chemical composition and properties of discussed minerals. In particular, total amount and ratios of large cations, and also degree of hydration do not practically influence values of interplanar distances. As well as in other zeolites, not only in aluminosilicate ones, but also in their rare-metal-bearing analogues with mixed tetrahedral-octahedral framework the unit cell parameters and, accordingly, the interplanar distances in komarovites significantly depend on composition of framework and slightly on variations in extra-framework sites. Probably the main factor determining unit cell parameters of komarovite is a value of Nb/Ti-ratio as well as for labuntsovite group minerals (Chukanov *et al.*, 2003). It is shown in Table 1 that X-ray diagrams of cation-saturated natrokomarovite form Greenland and strongly decationized komarovite from Lovozero are practically indistinguishable, whereas high-titanium komarovite from Khibiny (№ 8 in Table 3) have decreased values of majority of interplanar distances in spite of its enrichment by large out-of-framework atoms (Pb, Ba).

Isomorphism in komarovites is complicated; no doubts these replacements take place simultaneously on some schemes. T. Balic'-

Zunic' with co-authors suggest the isomorphous scheme $Na^+Nb^{5+} \leftrightarrow Ca^{2+}Ti^{4+}$ with hypothetical end members with compositions: $Na_6CaNb_6Si_4O_{26}F_2 \cdot 4H_2O$ and $Ca_7Ti_6Si_4O_{26}F_2 \cdot 4H_2O$ (Balic'-Zunic' *et al.*, 2002). The increased content of calcium in most rich in titanium samples from Khibiny (№№ 8 – 9 in Table 3) can be evidence of that scheme is realized at some degree in nature. Our data show that isomorphism between niobium and titanium in komarovite series takes place in wide range and, probably, is continuous as well as in minerals of pyrochlore and labuntsovite groups. The charge balance can be achieved, for example, by typical for these groups way: $Nb^{5+} + O^{2-} \leftrightarrow Ti^{4+} + OH^-$.

The substitutions with participation of vacancies in extra-framework cation positions play very important role in komarovite series minerals. It is shown in Table 3 that the sum of large cations varies in widest limits: from 1.8 to 7.2 *atoms per formula units* (*apfu*). Most cation-saturated samples are characterized by highest content of sodium, whereas in significant vacant ones the role of divalent cations increases, i. e. the isomorphous scheme $2M^+ \leftrightarrow M^{2+} + \square$ where M^+ = Na, K; M^{2+} = Ca, Sr, Ba, Pb is realized. Location of significant part of O-atoms on bridge and «pendent» vertices of (Nb,Ti)-octahedra in pyrochlore module allows their protonization ($O^{2-} \rightarrow OH^-$) that permits to achieve yet greater degree of vacancity of extra-framework cation sites. That is assisted by substitution $F^- \rightarrow H_2O$, noted by T. Balic'-Zunic' with co-authors (2002). The IR-spectroscopic data (Fig. 2, Table 2) are shown that in komarovite from Lovozero there is small amount of hydronium $(H_3O)^+$. The content of large cations (Na, K, H_3O, Ca, Sr, Ba, Pb, REE, Th) in komarovites and pyrochlore group minerals are practically identical. Both are characterized by wide variations in ratios of these cations and in degree of vacancity of their sites. For komarovite series minerals, the majority of substitutions with participation of large cations takes place within the pyrochlore module. The presence of additional wide channels in places where between pyrochlore-like blocks there are «spreaders» in the form of $[Si_4O_{12}]$ rings strengthens zeolite character. The framework density of komarovite series minerals is 15.0 – 15.6 atoms per 1000 Å^3 that falls into interval of values for most broad-porous natural aluminosilicate zeolites.

Komarovite from Lovozero is the most strongly decationized member of the series; the sum of large (extra-framework) cations in it varies in limits 1.8 – 2.4 *apfu* (Table 3). As the same time, this mineral is not different from cation-saturated natrokomarovite by value of Nb/Ti-ratio. All data evidence that komarovite is a product of natrokomarovite alteration (leaching of sodium and additional hydration) and forms at late hydrothermal stages under alkalinity decrease. The similar phenomenon resulting in transition from some species to others is well known for many high-sodic minerals from hyperagpaitic assemblages, first of all for representatives of the lomonosovite group (lomonosovite → murmanite; vuonnemite → epistolite), the lovozerite group (zirsinalite → lovozerite; kazakovite → tisinalite; kapustinite → litvinskite), the keldyshite series (parakeldyshite → keldyshite) (Khomyakov, 1990; Pekov *et al.*, 2003). Significantly vacant members of the pyrochlore group, which was formed by leaching of sodium and calcium from full-cationic analogues, are also spread in nature. Products of successive stages of natrokomarovite alteration containing different amounts of sodium were observed by us in the «Belovitovoye» pegmatite at Mt. Kukisvumchorr (Khibiny). All that allows thing the process of decationization of natrokomarovite in water medium (under late hydrothermal and hypergene conditions) proceed easily.

Zeolite-like structure of komarovite series minerals permits the presence of strong ion exchange properties at them, similarly to the pyrochlore group members (Nechelyustov, Chistyakova, 1986). It is very probably that observed ratios of extra-framework cations in proper komarovite are achieved by natural ion exchange at late hydrothermal stages: replacement of Na^+ by larger and/or high-valent cations (Ca, Sr, Ba, Pb, REE, Th, H_3O) easily realizes in reactions of this type. The example of high-lead komarovite from Khibiny is very bright. The saturation of this mineral by lead, freeing by dissolving of galena from pegmatite at late hydrothermal stage, can realize only after the leaching of sodium or simultaneously with it. As a whole, the content of large cations in komarovite reflects the geochemical speciality of latest stages of hydrothermal process: the samples from Lovozero are more enriched by strontium, and ones from Khibiny — by barium and calcium.

The independent crystallization of komarovite, zeolite-like mineral with strong cation deficiency, from solution is seemed extremely improbable. From the experimental data it is known (Barrer, 1985) that phases with such open-worked structures can arise only at participation of large cations, which the framework forms around; the same cations neutralize its surplus negative charge (the theory of this phenomenon are discussed by N.V. Belov in his «Second Chapter of Silicate Crystal Chemistry», see for example: Belov, 1976). Thus, by A.P. Khomyakov's terminology, komarovite seems to be the typical transformational mineral species, i.e. incapable to heterogeneous origin, but forming only by solid-state transformation of the mineral-predecessor, full-cationic natrokomarovite. It fall into the same genetic group as murmanite, epistolite, lovozerite, tisinalite, litvinskite, keldyshite, kalipyrochlore, and a number of other minerals formed by decationization and hydration of corresponding proto-phases. That is the additional argument in favour of that komarovite and natrokomarovite are considered as different mineral species. The ideal general formula for komarovite series members can be write down as $(Na,M)_{6-x}Ca(Nb,Ti)_6[Si_4O_{12}](O,OH)_{14}(F,OH)_2{\cdot}nH_2O$ where M = Ca, Sr, Ba, K, Pb, REE, Th etc. according to data of T. Balic'-Zunic' with co-authors (2002) and our results. The formal border between komarovite and natrokomarovite can be proposed on chemical composition with $x = 3$, taking in account «the rule 50%»: the series members with $x < 3$ will concern to natrokomarovite, and with $x > 3$, i. e. with prevalence of vacancies in sodium positions, to komarovite. The name *natrokomarovite* seems to be more correct than *Na-komarovite*, because the latter does not correspond the rules of modern nomenclature, according which the symbol of chemical element must not be stand as a prefix of mineral species name and be separate from it by hyphen (*Na-komarovite* is only such case: Mandarino, 1999).

Practically all finds of komarovite series minerals are made in pseudomorphs after vuonnemite, which is not accidentally. Niobium and titanium are ordered in the crystal structure of vuonnemite (Drozdov *et al.*, 1974; Ercit *et al.*, 1998) that caused the stable ratio Nb:Tic ≈ 2. This feature of the vuonnemite crystal structure allows to niobium to accumulate in hyperagpaitic pegmatites separating from close in properties, but significant more widespread titanium. Vuonnemite is an anhydrous hypersodic mineral crystallized in significant amounts at «dry» hyperagpaitic stage of pegmatite formation. At alkalinity decrease and water activity increase, it becomes unstable and easily replaced by numerous other niobium minerals, superseding each other depending of conditions. In general, they are immediate part of pseudomorphs after vuonnemite that is connected to low mobility of Nb^{5+} in relatively low-alkaline hydrothermal solutions (Azarova *et al.*, 2002). Natrokomarovite is one of these minerals. This is a zeolite-like hydrous phase, and it is represented the most probable to crystallize under temperatures not above 200 – 250°C. Thus, komarovite, being the product of decationization of natrokomarovite, must be yet more low-temperature; most likely, it can form under hypergene conditions.

The study of mineral relations in pseudomorphs after vuonnemite from Lovozero by means of electron microscope has shown that komarovite was formed after labuntsovite group minerals and, in its turn, replaced by strontiopyrochlore. On the contrary, in the samples from Khibiny there are late veinlets of nenadkevichite in pseudomorphs after vuonnemite consisting of natrokomarovite, Nb,Ti-oxides, and apatite (probably the latter inherits phosphorus from vuonnemite).

Komarovite series members are concerned to oxosilicates, been characterized by intermediate content of SiO_2 (15 – 19 wt %) between (Nb,Ti)-silicates of the labuntsovite group (35 – 45% SiO_2) and (Nb,Ti)-oxides (pyrochlore group minerals, gerasimovskite — not more than 3 – 5% SiO_2). The place of natrokomarovite in general scheme of the evolution of niobium mineralization in high-alkali pegmatitic-hydrothermal systems, most likely, are caused by following: it arises as an intermediate (and, to all appearances, relatively unstable) product under fluctuations of silica activity in hydrothermalites. The changing of niobium minerals takes place in accordance with the direction of evolution of solutions chemistry. At gradual decrease of activity of SiO_2 the following scheme is realized: niobium members of the labuntsovite group → natrokomarovite → komarovite → oxides (the members of the pyrochlore group, gerasimovskite) as well as under the increase of silica activity there is an inverse order: oxides → natrokomarovite → labuntsovite group minerals. It is not except that presence of silicon in many analyses of pyrochlore, including electron microprobe ones, was caused exactly by presence of komarovite-like fragments.

In conclusion we shall note that easiness of replacement of komarovite series members by minerals of labuntsovite and pyrochlore groups has also structural presuppositions. Natrokomarovite and komarovite contain prepared «construction elements» of these minerals, pyrochlore blocks and silica-oxide rings of labuntsovite type, i. e. the komarovite series is a original «intermediate unit» between pyrochlore and labuntsovite groups not only in chemical but also in structural relation. That gives doubtless energetic advantage at corresponding reactions: in order to transform komarovite into pyrochlore or into labuntsovite-like mineral it is enough to «disassemble» its crystal construction not on «bricks» (atoms), but only on blocks. Perhaps the «decay» of natrokomarovite and komarovite on silicate and oxide minerals, labuntsovite-like mineral and pyrochlore, takes place in nature. The rarity of komarovite series members is most likely explained by easiness of such transformations.

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References

Azarova Yu.V., Pekov I.V., Chukanov N.V., Zadov A.E. Products and processes of alteration of vuonnemite under low-temperature transformations in hyperagpaitic pegmatites // Zapiski VMO. **2002.** № 5. P. 112–121. (Rus.)

Balic'-Zunic' T., Petersen O.V., Bernhardt H.-J. & Micheelsen H.I. The crystal structure and mineralogical description of a Na-dominant komarovite from the Ilimaussaq alkaline complex South Greenland // N. Jb. Miner. Mh. **2002.** № 11. P. 497–514.

Barrer R. Hydrothermal Chemistry of Zeolites. (Gidrotermal'naya Khimiya Tseolitov). Moscow, Mir. **1985.** 420 pp. (Rus.)

Belov N.V. Essays on Structural Mineralogy. (Ocherki po Strukturnoi Mineralogii). Moscow, Nedra. **1976.** 344 pp. (Rus.)

Chukanov N.V. IR-spectra of silicates and aluminosilicates // Zapiski VMO. **1995.** № 3. P. 80–85. (Rus.)

Chukanov N.V., Pekov I.V., Zadov A.E., Voloshin A.V., Subbotin V.V., Sorokhtina N.V., Rastsvetaeva R.K., Krivovichev S.V. Minerals of the Labuntsovite Group. (Mineraly Gruppy Labuntsovita). Moscow, Nauka. **2003.** 323 pp. (Rus.)

Drozdov Yu.N., Batalieva N.G., Voronkov A.A., Kuz'min E.A. Crystal structure of $Na_{11}Nb_2TiSi_4P_2O_{25}F$ // Dokl. Akad. Nauk SSSR. **1974.** V. 216. №1. P. 78–81. (Rus.)

Ercit T.S., Cooper M.A., Hawthorne F.C. The crystal structure of vuonnemite, $Na_{11}TiNb_2(Si_2O_7)_2(PO_4)_2O_3(F,OH)$, a phosphate — bearing sorosilicate of the lomonosovite group // Can. Miner. **1998.** Vol. 36. P. 1311–1320.

Gaines R.V., Skinner H.C.W., Foord E.E., Mason B., Rosenzweig A. Dana's New Mineralogy. 8th Ed. **1997.** John Wiley & Sons Inc., New York. 1819 pp.

Khomyakov A.P. Mineralogy of Hyperagpaitic Alkaline Rocks. (Mineralogiya Ultraagpaitovykh Shchelochnykh Porod). Moscow. 1990. 196 pp. (Rus.)

Krivokoneva G.K., Portnov A.V., Semenov E.I., Dubakina L.S. Komarovite: silificated pyrochlore // Dokl. Akad. Nauk SSSR. **1979.** V. 248. №2. P. 443–447. (Rus.)

Makovicky E. Modularity — different types and approaches // Modular Aspects of Minerals (ed. by S.Merlino). Eur. Miner. Union, Notes in Miner. Budapest. **1997.** P. 315–343.

Mandarino J.A. Fleischer's Glossary of Mineral Species. Tucson. **1999.** 225 pp.

Nechelyustov G.N., Chistyakova N.I. Ion exchange in natural samples of pyrochlore // Miner. Zhurnal. **1986.** V. 8. № 4. P. 57–64. (Rus.)

Pekov I.V. Lovozero Massif: History, Pegmatites, Minerals. Moscow, OP, **2000.** 480 pp.

Pekov I.V., Chukanov N.V., Yamnova N.A., Egorov-Tismenko Yu.K., Zadov A.E. A new mineral kapustinite, $Na_{5.5}Mn_{0.25}ZrSi_6O_{16}(OH)_2$, from Lovozero massif (Kola Peninsula) and new data on genetic crystallochemistry of the lovozerite group // Zapiski VMO. **2003.** № 6. P. 1–14. (Rus.)

Portnov A.M., Krivokoneva G.K., Stolyarova T.I. Komarovite, a new niobosilicate of calcium and manganese // Zapiski VMO. **1971.** № 5. P. 599–602. (Rus.)

Semenov E.I. Mineralogy of Ilimaussaq Alkaline Massif. (Mineralogiya Shchelochnogo Massiva Ilimausak). Moscow, Nauka. **1969.** 164 pp. (Rus.)