NEW DATA ON MINERAL ASSEMBLAGES WITH BITUMINOUS MATTER IN PEGMATITES OF THE KHIBINY MASSIF

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The new occurrences of solid bituminous substances (SBS) have been found in peralkline pegmatites of the Khibiny massif, Kola Peninsula, Russia. Mineral assemblages containing rounded and drop-like segregations of SBS ranging from 1 to 10 mm in size are described. In most cases, SBS are ingrown into the grains of microporous titanium, niobium, and zirconium silicates and locally overgrow their surface. Microinclusions of Th and *REE* minerals frequently occur within the SBS segregations. The new findings confirm a hypothesis of catalytic role of the zeolite-like titanium, niobium, and zirconium silicates to form SBS, as well as key role of organic matters to transfer and concentrate Th and *REE* during hydrothermal stage of the pegmatite formation. At final stage, most thorium and part of *REE* incorporate into mineral phases, which saturate SBS, whereas Ca (occasionally together with part of Th and *REE*) remains in organic phase as carboxylate salts and/or organometallic compounds.
2 tables, 5 figures, 20 references .

Introduction

The solid bituminous substances (SBS) are repeatedly documented in the pegmatite bodies of the Khibiny-Lovozero alkaline complex, Kola Peninsula, Russia. In these bodies, SBS being endogenetic are characteristic components of the late hydrothermal assemblages and frequently form clusters reaching several cm in size (Antonov *et al.*, 1933; Labuntsov, 1937; Sokolova, 1965; Zezin & Sokolova, 1967; Loskutov & Polezhaeva, 1968; Florovskaya *et al.*, 1968; Kostyleva-Labutsova *et al.*, 1972; Pekov, 1998, 2001; Kartashov *et al.*, 2006). Commonly, organic matters are intimately associated with the microporous silicates, which contain Ti, Nb and Zr atoms in heteropolyhedral frameworks: the SBS segregations are ingrown into aggregates of these minerals and overgrow their surface. Since this relation is so stable and clear, we have set up the first hypothesis that the zeolite-like titanium, niobium, and zirconium silicates are catalysts for synthesis of bituminous matter (Chukanov *et al.*, 2005a, b; 2006) all the more so analogous synthetic zeolite titanium, niobium, and zirconium silicate compounds are sorbents of small molecules and effective catalysts for the numerous organic-assisted reactions (see review by Chukanov *et al.* (2004)). It should be noted that peralkaline pegmatites and especially their hydrothermal assemblages are unique objects in abundance and diversity of microporous mineral phases with heteropolyhedral frameworks designed on the basis of SiO_4 tetrahedra and octahedral coordinated atoms of the transitional elements and first of all Ti, Nb, and Zr (Chukanov & Pekov, 2005; Pekov & Chukanov, 2005).

As reported in above cited papers, SBS from the Khibiny pegmatites are generally depleted in sulfur and are enriched in water and derivatives of polycyclic aromatic hydrocarbons containing hydroxyl, carbonyl, and carboxylate groups. During hydrothermal mineralization, they concentrate thorium, as well as alkaline-earth and rare-earth elements. In particular, megascopic clusters of oxidized bituminous matters from the Khibiny pegmatites are usually accompanied with thorium and/or *REE* mineralization. The oxidized SBS with rare high valence (Th, U, *REE*, Nb, Zr, Ti) and alkaline-earth elements are complex microheterogeneous systems containing mineral (the most frequent silicates of thorium and calcite), organometallic (with *REE*, Ca, Sr, Ba), and organic phases, which can be formed in result of decomposition of the primary organometallic substrate at decreasing of temperature. On the other hand, thorium and *REE* minerals formed in peralkaline pegmatites during hydrothermal stage commonly contain numerous inclusions of SBS (in contrast to associated Th- and *REE*-free minerals). As a result, we set up the second hypothesis that oxidized derivatives of polynuclear arenes identified in SBS are complex-forming compounds for Th, *REE*, Ba, Sr, Ca and contribute to the transfer and concentration of these elements at low temperatures.

New findings of SBS in the Khibiny pegmatites described in this paper gave additional data to check both assumptions.

Materials

Pegmatite at Mt. Khibinpakhcorr (Khbp-1). Aegirine-feldspar pegmatite vein hosted in khibinite at Mt. Khibinpakhcorr was found by Z.V. Shluykova in 1959. This vein was traced from West to East for 8 m with thickness ranging from 0.5 to 1.2 m. The western area of the vein is composed of microline, arfvedsonite, aegirine, eudialite, enigmatite, and accessory loparite, whereas central and eastern parts, mainly hydrothermal minerals, including analcime, natrolite, catapleite and others. The labutsevite-group minerals are the most diverse: heterogeneous in composition (with zones sharply enriched in Ca or Sr) colorless crystals of tsepenite-Na and paratsepenite-Na overgrow (local epitactically) orange crystals of the earlier labuntsevite-Mn and lemmleinite-Ba. Microheterogeneous segregations enriched in SBS are mainly hosted in the labuntsevite crystals and less frequent, tsepenite and catapleite. In most cases, they occur as black spherulites up to 1 mm in diameter ingrown into the labutsevite crystals or overgrown their surface.

Pegmatite at Mt. Koashva (Koa-2) developed by quarry in the summer 2005 is subhorizontal 3 m long and 0.5 m thick lens located at the contact between urtite and nepheline-apatite orebody. Mineral assemblages of three stages are recognized in the pegmatite. Potassium feldspar, nepheline, dark grey sodalite, alkaline pyroxene and black amphibole, eudialite, lamprophyllite, and rinkite were deposited during the first stage. Green acicular aegirine, villiaumite, lomonosovite, mineral of the lovozerite group (zircinalite?), chkalovite, fluorcaphite, sphalerite, and a few galena and phlogopite were deposited during the second dry ultraagpaitic stage. Minerals, which replace the earlier phases and crystallize in cavities, are attributed to the third stage. These are natrolite (composes the main part of the pegmatite core), catapleite (occurs as complete pseudomorphs after lovozerite-like mineral), sitinakite, lemmleinite-K, vinogradovite (these three titanium silicates completely replace lomonosovite and crystallize in caverns), lilac fluorapatite (epitactically overgrows fluorcaphite and occurs as sustentative crystals in caverns), astrophyllite, fine-fibre pectolite, umbite (pseudomorphs after eudialite), sazykinaite-(Y), amichite, elpasolite, and unidentified lamellar hydrous (Cu,Fe)-sulfides. Among natrolite and in caverns, there are numerous large (up to 1 cm) segregations of black bituminous substance apparently formed during stage 3. Continuous rims and chains of spherulites of this bituminous substance frequently surround pseudomorphs of catapleite after the lovozerite-group ingrown into natrolite.

Pegmatite at Mt. Kukisvumchorr (Kuk-3). The 10 cm thick vein body mainly composed of natrolite with subordinate aegirine and accessory mackinawite has been developed by the underground working of the Kirovsky Mine (Mt. Kukisvumchorr). This vein cut urtite close to the contact with the nepheline-apatite body and contains the small pods composed of fine-grained segregations of pyrochlore and yellow komarovite-like (Na,Ca)-niobosilicate, which are most likely pseudomorphs after the earlier alkaline niobosilicate (probably vuonnemite). Just these segregations host black bituminous substance with strong resinous to metal-like luster. Aggregates of pyrochlore and (Na,Ca)-niobosilicate are dense "stuffed" by awkward shaped segregations of this substance up to several mm in size.

The sample from **pegmatite at Mt Kukusvumchorr (Kuk-4)** is a fragment of core from the hole drilled in underground working at level +252, Kirovsky Mine. This drill hole crosses pegmatite veinlet composed of microcline with a few black acicular aegirine; marginal parts of this veinlet are enriched in

Fig. 1. Specimen from pegmatite at Mt. Kukisvumchorr (Kuk-4). Bituminous sabstance (dark) overgrows crystal of pyatenkoite-(Y). Photo by N.A. Pekova.

Table 1. **Content of elements with atomic numbers more than 10 in organic phases, wt.%**

Number of analysis	1	2	3	4	5	6	7	8	9
	Pegmatite at Mt. Khibinpakhchorr (Khbp-1)				Pegmatite at Mt. Koashva (Koa-2)		Pegmatite at Mt Kukisvumchorr (Kuk-3)		Pegmatite at Mt Kukisvumchorr (Kuk-4)
Na_2O	bdl	bdl	bdl	bdl	1.65	bdl	bdl	bdl	5.62
K_2O	bdl	bdl	bdl	bdl	0.56	bdl	0.28	1.31	0.96
CaO	3.41	3.54	3.89	3.71	0.69	0.44	bdl	bdl	1.56
SrO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.23
MgO	bdl	bdl	0.79	bdl	bdl	bdl	bdl	bdl	0.21
FeO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.44
ZnO	1.50	1.42	1.48	1.81	bdl	bdl	bdl	bdl	bdl
PbO	bdl	bdl	0.83	bdl	bdl	bdl	bdl	bdl	bdl
Al_2O_3	0.85	0.90	0.67	1.39	0.51	bdl	bdl	bdl	0.27
La_2O_3	6.08	6.66	6.15	6.21	bdl	bdl	bdl	bdl	bdl
Ce_2O_3	0.16	0.44	0.37	0.27	bdl	bdl	bdl	bdl	bdl
Pr_2O_3	1.09	0.66	0.67	0.58	bdl	bdl	bdl	bdl	bdl
Nd_2O_3	2.74	2.59	2.70	2.50	bdl	bdl	bdl	bdl	bdl
Sm_2O_3	0.62	0.09	0.16	bdl	bdl	bdl	bdl	bdl	bdl
ThO_2	bdl	bdl	bdl	bdl	3.84	3.67	bdl	bdl	6.23
SiO_2	bdl	bdl	bdl	1.15	1.88	1.50	bdl	bdl	13.07
S	0.58	0.49	0.43	0.45	1.91	0.41	1.61	2.40	0.38
Cl	bdl	bdl	bdl	bdl	0.66	0.14	bdl	bdl	0.12
$-O=S$	-0.29	-0.24	-0.21	-0.22	-0.95	-0.20	-0.80	-1.20	-0.19
$-O=Cl_2$	–	–	–	–	-0.15	-0.03	–	–	-0.03
Total	16.74	16.55	17.93	17.85	10.60	5.93	1.09	2.51	28.86

Notes: bdl is below detection limit by electron microprobe aegirine and contain nepheline and rinkite. The axial zone of the veinlet comprises white to colorless microcline with a few black acicular aegirine. The walls of cavities located in the axial zone are overgrown by rhombohedral crystals of pyatenkoite-(Y) $Na_5(Y,HREE)TiSi_6O_{18}\cdot 3H_2O$ up to 1.5 mm across. Relationships of *REE* in the Kukisvumchorr pyatenkoite-(Y) are interesting with the predominance of erbium (Pekov *et al.*, 2003) that is rare for minerals from peralkaline massifs. These crystals and surrounding microcline are covered by crusts of brown (to black) solid bituminous substance (Fig. 1). Rounded and drop-like segregations of this substance up to 5 mm in diameter are also occur; numerous small (< 0.1 mm) inclusions of steacyite $Th(Na,Ca)_2K_{1-x}Si_8O_{20}$ have been identified in these segregations.

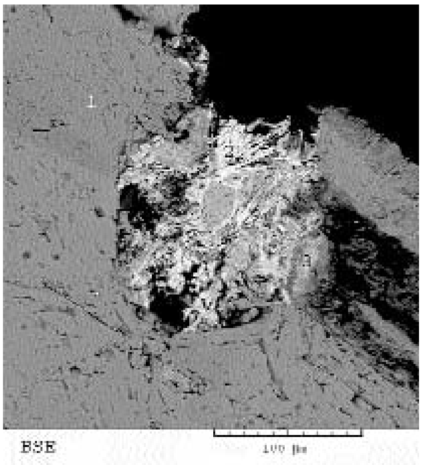

Fig. 2. Specimen from pegmatite at Mt. Khibinpakhchorr (Khbp-1). (1) Labuntsevite-Mn, (2) "Silicooxide of Mn and REE". (3) Rancieite.

Electron microprobe study

Secondary and back-scattered electron images and distribution mapping of selected elements were made with a CamScan MV2300 scanning electron microscope equipped with a YAG-detector of secondary and back-scattered electrons and energy-dispersion system with a Link INCA Energy semiconductor (Si-Li) detector, A.N. Nekrasov, analyst, Institute of Experimental Mineralogy, Russian Academy of Science. During scanning, beam diameter was 0.157 µm at accumulation time of signal in each point of 0.5 ms. An accelerating potential of 20 kV and current intensity of 0.52 – 0.56 nA were used.

The bituminous substances forming inclusions in labuntsevite-Mn (pegmatite Khbp-1, Mt. Khibinpakhchorr) and segregations of SBS from pegmatite at Mts. Koashva (pegmatite Koa-2) and Kukisvumchorr (pegmatites Kuk-3 and Kuk-4) are described in this paper. Like to segregations previously documented by Chukanov *et al.* (2005, 2006), these are microheterogeneous intergrowths with two types of phases: substantially organic and mineral (Figs. 2 – 4). Organic phases are characterized by homogeneous BSE images, low totals of analyses (generally not higher than 20%), and constant presence of sulfur (0.4 – 2.4 wt.%), as well as calcium and/or potassium (Table 1). Mineral phases intergrown with SBS are diverse in chemical composition (Table 2). Si, Mn, *REE*, Th, and alkaline (Na, K), alkaline-earth (ca, Sr, Ba) elements are the most typical components in these phases.

Fig. 3. Specimen from pegmatite at Mt. Khibinpakhchorr (Khbp-1). (1) Labuntsevite-Mn, (2) "Silicooxide of Mn and REE". (3) Ti,Th-silicate.

In contrast to the Khibiny "carbocer" and most other samples of SBS, which we previously described, the high concentration of Th and *REE* were identified not only in mineral phases, but ocassionally, in organic matrix. Organic phase of SBS from pegmatite Khbp-1 concentrates *REE* and is Th-free, with La (6.1 – 6.7 wt.%) being

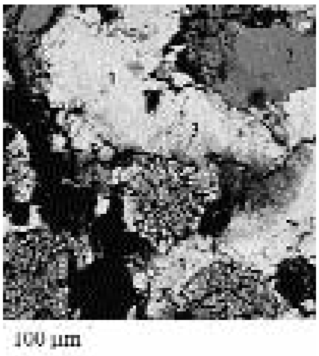

Fig. 4. Specimen from pegmatite at Mt. Koashva (Koa-2). (1) Thorium titanosilicate. (2) Lemmleinite-K. (3) Biotite. Organic matter is dark.

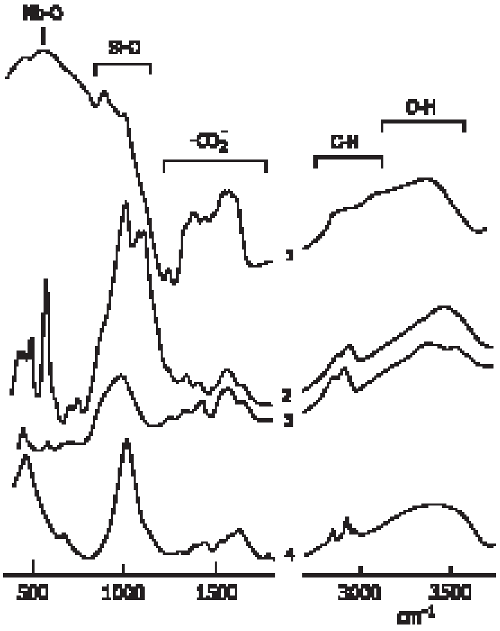

Fig. 5. IR spectra of microheterogeneous segregations with SBS from pegmatites at Mt. Kukisvumchorr (Kuk-3 (1), Kuk-4 (2)) Mt. Koashva (Koa-2 (3)), and Mt. Khibinpakhchorr (Khbp-1 (4)).

dominant among *REE* and Nd (2.5 – 2.7 wt.%) and Pr (0.6 – 1.1 wt.%) being sharply predominated over Ce (0.2 – 0.4 wt. %). SBS from pegmatites Koa-2 and Kuk-4 are enriched in Th and are *REE*-free. Rare elements are absent in organic matter from pegmatite Kuk-3 (Table 1).

Electron microprobe data for mineral phases intimately associated with SBS are given in Table 2. Labuntsevite-Mn $Na_4K_4Mn_2Ti_8(Si_4O_{12})_4(OH,O)_8 \cdot 10H_2O$, lemmleinite-K $Na_4K_8(Ti,Nb)_8[Si_4O_{12}]_4(OH,O)_8 \cdot 8H_2O$, rancieite $(Ca,Mn^{2+})Mn^{4+}{}_4O_9 \cdot 3H_2O$, umbite or kostylevite $K_2ZrSi_3O_9 \cdot H_2O$, and steacyite $(Na,Ca)_2K_{1-x}ThSi_8O_{20}$ (here and further, idealized formulae are given) were identified by composition and partially by infrared spectroscopy. These minerals as well as Nb-rich silicate $(Na,Ca,K)_3(Nb,Ti)_2Si_{1-x}(O,OH)_xF \cdot nH_2O$, thorium titanosilicates $(K,Ba)_{1.5}(Ca,Na)(Th,REE)(Ti,Nb)_3(Si,Al)_8(O,OH)_x \cdot nH_2O$ and $NaCaK_{0.5}MnTh_4REE_{1-x}(Ti,Nb)_2Si_8(O,OH)_x \cdot nH_2O$, and silicate of zinc and thorium $(Na,Ca,K)_2(Zn,Ti)_2Th_4REE(Si,Al)_8(O,OH)_x \cdot nH_2O$ are stoichiometric and their formulae are calculated with coefficients close to integral. The compositions of so called Mn and *REE* silicooxide (Table 2, analyses 4 – 6) probably attributed to cryptocrystalline mixtures are variable and are characterized by low totals.

Both Th and *REE* are present in minerals of pegmatite Khbp-1. Like to content of rare earth elements in the intergrown organic phases, *REE* in minerals are characterized by the La maximum. Rare elements in the mineral phases and SBS from pegmatites Koa-2 and Kuk-4 are dominated by thorium (30.7 – 46.8 wt.%), but in the sample from pegmatite Koa-2, *REE* (4.6 – 6.9 wt.%) with the Ce maximum are present. Thorium is absent in the mineral phases from pegmatite Kuk-3, but a few *REE* (2.55 – 3.19 wt.%) with predominance of Ce is observed in these phases.

According to composition of organic substances and comparison with composition of intimately associated mineral phases from the same pegmatites, rare elements can be concluded to tend forming proper mineral phases. However, in contrast to carbocer and some other microheterogeneous segregations with SBS (Chukanov *et al.*, 2005a, 2005b, 2006), the clear fractionation of rare elements between different organic and mineral phases is not observable.

Infrared spectroscopy

Infrared spectra of samples in KBr disks were measured on a Specord 75 IR dual-beam spectrophotometer. Spectrum of the pure KBr disk was deducted during recording in automatic mode.

The most reliable diagnostic feature of the hydrocarbon groups is the relatively narrow bands of C-H-stretching vibrations within range 2800 – 3100 cm^{-1} in the infrared spectrum, with the doublet within range 2840 – 2980 cm^{-1} corresponding to the aliphatic groups CH_2 and CH_3. The symmetric stretching vibrations of the methylene and methyl groups have wavenumbers 2843 – 2863 and 2860 – 2870 cm^{-1}, respectively, while asymmetric stretching vibrations, 2916 – 2936 and 2952 – 2972 cm^{-1}, respectively. The C-H bonds pertaining to unsaturated hydrocarbon groups (in alkenes and aromatic compounds) are characterized by the increased frequencies of the stretching vibrations (2990 – 3110 cm^{-1}). The band with the absorption maximum at 2835 cm^{-1} is characteristic of methoxygroup O-CH_3 linked to the aromatic ring.

Numerous absorption bands within range 1210 – 1740 cm^{-1} are the most reliable feature of

Table 2. **Chemical composition of mineral phases intergrown with SBS**

Number of analysis	1	2	3	4	5	6	7
	Pegmatite at Mt. Khibinpakhchorr (Khbp-1)						
Na_2O wt.%	5.64	4.73	0.88	bdl	bdl	bdl	bdl
K_2O	7.07	6.74	3.19	bdl	bdl	bdl	bdl
CaO	bdl	bdl	2.12	0.39	0.52	0.54	3.87
BaO	10.19	12.17	4.04	1.64	1.25	0.68	3.20
MnO	2.50	2.37	1.18	30.56	28.74	29.62	64.20
FeO	0.59	0.78	0.58	8.65	10.90	11.01	0.64
ZnO	bdl	bdl	bdl	0.87	0.71	0.84	0.60
Al_2O_3	bdl	bdl	0.72	2.99	3.64	3.60	bdl
La_2O_3	bdl	bdl	2.03	3.92	4.27	3.71	bdl
Ce_2O_3	bdl	bdl	1.66	1.18	1.42	1.60	bdl
Pr_2O_3	bdl	bdl	0.35	1.05	0.65	1.32	bdl
Nd_2O_3	bdl	bdl	1.46	3.55	2.83	3.54	bdl
ThO_2	bdl	bdl	8.49	bdl	0.56	bdl	bdl
SiO_2	40.56	38.94	30.51	4.32	6.51	6.20	bdl
TiO_2	26.37	23.98	11.15	0.83	0.59	0.57	bdl
Nb_2O_5	1.03	3.54	5.37	bdl	bdl	bdl	bdl
Total	94.27	93.57	73.73	60.37	63.32	64.00	74.59
Na apfu	4.32	3.77	0.43	–	–	–	–
K	3.56	3.52	1.04	–	–	–	–
Ca	–	–	0.57	0.38	0.34	0.38	0.66
Ba	1.58	1.97	0.40	0.60	0.29	0.17	0.09
Mn	0.83	0.83	0.26	24.02	14.94	16.16	4.04
Fe	0.21	0.28	0.13	6.70	5.60	5.93	0.04
Zn	–	–	–	0.60	0.33	0.40	0.03
Al	–	–	0.22	3.26	2.63	2.72	–
La	–	–	0.19	1.34	0.96	0.88	–
Ce	–	–	0.15	0.40	0.31	0.38	–
Pr	–	–	0.03	0.36	0.15	0.31	–
Nd	–	–	0.13	1.18	0.62	0.81	–
Th	–	–	0.50	–	0.08	–	–
Si	16.00	16.00	7.78	4.00	4.00	4.00	–
Ti	7.83	7.41	2.14	0.58	0.28	0.28	–
Nb	0.18	0.65	0.62	–	–	–	–
Basis of calculation	Si=16	Si=16	Si+Al=8	Si=4	Si=4	Si=4	Total cations =5

Notes: Labuntsevite-Mn (1, 2), Ti,Th-silicate (3), hydrous silicooxide? (4-6), rancieite (7), lemmleinite-K (8), umbite or kostylevite (9), Ti,Th-silicates (10-12), Zn,Th-silicate (13), Nb-rich silicate (14-16), and steacyite (17). These minerals are also contain SrO (7 - 1.23, 14 - 5.22, 15 - 3.49), MgO (1 - 0.23, 2 - 0.32, 7 - 0.85, 11 - 0.72), ZrO_2 (9 - 24.10), Cl (4 - 0.54, 5 - 0.94, 6 - 1.00), -O=Cl_2 (4 - 0.12, 5 - 0.21, 6 - 0.23), F (14 - 5.59, 16 - 4.57), -O=F2 (14 - 2.35, 16 - 1.92); apfu are as follows Sr (7 - 0.05, 14 - 0.20, 15 - 0.14); Mg (1 - 0.18, 2 - 0.21, 7 - 0.09, 11 - 0.35), Zr (9 - 3.23); Cl (4 - 0.85; 5 - 0.98; 6 - 1.09); F (14 - 1.13, 16 - 1.13). bdl is below detection limit by electron microprobe.

Number of analysis	8	9	10	11	12	13	14	15	16	17
			Pegmatite at Mt. Koashva (Koa-2)				Pegmatite at Mt Kukisvumchorr (Kuk-3)			Pegmatite at Mt Kukisvumchorr (Kuk-4)
Na_2Owt.%	4.49	1.19	2.12	2.42	1.57	1.54	10.44	9.42	9.56	4.41
K_2O	14.67	19.66	1.05	2.09	1.03	0.77	1.57	1.90	1.83	3.93
CaO	bdl	bdl	1.25	1.90	2.24	1.52	10.56	10.93	11.55	5.41
BaO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	bdl	bdl	2.54	6.37	2.95	bdl	bdl	bdl	bdl	bdl
FeO	bdl	bdl	bdl	bdl	bdl	bdl	0.78	1.41	0.91	0.77
ZnO	bdl	bdl	bdl	bdl	bdl	4.83	bdl	bdl	bdl	bdl
Al_2O_3	bdl	bdl	0.58	bdl	bdl	0.84	bdl	bdl	bdl	bdl
La_2O_3	bdl	bdl	0.99	1.44	0.68	1.70	bdl	1.19	0.58	bdl
Ce_2O_3	bdl	bdl	2.62	3.36	3.09	3.81	bdl	2.00	1.72	bdl
Pr_2O_3	bdl	bdl	bdl	0.40	0.75	0.15	bdl	bdl	0.25	bdl
Nd_2O_3	bdl	bdl	0.95	0.87	1.48	1.26	bdl	bdl	bdl	bdl
ThO_2	bdl	bdl	40.46	35.06	46.83	45.02	bdl	bdl	bdl	30.69
SiO_2	39.29	43.63	19.82	24.02	22.39	19.07	3.67	9.85	11.80	53.62
TiO_2	16.81	3.57	3.05	8.22	5.67	1.32	5.59	6.88	6.27	bdl
Nb_2O_5	17.80	2.93	1.47	4.24	2.37	bdl	59.55	54.60	46.00	bdl
Total	93.06	95.08	76.92	91.11	91.05	81.83	100.62	101.67	93.12	99.79
Na apfu	3.55	0.16	1.60	1.57	1.09	1.19	1.30	1.23	1.45	1.28
K	7.62	1.73	0.52	0.89	0.47	0.39	0.13	0.16	0.18	0.74
Ca	–	–	0.52	0.68	0.87	0.65	0.73	0.79	0.97	0.86
Ba	–	–	–	–	–	–	–	–	–	–
Mn	–	–	0.84	1.80	0.89	–	–	–	–	–
Fe	–	–	–	–	–	–	0.04	0.08	0.06	0.09
Zn	–	–	–	–	–	1.43	–	–	–	–
Al	–	–	0.27	–	–	0.39	–	–	–	–
La	–	–	0.15	0.18	0.09	0.25	–	0.03	0.02	–
Ce	–	–	0.37	0.41	0.40	0.55	–	0.05	0.05	–
Pr	–	–	–	0.05	0.09	0.03	–	–	0.01	–
Nd	–	–	0.14	0.11	0.19	0.18	–	–	–	–
Th	–	–	3.59	2.66	3.81	4.09	–	–	–	1.04
Si	16.00	3.00	7.73	8.00	8.00	7.61	0.56	0.66	0.93	8.00
Ti	5.14	0.19	0.90	2.06	1.53	0.39	0.27	0.35	0.37	–
Nb	3.27	0.09	0.26	0.64	0.39	–	1.73	1.65	1.63	–
Basis of calculation	Si=16	Si=3	Si+Al=8	Si+Al=8	Si+Al=8	Si+Al=8	Ti+Nb=2	Ti+Nb=2	Ti+Nb=2	Si=8

aromatic compounds with the O-bearing groups. In particular, the series of bands within range 1370 – 1600 cm^{-1} is attributed to the C-C-stretching vibrations in the aromatic rings. The carboxylate groups CO^{2-} absorb within ranges 1550 – 1670 cm^{-1} (antisymmetric stretching vibrations) and 1280 – 1430 cm^{-1} (symmetric stretching vibrations). These groups present in most segregations of SBS from Khibiny. Bonds C = O (carbonyl and carboxylate groups including dimers of carbonic acids) have characteristic bands at 1690 – 1740 cm^{-1} (Smith, 1979).

According to infrared spectroscopy, all studied microheterogeneous aggregates with SBS contain both aliphatic hydrocarbons and oxidized aromatic compounds, but in different proportions (Fig. 5).

The aromatic compounds with the carboxylate groups are predominant in the sample from pegmatite Kuk-3. The amount of bonds of hydrogen atoms with the aromatic hydrocarbon ring (shoulder at 3100 cm^{-1}) is insignificant; there are side aliphatic groups (broad shoulder within range 2800 – 2900 cm^{-1}).

The SBS from pegmatites Khbp-1, Koa-2, and Kuk-4 are assigned to the intermediate type. The significant amount of the aliphatic hydrocarbon groups presents in them along with the oxidized unsaturated organic compounds. The position of the strongest band of the C-H-stretcing vibrations (2910 – 1932 cm^{-1}) indicates the presence of the polymethylene chains $(CH_2)n$ in these samples.

The bands of O-H- and Si-O-stretching vibrations (ranges 3200 – 3700 and 880 – 1200 cm^{-1}, respectively) present in each studied sample of the bituminous matter. The silicate component is the substance with the isolated SiO_4 groups (Kuk-3, band at 897 cm^{-1}), steacyite (Kuk-4), and silicates with polymerized SiO_4 tetrahedra (Koa-2 and Khbp-1, bands at 986 и 1020 cm^{-1}, respectively). The strongest broad band at 567 cm^{-1} in the sample from pegmatite Kuk-3 is characteristic of niobium and titanium silicates with $(Nb + Ti):Si > 1$ and with pyrochlore-like block (komarovite, natrokomarovite, belkovite, fersmanite, and probable mongolite) in their structures. These mineral phases may be considered as intermediate between silicates and titano-niobates. The major mineral phase with $(Nb + Ti) >> Si$ (Table 2, analyses 14 – 16) from intergrowths with SBS in pegmatite Kuk-3 is most probable attributed to this type.

Discussion

Comparison with previous data reveals common and distinct features assigned to the studied objects. The common features are:

1. Relation of SBS to microporous titanium, niobium, and zirconium silicates. In the sample from pegmatite Khbp-1, microscopic segregations of SBS occur within crystal of labuntsevite-Mn. Megascopic segregations of SBS in the sample from pegmatite Koa-2 contain microscopic umbite or kostylevite, as well as lemmleinite-K. In pegmatite Kuk-3, SBS are intimately associated with Nb-rich silicate and in pegmatite Kuk-4 overgrow titanosilicate pyatenkoite-(Y).
2. Presence of miscroscopic mineral phases containing *REE* and/or Th: titan-thorium and zinc-thorium silicates, Mn and *REE* silicooxide, Nb-rich silicate, and steacyite.
3. Microheterogeneous structure of the bituminous clusters (intimate intergrowths between SBS and mineral phases are observed).
4. Presence of sulfur in organics.

In most previously reported bituminous matters from peralkaline pegmatites, high valence rare elements (Ce, La, Nd, Y, Th, U, and Ti) are incorporated into inclusions of microscopic mineral phases, whereas the organic matrix mainly contains alkaline-earth elements, with the high grade of interphase partitioning of rare elements being observable (Chukanov *et al.*, 2005a, 2006). In the above described assemblages, this partitioning is not so pronounced, with presence of large amount of *REE* (pegmatite Khbp-1) or Th (pegmatites Koa-2 and Kuk-4) in organics being observed.

The term carbocer was previously noted as ineffectual in regard to hydrothermal rocks from pealkaline massifs of Kola Peninsula, because *REE* were falsely determined instead of Th (Chukanov *et al.*, 2003) in primary described material (Labuntsov, 1937). The finding of SBS containing 10 wt.% REE_2O_3 in pegmatite Khbp-1 (Table 1) allows a rehabilitation of the term carbocer. According to above data, in considered objects, both the crystal chemical mechanism and affinity of the different type organic molecules to definite metals can be suggested to work during fractionation of elements similar in properties between phases (including separation of Th from *REE* and fractionation of lanthanides).

Above mentioned data confirm previous conclusion that the evolution of the carbonic matters during hydrothermal stage of the formation of peralkaline pegmatites is intimately related to Th, *REE*, Ti, Zr, and Nb, which are generally distinguished by the low activity and mobility at low temperatures. In this case, the conclusion by V.I. Vernadsky (1954) with regard to geochemistry of such elements is representative. Let us cite it with small breviaries:

> *"The whole geochemistry of thorium is defined by its attractive feature differing this element from uranium... Thorium pertains to the chemical elements, which are out of geochemistry of water, rather geochemistry of aqueous solutions. It does not go into solution and does not enter aqueous equilibriums of the Earth, and it should be assumed that its concentration in the Earth environment must be poor... In this regard, it pertains to paragenetic chemical elements to which Zr, Hf, ..., elements of rare earths, Nb, and Ta are attributed. For thorium... both vadose minerals crystallized from aqueous solutions and hydrothermal ones"*

It is important that along with thorium, Vernadsky distinguishes *REE*, Zr, Nb (Ti can be added to them) as elements "out of geochemistry of aqueous solutions". At first sight, this conclusion conflicts with the prevalence of so called "amphoterosilicates" (essentially alkaline hydrous titanium, zirconium and niobium silicates, which are zeolite-like minerals with low-dense heteropolyhedral frameworks), as well as *REE* and Th minerals in hydrothermal assemblages of the Khibiny-Lovozero complex. This contradiction is withdrawn if take into account that Vernadsky did not consider an opportunity of transport of low mobile elements in aqueous medium as complexes with hydrophilic ligands.

Probable mechanisms for participation of organic matters to transfer rare elements (mainly Th and *REE*) in hydrothermal rocks of the Khibiny-Lovozero complex can be defined subject to observed paragenetic relationships between organic and mineral phases in these objects. In particular, above described parageneses confirm the clear spatial relation between the segregations of condensed organic substance, amphoterosilicates, and *REE* and Th minerals. The SBS overgrowths of aggregates of titatium, niobium, and zirconium minerals, microscopic ingrowths of organics into thorium minerals of hydrothermal stage, and rims enriched in SBS around *REE* minerals testify this. By analogy with the synthetic microporous matters with heteropolyhedral frameworks, titanium, niobium, and zirconium silicates in pegmatite are suggested to be catalysts of polymerization, reforming, and selective oxidizing to form oxygen-bearing SBS from the low-molecular hydrocarbons. At the same time, the participation of organic matters to transport not only thorium and rare earth elements, but Ti, Nb, and Zr should not be excluded. Both crystallization of minerals of the elements, which are low mobile in aqueous medium and ingrowths of microscopic phases containing these elements in SBS indicate this. Thus, the new data (Tables 1, 2) confirm the hypothesis of the intimate genetic relationship of Th, *REE*, Ti, Nb, and Zr with the bituminous substances in the late derivatives of peralkaline plutons. At the late hydrothermal mineralizing stage of the Khibiny massif, the SBS concentrate Th, *REE*, Ti, Nb, and Zr. This relationship is very important for geochemistry of thorium. Relation of these elements to SBS can be explained by their ability to form the stable complex compounds with organics formed at the late hydrothermal stage. The rise of these compounds favours transport, concentration, and separation of Th, *REE*, Ti, Nb, and Zr at low temperature.

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