

On the Problem of the Formation and Geochemical Role of Bituminous Matter in Pegmatites of the Khibiny and Lovozero Alkaline Massifs, Kola Peninsula, Russia

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Abstract—Solid bituminous matter (SBM) typically occurs in the late hydrothermal assemblages of pegmatites of the Khibiny and Lovozero massifs, being confined to a microporous framework Ti-, Nb-, and Zr-silicates, which are sorbents of small molecules and efficient catalysts of the polymerization, reforming, and selective oxidation of organic matter. Bituminous matter from the pegmatites of the Lovozero Massif typically have elevated contents of aliphatic hydrocarbons, sulfur, and sodium, but are depleted in oxygen and trace elements. SBM from the pegmatites of the Khibiny Massif are depleted in sulfur and enriched in oxygen-bearing derivatives of polycyclic aromatic hydrocarbons. Being complexing agents for Th, REE, Ba, Sr, and Ca, they play a key role in the transfer and accumulation of Th and in the accumulation of alkali earth and rare earth elements during the hydrothermal stage of mineral formation. Oxidized SBM bearing rare and alkali earth elements are complex microheterogeneous systems, which contain mineral (Th silicates, calcite, etc.), metalorganic (with REE, Ca, Sr, Ba), and predominantly organic phases formed by the exsolution of initial metalorganic material with decreasing temperature.

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INTRODUCTION

Alkaline rocks often have elevated contents of hydrocarbon gases and condensed organic matters. In particular, the average carbon content in these compounds in the rocks of the Khibiny Massif is as high as 0.04 wt % and increases by one order of magnitude in the ijolite–urtites altered by postmagmatic processes, whereas the host Precambrian rocks contain, on average, 0.005–0.01 wt % organic carbon, with the highest values being no more than 0.04 wt % [1].

The gases extracted from closed pores in the Khibiny alkaline rocks (averaged sample over the massif) contain 16.5 cm³/kg hydrocarbons, and microinclusions in the alkaline rocks of the Lovozero Massif contain from 3.8 to 18.3 cm³/kg gases [2], maximally >100 cm³/kg [3].

It was repeatedly noted that the pegmatites and postmagmatic rocks of the Khibiny and Lovozero massifs are significantly enriched in organic carbon compared with the magmatic rocks and often contain even visible aggregates of solid bitumenlike matter (SBM). The pegmatites of the two agpaitic massifs contain practi-

cally all types of solid, liquid, and gaseous carbonaceous compounds, as well as graphite and amorphous carbon [1, 4–9]. This can be exemplified by pegmatite veins with villiaumite–carbonate mineralization in the Khibiny rischorrite, which were cut by the Kirovsk underground mine at Mount Kukisvumchorr. Mineralized cavities in the pegmatites contain natroxalate crystals and spherules of black SBM, which are associated with soda minerals, thorium carbonate (tuliokite), zeolite, vinogradovite, fersmanite, rasvumite, and others.

In terms of physical properties and content of fractions soluble in organic solvents, solid and viscous bituminous matters in the Khibiny pegmatites are divided, by analogy with bitumens from other rocks [10, 11], into anthraxolite, impsomite, albertite, asphaltite, asphalt, and maltha [1, 12]. The most abundant type of solid hydrocarbons in postmagmatic rocks is kerite, which occurs as two varieties: impsomite (higher kerite) and albertite (lower kerite). For instance, impsomite was found among the products of hydrothermal alteration of eudialyte, lomonosovite, and delhayelite in a giant peg-

matite of the Material'naya adit at Mount Yukspor, Khibiny. The impsonite content in the rocks reaches, in places, 20–30%. The largest aggregates (up to 5 mm) and abundant accumulations were found in close association with natrolite, murmanite, nenadkevichite, etc. in a feldspar–sodalite–natrolite pegmatite vein at the Kukisvumchorr deposit [1, 6]. The Khibiny impsonites have an elevated ash content (typically 5–10%).

The carbonaceous matter in the Khibiny pegmatites is able to accumulate REE. This can be exemplified by so-called carbocer, which was first described in natrolitized pegmatite from the upper reaches of the Lopar valley. The soluble fraction of the carbocer ash contains 8.2% REE₂O₃ [13]. According to [1], the *carbocer* contains 71.94% C, 7.01% H, 1.12% N, 0.12% S, and 18.98% O at 15% ash (the ash composition was not published). The high-ash SBM from the natrolitized pegmatite vein at Mount Kukisvumchorr [14] contains 7.2% ThO₂ and only 1.1% REE₂O₃, while the main mass consists of amorphous organic matter (57–60% C, 5.1% H) and water (22–33%).

Organic matter is also abundant in the late derivatives of the alkaline rocks of the Lovozero Massif, in which it forms macroscopically discernible aggregates. The SBM-bearing objects can be exemplified by two large hydrothermally altered pegmatite bodies at Mount Alluaiv: the Shomiokitovoe body with yttrium and oxalate mineralization, unique for agpaite rocks, and the El'piditovoe body [15]. Both of the bodies contain abundant SBM aggregates in association with microporous zeolitelike Ti-, Nb-, and zirconosilicates (korobitsynite, nenadkevichite, elpidite, etc.).

Many researchers believe that hydrocarbon gases in these massifs were synthesized abiogenically from CO, CO₂, H₂, and H₂O mainly during the magmatic stage [1, 4, 5, 16, 17], though some authors (for example [18]) admit that organic matters could be partially extracted from host rocks. Recent data [19] suggest a possible mantle source for methane and heavy hydrocarbons (alkanes, polycyclic aromatic hydrocarbons, and others).

Geological conditions of occurrence indicate that gases and SBM in the Khibiny and Lovozero massifs are of an abiogenic origin and were formed syngenetically with alkaline rocks and their derivatives. In particular, the contents of hydrocarbon gases correlate with the chemical composition of the rocks, in particular, with the Al content, which could have served as a catalyst in methane synthesis. Young veins and fault zones cutting across the massifs contain only insignificant amounts of these gases [5]. In addition, the types of carbonaceous matter, like mineral assemblages, show regular changes from the magmatic through pegmatite and hydrothermal stages [1].

The organic compounds of the Khibiny and Lovozero massifs have been studied by many geologists [1, 4, 5, 6, 7, 14, 16, 20–24]. According to isotopic data of Kogarko with coauthors [23], the alkaline magma of

Khibiny was not contaminated with crustal material. Based on the carbon isotope composition of the alkaline rocks of the Khibiny, Lovozero, and Ilimaussaq massifs, Galimov and Petersil'e [21] concluded that primary carbon in the magmatic melts originated from mantle graphite carbon. In [22], the authors noted that bitumens and gases were derived from endogenous carbon of different sources. Elementary carbon (graphite) is enriched in C¹³ ($\delta C^{13} \approx -0.7$) relative to bound carbon occurring as compounds or alloys, i.e., carbides ($\delta C^{13} \approx -2.4$). Kogarko with coauthors [24] studied gases entrapped by eudialyte from the III intrusion phase of the Lovozero Massif. When determining the composition of the gas phase of the inclusions and calculating thermodynamic parameters, the authors solved the problem of the coexistence of a gas mixture of CH₄, H₂, and N₂ with minerals of agpaite nepheline syenites bearing significant amount of the oxidized forms of the elements. The authors suggested that such aqueous solutions were formed by the accumulation of volatiles in the residual melt, and this gradually led to the transition from a silicate melt to a fluid. Thus, the initial aqueous fluid bearing significant amounts of CH₄ and H₂ can release water during late magmatic stages, when minerals of the alkaline rocks are hydrated and a single fluid is split into two phases, predominantly aqueous liquid and gas, which accumulates the most volatile components (CH₄, H₂, N₂). The exsolution of reduced fluid is also facilitated by a significant decrease in CH₄, H₂, and N₂ solubility in the aqueous phase with decreasing temperature. Thus generated reduced gas with high H₂ and CH₄ contents should have been in disequilibrium with minerals of the alkaline rocks. However, the rate of redox reactions with fluid participation sharply decreases at temperatures lower than 350–300°C (as follows from kinetic and isotopic data on hydrothermal solutions) thus preventing an equilibrium to be attained. The initial fluid could form at temperatures higher than 400°C and contained significant amounts of CO₂, which interacted with H₂ during subsequent cooling to form CH₄ [24]. The latter could then produce more condensed hydrocarbons [3, 5, 16].

The formation of methane during the magmatic stage could be governed by one of the following reactions: $C + 2H_2 \rightarrow CH_4$ [5]; $4CO + 2H_2O \rightarrow CH_4 + 3CO_2$ [17]; $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ [25]. Then methane could generate more complex carbon-bearing compounds. From the viewpoint of the catalytic synthesis of hydrocarbons, the high content of amorphous soot carbon in the agpaite rocks can be explained by its precipitation on possible catalyst minerals (nepheline and other aluminosilicates), a process similar to surface catalyst spoiling, which is well known in organic synthesis [1, 5].

A brief review of the literature data demonstrates a trend in the transformation of organic matter during the evolution of alkaline massifs, from the magmatic to the

hydrothermal stages. However, most papers devoted to this problem consider hydrocarbon gases in magmatic rocks, whereas data on bituminous matter in pegmatites are still scarce. Our research was centered on paragenetic relations, microstructure, and the chemical and phase composition of SBM from the late hydrothermal associations, which are the last in the evolution of pegmatite systems related to the agpaite alkaline rocks of the Khibiny and Lovozero massifs. It is important to mention that bituminous matter is universally confined to aggregates of zeolitelike microporous aqueous Ti-, Nb-, and Zr-silicates, which can be regarded as catalysts in the polymerization and other complex transformations of organic compounds. The material presented below also demonstrates the universal and close association of SBM with La, Y, and Th minerals, indicating the important role of organic matter in the transfer and accumulation of Th and REE during the low-temperature stages of the formation of alkaline pegmatites.

SAMPLES

We studied a representative collection of SBM from various hydrothermal assemblages related to the pegmatites of the Khibiny and Lovozero massifs.

Samples (1–4), carbocer, were collected by A.N. Labuntsov in zeolitized pegmatites among rischorrites of the Khibiny Massif and were donated to the Fersman Mineralogical Museum, Russian Academy of Sciences (MM RAS) in 1939–1946. These samples were described in detail in [13, 14, 20]. Carbocer in all the samples forms brittle, black, and irregularly shaped or spherical aggregates up to 4–5 mm in size, with a dull fracture. The sampling localities according to the labels were as follows.

Sample 1 (no. 40749, MM RAS) was taken from the third tributary of the Vuonnemiok River.

Sample 2 (no. 41426, MM RAS) was taken from a rinkolite–natrolite vein (Mount Kukisvumchorr, slope of the Lopar valley).

Samples 3 and 4 (nos. 41156, 44322, MM RAS) are from lovchorrite–apatite vein, Mount Apatitovaya, slope of the Lopar valley.

The carbocer in sample 1 from the Vuonnemiok River valley associates with astrophyllite, pectolite, and yuksporite [20]. The carbocer in sample 2 closely associates with white powdery tetranatrolite (our data).

Sample 5 was kindly given by M. N. Sokolova, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (original no. 1333). The sample was taken from the Kirovsk underground mine, Kukisvumchorr apatite deposit, Khibiny. The mineral assemblage was described in detail in [6, 7]. In this paper, we studied a drop-shaped aggregate of bituminous matter 2.4 × 1.4 mm in size with a dull surface, which was extracted from an altered nenadkevichite

aggregate. It has a lustrous surface and is dull on the fracture surface and black in color.

Sample 6 (Mount Eveslogchorr, Khibiny) is a dark-gray spherical aggregate ~5 mm in size, dull on the fracture surface, and was found in coarse-columnar natrolite. Other associated minerals are albite, analcime, barite, leifite, thorite, and diverse minerals of the labuntsovite group [vuoriyarvite-(K), kuzmenkoite-(Zn), paratsepinite-(Ba), and tsepinite-(Ca)].

Sample 7 from the Ileritovoe pegmatite body (Kirovsk underground mine, Mount Kukisvumchorr, Khibiny) forms dark-brown rounded aggregates of SBM up to 1 mm in size in cavernous natrolite. The pegmatite is located among ijolite–urtites and shows a wide diversity in mineral composition. We found 70 (!) mineral species there, more than two-thirds of which belonging to hydrothermal assemblages, and occurring mainly in small cavities. These are Ti, Nb oxides (anatase, pyrophanite, pyrochlore, franconite), zeolites (gobbsite, natrolite, phillipsite), carbonates, including REE varieties (ankerite, ancylite-(La), burbankite, dawsonite, donnayite, calcite, carbocernaite, cordylite-(Ce), kukharenkoite-(La), mckelveyite, synchysite-(Ce), and srontianite), microporous Ti, Nb, and Zr silicates (vuoriyarvite-(K), gaidonnayite, hilairite, catapleiite, kukisvumite, labuntsovite-(Mg), labuntsovite-(Mn), nenadkevichite, tsepinite-(K), and elpidite), sulfides, and many other minerals, in particular, thorite.

Sample 8 consists of rounded brown and black aggregates in the core of a borehole drilled in an underground pit of the Kirovsk mine. The aggregates associate with pyatenkoite-(Y), microporous titanosilicate, $\text{Na}_5(\text{Y}, \text{HREE})\text{TiSi}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$. REEs contained in pyatenkoite-(Y) are dominated by Er, which is rare for minerals of agpaite massifs [15].

Samples 7 and 8 were provided for us by courtesy of A.S. Podlesnyi.

Sample 9 was taken from Mount Koashva, Khibiny. Rounded aggregates (up to 5 mm in size) of the coal-black organic matter were found in the cavernous aegirine–pectolite–natrolite aggregate in the core of a large pegmatite body located at the contact of urtites with the agpaite body. The bituminous compounds are either included in massive natrolite or occur in cavities, where they are rimmed by late aegirine and natrolite. The accompanying minerals are sodalite, arctite, belovite-(Ce), fluorcaphite, partially altered lomonosovite, magnesioastrophyllite, lamprophyllite, amphibole, and sphalerite. The latest minerals are microporous hydrous Zr, Ti, and Nb silicates: sazykinaite-(Y), catapleiite, sitinakite, lemmleinite-K (including pseudomorphs after lomonosovite), as well as rhabdophane-(Ce).

Samples 10 and 11 were taken from a hydrothermally altered zone of the large Shomiokitovoe pegmatite body, Mount Alluaiv, Lovozero [26], which cuts across lujavrites, foyaites, and urtites of the differentiated complex. This body is noted for extremely high contents of Y and HREE accumulated in shomiokite-(Y)

$\text{Na}_3(\text{Y,HREE})(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$, as well as for having abundant soda and oxalate mineralization. Our samples are pitch-black drop-shaped aggregates up to 3 mm in size. In one case, they occur on the walls of a cavity in a sidorenkite–aegirine–albite rock, overgrowing the minerals, and on quartz, sphalerite, microporous Zr, and (Ti,Nb) silicates (elpidite and korobitsynite). The precipitation of organic matter was followed by trona crystallization. In other samples, organic matter occurs as a cavernous aggregate composed mainly of albite, with subordinate aegirine, shortite, sphalerite, epididymite, rhodochrosite, and microporous Ti and Nb silicates, such as vinogradovite (pseudomorphs after lomonosovite), korobitsynite, and nenadkevichite; the interstitial space is filled with powdered nahpoite.

Samples 12 and 13 taken from the El'piditovoe hydrothermally altered pegmatite body, Mount Alluaiv, Lovozero [26], which is hosted by the same rocks of the differentiated complex, are pitch-black spherical aggregates 2–3 mm across, brittle, brilliant on the fracture surface, which grow on albite combs, elpidite crystals, and massive, fine-grained pore aggregates of hydrous Fe and Na titanosilicate. The latter mineral is abundant in the hydrothermal zone of this pegmatite, but is poorly studied because of its small size.

Sample 14 was taken from a core of the large “dry” ultraaluminous Palitra pegmatite, which was recently penetrated by the underground mine at Mount Kedykverpakhk, Lovozero. The pegmatite was only insignificantly altered by late hydrothermal processes. The hydrous minerals (natrolite, ussingite, analcime) occur in subordinate amounts, but the anhydrous phases, including those soluble in water or easily hydrolyzing, are very diverse: villiaumite, natrosilite (in rock-forming amounts), lomonosovite, vuonnemite, kazakovite, manaksite, and others. Organic matter, which closely associates with sodalite, ussingite, natrosilite, villiaumite, manaksite, serandite, nordite, barioolite, chkalovite, sphalerite, and others, forms black rims up to 1 mm thick around grains of poorly studied Na, Th silicate.

METHODS AND INVESTIGATION RESULTS

Chemical Composition of Bituminous Matters

Although chemical composition of SBM from alkaline rocks was studied quite extensively, only the contents of light elements (H, C, N, O) and S are published in most of the papers. The compositions of bituminous matter from different rocks, including those from pegmatites of the Khibiny Massif, are summarized in [1]. The following variations of major components in the organic constituent of bituminous matter from pegmatites are reported (in wt %): from 64 (oxidized oillike matter) to 87 (antraxolite) C; from 4 (antraxolite) to 12 (oily bituminoids) H, from 0.8 to 1.2 N, and from 5 to 19 O. In terms of these components, the organic matter is close to the typical bitumens from sedimentary rocks.

The bituminous matter from the Khibiny pegmatites is characterized by elevated ash content, in most of the samples (from 4 to 10%, occasionally more), and high contents of trace elements.

Available data on the contents and modes of occurrence of elements with atomic numbers higher than 8 in carbonaceous matters from alkaline rocks and pegmatites, as well as on the oxygen and hydrogen distribution between organic matter, water, and inclusions of mineral phases are sparse and contradictory.

The local contents of mineral components in the SBM were determined on a Camebax-MBX microprobe equipped with an EDS Link AN 10000 and a Si–Li detector operating at a take-off angle of 40°, an accelerating voltage of 15.7 kV, a beam current of 1–1.5 nA, and an electron beam from 2 to 18 μm in diameter. The following standards were used: albite for Na and Al, orthoclase for K, SiO_2 for Si, wollastonite for Ca, SrSO_4 for Sr, BaSO_4 for Ba, MgO and diopside for Mg, Al_2O_3 for Al, iron for Fe, manganese for Mn, zinc for Zn, titanium for Ti, niobium for Nb, zirconium for Zr, LaPO_4 for La, CePO_4 for Ce, PrPO_4 for Pr, and NdPO_4 for Nd.

Images of the studied samples in secondary and reflected electrons and maps obtained in the characteristic X-ray radiation of selected chemical elements were obtained on a CamScan digital scanning electron microprobe equipped with a YAG detector of secondary and reflected electrons and a Link INCA Energy EDS with a Si–Li semiconductor detector. To improve the accuracy of the measurements, each sample was scanned 5 to 10 times, with 262144 points analyzed during each scanning session. The counting time at each point was 500 μs . These data were subsequently processed with the INCA Energy 200 program and program package developed at the Institute of Experimental Mineralogy, Russian Academy of Sciences. The investigations were performed at an accelerating voltage of 20 kV, absorbed electron current of 516 nA on a Co standard, and a specimen current of 540–560 nA. The beam size at the sample surface was 0.157 μm . The following standards were used: albite for Na, microcline for K, wollastonite for Ca, SrF_2 for Sr, MgO for Mg, iron for Fe, Al_2O_3 for Al, LaPO_4 for La and P, CePO_4 for Ce, PrPO_4 for Pr, NdPO_4 for Nd, ThO_2 for Th, SiO_2 for Si, FeS_2 for S, NaCl for Cl, yttrium for Y, zinc for Zn, niobium for Nb, arsenic for As, telluric for Te, and UO_2 for U.

The results are listed in Tables 1 and 2. It is seen from Table 1 that some components occur in most or even in all of the samples. It is interesting that the samples contain, along with widely spread Na, K, Ca, Al, Si, and S, which are typical of natural organic matter, also Th, whose average content in carbocers is 5.58 wt % and reaches 6.23 wt % in sample 8. Some samples contain REE and Sr in amounts above the clarke values.

Table 1. Average contents (wt %) of elements with atomic numbers >10 in the aggregates of bituminous matter from pegmatites of the Khibiny and Lovozero massifs

Component	Khibiny										Lovozero			
	Sample													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Na ₂ O	0.12	0.18	n.d.	n.d.	0.33	0.31	0.72	5.62	0.22	0.60	4.85	1.51	1.03	14.80
K ₂ O	n.d.	0.15	0.08	n.d.	0.06	0.16	7.07	0.96	0.11	n.d.	0.20	0.19	0.19	n.d.
CaO	4.97	7.42	1.86	5.43	0.16	5.58;	0.17	1.56	1.04	0.10	0.40	0.34	0.27	n.d.
SrO	n.d.	0.25	0.21	0.55	n.d.	1.03	0.35	0.23	n.d.	n.d.	n.d.	0.56	n.d.	n.d.
MgO	n.d.	n.d.	0.10	n.d.	0.05	0.25	0.05	0.21	0.08	0.15	n.d.	0.14	0.20	n.d.
FeO	n.d.	n.d.	n.d.	n.d.	n.d.	0.49	0.16	0.44	0.30	0.10	0.41	0.30	8.91	0.08
Al ₂ O ₃	0.18	0.12	0.18	0.28	0.46	0.45	7.55	0.27	0.11	0.07	n.d.	0.28	0.23	n.d.
La ₂ O ₃	n.d.	n.d.	n.d.	1.37	n.d.	0.60	n.d.	n.d.	n.d.	n.d.	0.27	n.d.	n.d.	n.d.
Ce ₂ O ₃	n.d.	n.d.	n.d.	1.64	n.d.	0.49	n.d.	n.d.	n.d.	n.d.	0.37	n.d.	n.d.	n.d.
Nd ₂ O ₃	n.d.	n.d.	n.d.	0.40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ThO ₂	4.00	0.38	2.37	5.58	n.d.	3.01	n.d.	6.23	2.66	n.d.	0.41	n.d.	n.d.	0.74
SiO ₂	1.85	0.42	1.33	1.80	0.40	2.64	27.26	13.07	1.82	0.59	1.18	0.78	8.74	12.97
S	0.25	0.40	0.15	0.29	1.24	0.52	0.12	0.38	0.26	1.66	4.23	2.11	1.36	0.26
Cl	n.d.	n.d.	0.07	n.d.	n.d.	0.10	0.07	0.12	n.d.	0.07	n.d.	n.d.	n.d.	n.d.
Total	11.37	9.32	6.34	20.37 ^{1*}	2.70	15.73 ^{2*}	43.52	29.08	6.81 ^{3*}	3.34	19.53 ^{4*}	6.29 ^{5*}	20.93	29.29 ^{6*}

Note: (n.d.) not detected. Total also includes: ^{1*} 2.83% Y₂O₃, 0.20% Pr₂O₃; ^{2*} 0.07% ZnO; ^{3*} 0.21% ZnO; ^{4*} 3.64% Nb₂O₅, 0.68% As₂O₅, 2.87% P₂O₅, 0.37% UO₃; ^{5*} 0.08% Te; ^{6*} 0.44% Nb₂O₅.

Table 2. Average contents (wt %) of elements with atomic numbers >10 in the “carbocer” organic matrix based on SAED data

Component	Sample no.											
	1			2			3			4		
	Analysis no.											
	1	2	3	4	5	6	7	8	9	10	11	12
Ca	7.02	5.91	3.66	5.68	5.78	5.97	1.62	3.18	3.17	3.45	3.41	3.94
Sr	n.d.	n.d.	0.27	0.34	n.d.	0.24	0.31	0.37	0.11	0.55	0.42	0.37
Ba	n.d.	0.19	n.d.	n.d.	n.d.	n.d.	0.34	0.14	n.d.	n.d.	0.16	n.d.
Pb	n.d.	n.d.	0.18	n.d.	0.14	n.d.	n.d.	n.d.	0.20	n.d.	0.27	n.d.
Y	n.d.	0.10	n.d.	0.15	n.d.	n.d.	0.15	n.d.	n.d.	2.43	1.69	2.55
La	n.d.	n.d.	n.d.	0.26	n.d.	n.d.	0.09	0.42	0.26	0.67	1.60	1.49
Ce	n.d.	n.d.	n.d.	0.25	n.d.	n.d.	n.d.	0.16	n.d.	0.67	1.49	1.20
Pr	n.d.	n.d.	0.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.34	0.34	0.23
Nd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.13	n.d.	0.10	0.31	0.19	0.52
Th	0.15	0.21	n.d.	n.d.	n.d.	n.d.	0.13	0.16	0.15	n.d.	n.d.	0.18
S	0.14	0.15	0.14	0.48	0.22	0.29	0.17	0.11	0.21	0.13	0.10	0.18
Total	7.31	6.56	4.45	7.16	6.14	6.50	2.94	4.54	4.20	8.55	9.67	10.66

Note: (n.d.) not detected. Na, K, Mg, Fe, Mn, Zn, Si, Al, Ti, Nb, Zr, U, P, As, also were not detected

The samples from the Khibiny Massif are lower in Na and S, significantly higher in Ca, and are enriched in Th compared to the samples from the Lovozero Massif. The samples from Khibiny universally show a predominance of ThO₂ over the total Σ REE₂O₃ (total REE concentration is no higher than 1 wt %). This is also typical of carbocers, and therefore, the term carbocer seems to be misleading.

The structure of the typical “carbocer” grain (sample 1) is shown in Fig. 1. A back scattered electron image and maps in the characteristic X-ray radiation of Th, Si, and Ca demonstrate the microheterogeneous polyphase structure of the studied sample with typical exsolution lamellae. Judging from their morphology, the exsolution lamellae were formed in two stages. Large lamellae with a size from a few tens to ~100 μ m enriched in Th and Si (supposedly containing organosilicon compounds and organothorium complexes) were formed at the first stage. The second stage involved the exsolution of thorite lamellae from 2 to 4 μ m, occasionally to 30 μ m in size in high-Th–Si phases. Based on SAED data, the thorite has the following major-element composition (wt %): 69.9 Th, 8.4 Si, and 15.3 O (semiquantitative estimate). The thorite-containing matrix with thorite lamellae contains dispersed Si and Th, whose modes of occurrence are unknown. Along with thorite, the bituminous matter contains calcite, occasionally as euhedral rhombohedral crystals up to 30–40 μ m in size (Fig. 1).

The carbocer of sample 2 (Fig. 2) has an unusual structure, in which Th, Si, and Ca are confined to scarce thorite and calcite intergrowths no more than 10 μ m in

size (white and gray domains, respectively, in the BSE image). The organic matrix of this sample has very low contents of elements with atomic numbers higher than 10. The sample differs from other “carbocers” in having higher contents of aliphatic hydrocarbon groups (C–H stretching vibrations at 2800–3000 cm⁻¹ in the IR spectrum; see below).

All other Th-bearing bituminous compounds from the Khibiny pegmatites are similar to typical “carbocers” in chemistry, phase composition, and structure. The exsolution lamellae of mineral phases in the organic matrix of samples 6, 8, and 9 are shown in Fig. 2. Sample 8 contains relatively small lamellae of steacyite, high-Si thorium silicate (identified from the IR spectrum and chemical composition), instead of thorite.

The SAED analysis of the “carbocer” organic matrix beyond mineral inclusions (Table 2) showed a predominance of Ca among the “heavy” elements; Sr, Ba, and REE also occur. The Th content of less than 0.2 wt % indicates that most Th was exsolved as Th silicates during phase unmixing, whereas Sr, Ba, REE, and a significant part of the Ca and S remained in the organic (metalorganic) phases mainly as carboxylate complexes, as is seen from the IR data below.

The mineral inclusions in the bituminous matters from the hydrothermal rocks of Mount Alluaiv (Lovozero) are less abundant than those in samples from the Khibiny Massif. They are randomly distributed in the organic matrix and are mainly Na carbonate and Na and Fe silicates. Given the random spatial distribution, the mineral inclusions could be mechanically entrapped in SBM. The contents of the elements in the organic

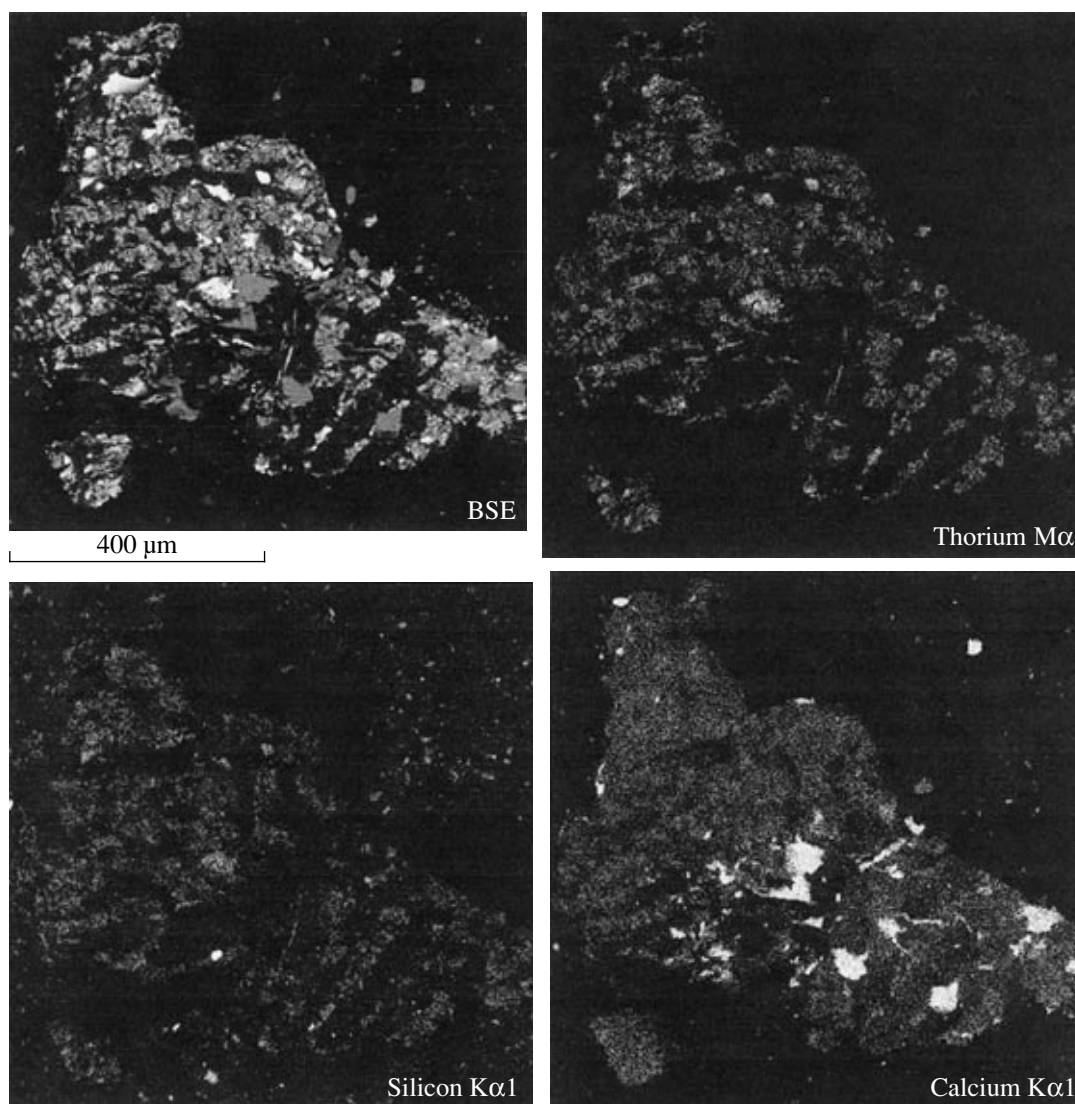


Fig. 1. Back-scattered electron image and a map in the characteristic X-ray radiation of Th, Si, and Ca for carbocer (sample 1).

matrix of sample 12 determined by microprobe analysis are as follows (wt %): 1.8–2.5 S, 0–0.1 As, 0–0.2 Te, 0.1–0.9 Sr, 0.2–0.3 Fe, 0.1–0.3 Ca, 0–0.3 K, 0–0.2 Ti, and 0–0.7 Si. The matrix of sample 11 contains only 3.5–3.6% S and 0.6–0.7% As.

IR study of Bituminous Matter

X-ray diffraction data (see below) showed that bituminous aggregates in the alkaline pegmatites are predominantly or completely composed of X-ray amorphous matter. The microstructure of these aggregates was studied by IR absorption spectroscopy. IR-spectra of SBM pressed in the form of pellets with KBr were recorded on a Specord 75IR two-beam spectrophotometer within a wavelength range of 400–4000 cm^{-1} , with a pellet of pure KBr used for compensation.

The results of our investigations show that SBM from the Khibiny and Lovozero pegmatites strongly differ in spectroscopic characteristics. The most intense bands in the IR spectra of the all Khibiny samples are ascribed to oxygen-bearing organic groups. These are primarily the stretching bands of carboxylate groups bound with aromatic rings at 1250–1440 and 1540–1590 cm^{-1} (Figs. 3, 4). The aromatic derivatives have lower frequencies of CO stretching vibrations as compared to the analogous aliphatic bands of carboxylate compounds and wider bands compared to those of crystalline aromatic carboxylate salts (for example, the spectrum of hydrous Al mellate, mellite, Fig. 3). Double C–O bonds (carboxyl and carboxylate groups) occur at 1680–1710 cm^{-1} , which is also typical of aromatic compounds. The IR spectrum of carboxylate groups exhibits, in addition to the band at 1680–1710 cm^{-1} , a stretching band (or series of bands) of

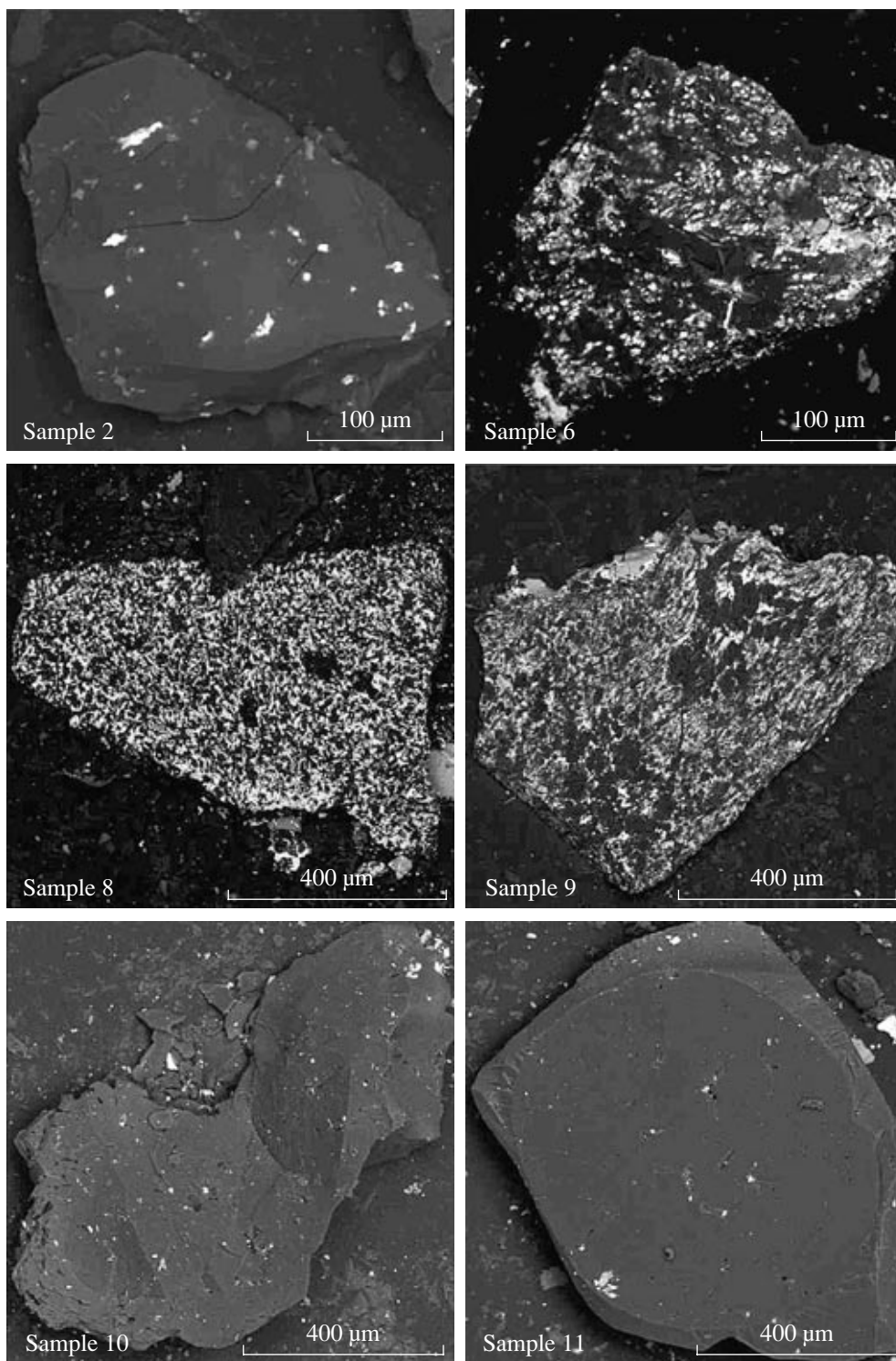


Fig. 2. Back-scattered electron images of SBM samples from pegmatites of Khibiny (Sample 2, 6, 8, 9) and Lovozero (samples 10, 11).

weakly acid hydroxides (typical region of 2520–2680 cm^{-1}). Much oxygen in the SBM of the Khibiny pegmatites occurs as C–OH groups (possibly, phenol groups) and water molecules, which form relatively strong hydrogen bonds corresponding to broad bands at

3000–3500 cm^{-1} . The presence of molecular water is evidently caused by the hydrophilic properties of carboxyl, carboxylate, and hydroxyl compounds.

The quasilinear fluorescent spectra [1] show that the alkaline rocks and pegmatites of the Khibiny Massif

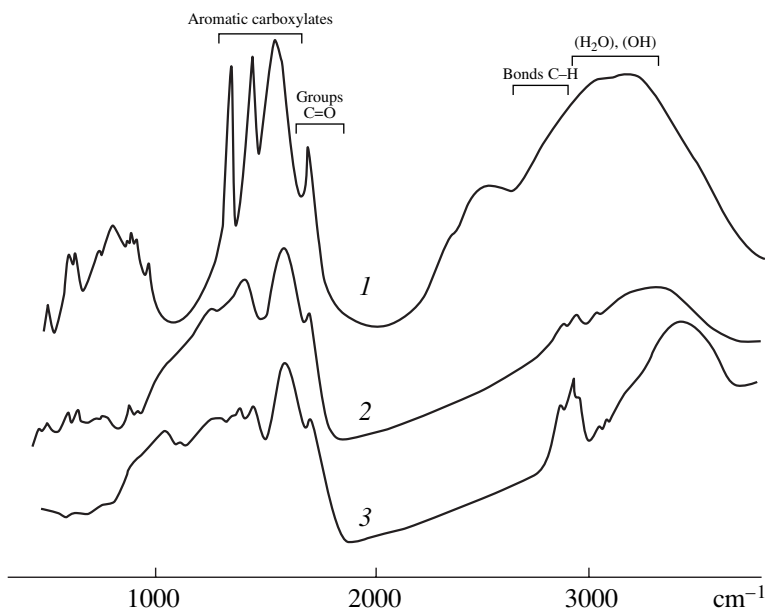


Fig. 3. IR spectrum of mellite (curve 1) and SBM from the Khibiny pegmatites (curve 2 and 3 are, respectively, samples 5 and 9).

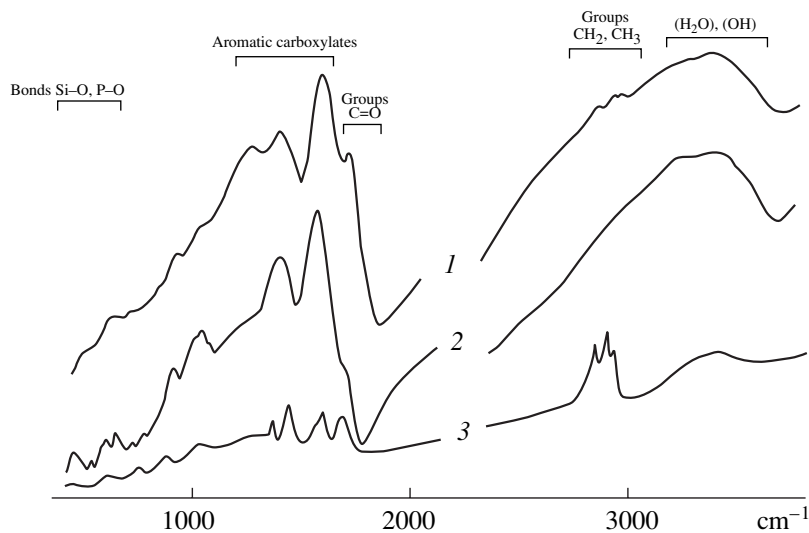


Fig. 4. IR spectra of "carbocers" from Khibiny (curves 1 and 2 are, respectively, samples 3 and 1) and bituminous matter scattered in villiaumite of the third generation associated with Na,Th silicate in the Palitra pegmatite, Mount Kedykverpakhk, Lovozero (curve 3).

have high contents of polycyclic aromatic hydrocarbons. Their total content in the rock is as high as $3 \times 10^{-7}\%$, which is significantly higher than that of polycyclic aromatic hydrocarbons in the rocks and pegmatites of the Il'meny Massif, which was less affected by hydrothermal processes. In particular, the five-cycle 3,4-benzopyrene, six-cycle 1,12 benzoperylene, and seven-cycle coronen were identified in the bitumoids extracted from the Khibiny rocks. However, IR data indicate that bituminous compounds from the Khibiny pegmatites contain only oxidized derivatives of polycyclic arenes.

Thus, the bituminous matter from the Khibiny pegmatites can be regarded as direct analogues of high-molecular heterocyclic oil components, in particular, asphaltogenic acids, which are known as efficient complexing agents and sorbents of Th and U [27].

Two samples from Khibiny, sample 2 (low-Th "carbocer") and sample 5 (Th-free "carbocer"), differ from other Khibiny samples in having higher contents of aliphatic hydrocarbon groups (CH_2 and CH_3 stretching vibrations at $2850\text{--}2960\text{ cm}^{-1}$, Fig. 4). Their spectra

also display narrow bands of aromatic C–H groups (a range of 3000–3100 cm^{-1}). The low-intensity bands corresponding to C–H bonds indicate a high extent of condensation of the aromatic rings in the Khibiny bituminous matter.

Another pattern is observed in SBM from pegmatites at Mount Alluaiv of the Lovozero Massif (samples 10–13). The strongest bands are ascribed to aliphatic hydrocarbon groups. These are C–H stretching bands at 2877, 2930, and 2960 cm^{-1} and narrow CH_2 and CH_3 bands of bending vibrations at 1450 and 1376 cm^{-1} . The weak C–C stretching band at 875 cm^{-1} is ascribed to the same groups. The bands of oxygen-bearing organic groups at 3430, 1697, and 1600 cm^{-1} are relatively weak, in spite of the fact that their extinction coefficients are more than one order of magnitude higher than those of the bands of hydrocarbon groups. Thus, samples 10–13 are amorphous matter, consisting mainly of highly-branched aliphatic hydrocarbons [the absence of bands at 720–750 cm^{-1} suggests a low content of linear fragments $(\text{CH}_2)_n$ with $n > 4$]. The IR spectrum of sample 14 also shows the predominance of aliphatic hydrocarbons, however the bands of oxygen-bearing groups at 3400–3450 and 1500–1700 cm^{-1} are more intense than those in samples 10–13. Scattered oxidized bituminous matter was also found in the IR spectrum of a cleavage plate of villiamite from sample 14 (bands at 1690, 1585, 1440, 1375, and 1265 cm^{-1}). However, this matter is dominated by the aliphatic hydrocarbon constituent.

X-ray Diffraction Data

The X-ray diffraction analysis of bituminous matter in pegmatites from both massifs was performed on a DRON-3 diffractometer (CuK_α radiation, voltage of 34 kV, and current of 32 μA) using an automated system of X-ray DRON diffractometers. Organic matter was identified following the recommendations in [28]. The X-ray powder diffraction data on the four main types of SBM preliminarily revealed by IR spectroscopy and X-ray diffraction analysis are shown in Fig. 5. It should be noted that the SBM types were arbitrarily distinguished since they show gradual transitions.

The diffraction curve of a typical Khibiny “carbocer” (first type, sample 3) represents a superposition of reflections from an aromatic constituent with a maximum at 3.5 Å and series of narrow bands, the strongest of which belong to thorite (corresponding interplanar spacings are 4.74, 3.59, 2.86, 2.70, 2.22, 1.89, and 1.84 Å). The mineral component in sample 8 is thorium silicate, and steacyite, instead of thorite.

The second type exemplified in sample 6 (Fig. 5) includes SBM with a predominant aromatic constituent (diffraction maximum at 3.8 Å) and subordinate crystalline mineral intergrowths. This type is also characteristic of the pegmatites of the Khibiny Massif.

The third type, exemplified by Sample 9 (Fig. 5), demonstrates the simultaneous presence of significant amounts of aromatic and aliphatic organic compounds, which is expressed in an asymmetric diffraction halo. The position of the diffraction maximum ($d > 4$ Å) corresponds to the aliphatic component, while the shoulder (inflection at $d < 4$ Å) corresponds to the aromatic constituent. SBM of this type typically contain insignificant amounts of silicate and carbonate intergrowths, which are difficult to identify because of their small sizes and, often, the absence of analogues among known minerals. The bituminous matter of this type is most typical of the pegmatites of the Khibiny Massif (sample 5 and others), with the only exception being sample 14 from the Lovozero Massif.

The fourth type of SBM with an organic component predominated by aliphatic hydrocarbons exhibits a relatively narrow diffraction maximum at ~ 4.2 Å and was found only in the Lovozero pegmatites (samples 10–13).

DISCUSSION

Our data, considered together with data previously published elsewhere, indicate that the macroscopic aggregates of condensed organic matter occur mostly among late mineral assemblages, which were formed during the hydrothermal stage of the formation of apatitic pegmatites of the Khibiny and Lovozero massifs. The SBM is distinctly confined from the one side to domains enriched in zeolites and, especially, in zeolite-like microporous hydrous Ti, Nb, and Zr silicates (elpidite, catapleite, vinogradovite, labuntsovite group minerals, hilairite, lovozerite, and others), and from the other, to the accumulations of REE-, Y-, and Th-bearing minerals, or is restricted to carbonate and sulfide occurrences. More rarely, the organic matter can associate with heterophillosilicates (murmanite, lomonosovite, astrophyllite, and lamprophyllite group minerals).

We believe that the pervasive spatial association of bitumenlike matter with microporous hydrous Ti, Nb, and Zr silicates is hardly a mere coincidence, but reflects a genetic relation. It is known that both Ti-organic complexes (in homogeneous systems) and synthetic zeolite-like Ti silicates (in heterovalent reactions) operate as catalysts during the reforming (transformation of low-molecular aliphatic hydrocarbons into aromatic ones), polymerization of undersaturated hydrocarbons, and the selective oxidation of many organic compounds. In particular, modified microporous Ti silicates ETS-10 and ETAS-10 are efficient in reforming the n-hexane [29], while ETS-10 additionally catalyzes the polymerization of alkyne [30]. Synthetic microporous Nb silicate AM-11, whose structure has not been studied as of yet, catalyzes the synthesis of the dimethyl ether from methanol in a flow reactor [31]. Under these conditions, the reaction proceeds mainly at the external active centers of the catalyst, which are characterized by elevated Brønsted acidity. In a closed reactor, methanol forms mainly a mixture of hydrocar-

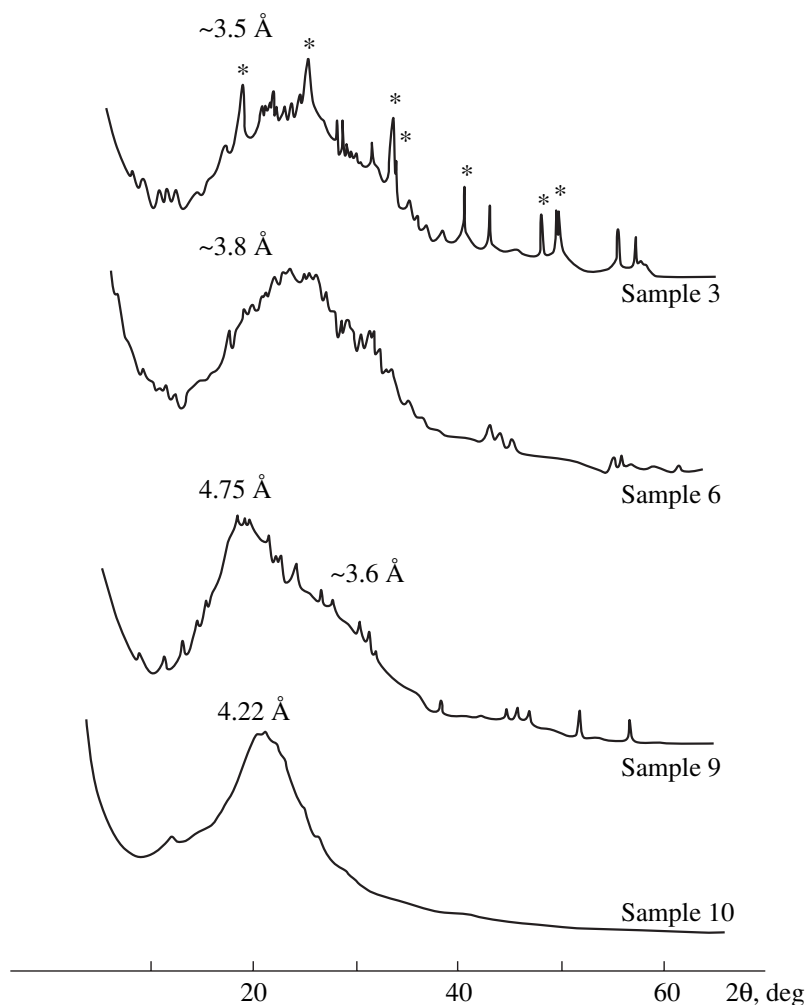


Fig. 5. XRD pattern of SBM from Khibiny (samples 3, 6, 9) and Lovozero (sample 10).

bons (from C_1 to C_5) on AM-1. There are a great number of reactions of the selective oxidation of diverse organic substrates (aliphatic and undersaturated, including aromatic hydrocarbons, alcohol etc.), which are catalyzed by synthetic microporous Ti and Nb silicates under heterogeneous conditions [32]. Some of the used catalysts are direct analogues of the natural minerals that are typical of the late hydrothermal assemblages of alkaline pegmatites. ETS-10, a chemical analogue of zorite, a zeolite-like Ti silicate, is most often used in chemical technologies. Many synthetic microporous Ti silicates are not only catalysts, but also active adsorbents, which take up small molecules from gases and solutions and accumulate them near catalytic centers. In particular, ETS-10 and its analogues obtained by ion exchange efficiently adsorb H_2 , CO , N_2 , NO , C_2H_4 , and NH_3 [33–35]. The same role is presumably played by aluminosilicate zeolites, which are widely applied as selective catalysts of different reactions in the organic synthesis [36].

The polymerization synthesis of solid organic matter in alkaline pegmatites presumably proceeded not only in heterogeneous but also in homogeneous systems. The possibility of their homogeneous formation is supported by the presence of Ti in many samples, in which Ti does not belong to any mineral and is presumably incorporated in some relict catalytic centers. Nb is more rarely contained in SBM. Ti typically occurs in all types of the organic matter: aliphatic and aromatic, with high and low contents of the functional groups (OH, CO_2^- , $C=O$, and others). This element shows an uneven distribution in the Khibiny samples. Its contents in most local analyses are below the detection limit, with the highest TiO_2 contents (at analyzed area of $254 \mu m^2$) reaching 1.4 wt % in sample 2, 1.7 wt % in sample 3, 1.2 wt % in sample 4, and 1.3 wt % for sample 9 etc. Ti shows a more systematic distribution in the weakly oxidized SBM from the Lovozero pegmatites. In particular, the average TiO_2 content in sample 10 is 0.12 wt %, reaching 0.3 wt %.

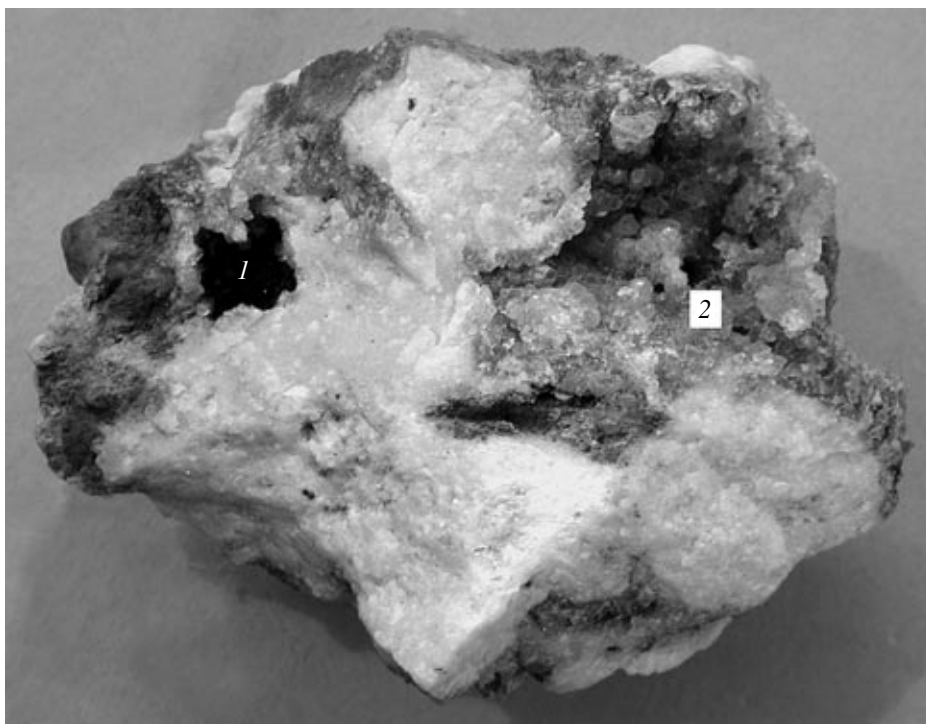


Fig. 6. Mineralized pockets from hydrothermal zone of the Shomiokitovoe pegmatite body (Lovozero) with korobitsynite, elpidite and black SBM (1) and without microporous Ti-, Nb-, and Zr-silicates and SBM (2).

The heterogeneous-catalytic formation of solid organic matter can be clearly illustrated by the albite zone in the Shomiokitovoe pegmatite body, in which cavities both with and without korobitsynite–elpidite intergrowths are spaced only a few centimeters apart. The former are filled by uninterrupted films of black bitumenlike matter, while the latter bear none of this material (Fig. 6).

Thus, strong differences were found between macroscopic SBM aggregates in the pegmatites of the Khibiny and Lovozero massifs. Samples from the Khibiny pegmatites contain mainly polyaromatic components or belong to intermediate types with variable (typically low) contents of aliphatic hydrocarbons and alkyl groups. They are characterized by significant amounts of bound oxygen, mainly in carboxylate, carboxyl, carbonyl, and hydroxyl groups, operating as selective complex agents for Th [28] and, to a lesser extent, for some other elements (Ca, Sr, Ba, Y, and REE). As compared to Lovozero samples, the Khibiny samples are lower in S and don't contain elements such as P, As, Te, and Nb.

Conversely, the SBM forming macroaggregates in the pegmatites of the Lovozero Massif (samples 10–13) consists mainly of hydrocarbons, being, respectively, depleted in oxygen-bearing organic groups and water, as well as in Th, alkali-earth and rare-earth elements. However, oxygen-bearing polyaromatic compounds universally occur in close intergrowths with the latest Th, Sr, and REE minerals in the Lovozero pegmatites.

The organic compounds of this type are most abundant in the Palitra pegmatite at Mount Kedykverpakhk (sample 14), in which they form macroscopic rims around the Na–Th silicate and microscopic inclusions identified by IR spectroscopy in villiaumite. In the latter case, polyaromatic compounds contain both carboxylate and free acid (carboxyl) groups.

Thus, the late pegmatite stages in both of the massifs are characterized by a close association of aromatic carboxylate compounds and Th minerals. At the same time, the composition of the organic matter points to a more reducing environment in the Lovozero Massif as compared to that of the Khibiny Massif, at least during the late evolutionary stages of these massifs. These data are consistent with wide occurrence of endogenous soda mineralization, the presence of carbonatites in the Khibiny Massif, and with their uncomparably lower abundance in the Lovozero massif at a higher Na content.

CONCLUSIONS

(1) Solid bituminous matter is a typical component of the hydrothermal assemblages in the Khibiny and Lovozero pegmatites.

(2) SBM is typically closely associated with microporous framework Ti, Nb, and Zr silicates, which could serve as catalysts in the synthesis of bituminous matter. This is highly possible, since analogous synthetic zeolitelike Ti, Nb, and Zr silicate materials are

known as adsorbents of small molecules and efficient catalysts of the polymerization, transformation, and selective oxidation of organic substrates. The organic matter in the alkaline pegmatites is also spatially related to heterophyllosilicates and aluminosilicate zeolites.

(3) Bituminous matter from the pegmatites of the Lovozero Massif typically has elevated contents of aliphatic hydrocarbons, sulfur, and Na, but is depleted in oxygen and trace elements.

(4) SBM from the pegmatites of the Khibiny Massif has low S contents and is enriched in derivatives of polycyclic aromatic hydrocarbons (containing hydroxyl, carbonyl, and carboxylate groups), as well as in water. They accumulate Th, alkali-earth, and rare-earth elements during the hydrothermal stage.

(5) The oxidized derivatives of polycyclic arenes found in SBM are complexing agents for Th, REE, Ba, Sr, and Ca and facilitate the transfer and accumulation of these elements at low temperatures. Macroscopic accumulations of oxidized bituminous matters in the pegmatites of the Khibiny Massif are typically associated with Th and/or REE mineralization.

(6) Oxidized SBM with rare-earth and alkali-earth elements are complex microheterogeneous systems bearing mineral (most often Th silicates and calcite), metalorganic (with REE, Ca, Sr, and Ba), and essentially organic phases, which formed owing to the exsolution of the initial metalorganic compounds with decreasing temperature.

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