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CARBONACEOUS MATTERS IN PEGMATITES OF DIFFERENT GENETIC TYPES AND THEIR ROLE IN FORMATION OF MINERAL ASSOCIATIONS

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Comparative investigation of carbonaceous matters from pegmatites of different formations has been performed. These formations are as follows: high alkaline (Khibina and Lovozero massifs, Kola Peninsula), rare metal granitic (Viitaniemi, Finland), granitic of mica type (Northern Karelia), and alkaline granite amazonitic (Western Keyvy, Kola Peninsula). The existence of steady genetic relation between reduced forms of carbon and several characteristic incoherent rare "bitumenphilic" elements (U, Th, *REE*, Zr, Hf, Nb, Ta, W, Sn) and titanium has been shown as well. Possible mechanisms of the formation and the transformation of carbonaceous matters in pegmatites of different genetic types, their structure and role in processes of mineral genesis are discussed.
2 tables, 11 figures and 46 references.

Keywords: pegmatites, rare elements, bitumen, thucholite, carburan, carbocer.

Introduction

Reduced forms of carbon (graphite, amorphous carbon, bitumen matters) are regular accessory components of many late- and post-magmatic paragenesises connected with formations of different types.

In publications there are specific terms "thucholite" and "carburan" for aggregates of carbonaceous matters from granitic pegmatites enriched in radioactive elements. The term "thucholite" (given according to the chemical composition – ThUCHO-lite) was firstly used (Ellsworth, 1928a) for uranium- and thorium-bearing carbonaceous matter from granite-pegmatitic vein intersecting Precambrian gneisses near the village Konger (Ontario, Canada). Thucholite forms there pseudomorphs after uraninite and original aggregates. Afterwards analogous matter was found in several other pegmatites of Canada: on the territory of the Ontario province (Spence, 1930; Jonasson *et al.*, 1977; Stevenson *et al.*, 1990) and Quebec province (Ellsworth, 1928b; Spence, 1940). Occurrence of thucholite in association with zircon (cyrtolite), titanite, allanite, uraninite, rarely with samarskite is typical for these objects. In the granites of Western Sudets (Poland), aggregates of thucholite occur in the areas with thorite and gummite mineralization (Milulski, 2007). Phase heterogeneity of uranium-bearing bituminous matters from different formations of Great Britain, Scandinavia and Southern Africa was investigated in details (Eakin, Gize, 1992). Nowadays the name "thucholite" (in wide sense) is often used for all mineralized carbonaceous matters from granitic pegmatites. Uranium-bearing carbonaceous matter from granite—pegmatitic veins of the Northern Karelia was firstly characterized by A.E. Fersman (1931) and afterwards described under the name "carburan" (Labuntsov, 1939; Zhirov, Bandurkin, 1968). It is a light, brittle and hygroscopic black colored matter containing up to 90 wt.% of carbon and able to fire on air. Its ash residue contains mainly oxides of U and Pb as well as Fe, Th, Y, Nb, Zr, Sr and trace amounts of other elements (Ti, Sn, Be, Ba a.o.). Two varieties of carburan are distinguished: rounded aggregates among rock-forming minerals and pseudomorphs after crystals of uraninite. Carburan occurred in the paragenesis with unchanged uraninite as well as with titanite, allanite, cyrtolite, xenotime, and monazite. S.M. Popov (1957) considers carburan as a product of later pneumatolytic activity. In granitic pegmatites of Norway, carbonaceous matter is formed at the same stage with uraninite, monazite, allanite, thorite, yttrofluorite, and xenotime. In the pegmatitic vein Ytterby (Sweden), carburan type matter occurs in the association with fergusonite, yttrotantalite, gadolinite, cyrtolite, and xenotime (Fersman, 1931). In the Northern Karelia and in the Kola

Peninsula carburan is characteristic to plagioclase—quartz—muscovite pegmatitic veins. The consequence of accessories formation in these pegmatites is as follows: allanite → monazite → xenotime + cyrtolite + uraninite → pyrrotine + carburan → pyrite → chalcopyrite (Zhirov, Bandurkin, 1968).

Organic matters are characterized by a wide distribution in high-alkaline magmatic rocks and their pegmatites (Chukanov *et al*., 2005, 2006; Nivin *et al*., 2005). Characteristic feature of bituminous matters from agpaitic pegmatites is their ability to concentrate some rare elements, e.g. Th and *REE*.

Despite a large amount of publications concerning carbonaceous matters, there are several problems connected with their genesis still remaining unsolved. They include the following questions:

— source of carbon (magma or contamination by the matter of enclosing rocks);

— mechanisms of carbon reduction;

— mechanisms of concentration of rare elements;

— role of organic matter in the processes of mineral formation;

— is the affinity of several rare elements to the organic matters a universal characteristics of these ("bitumenphilic", "coalphilic") elements, or it is firstly connected with the geological formation type.

In the present work new data have been obtained on the relationships between organic matters and the processes of mineral formation in pegmatites of different types.

Objects of investigation

Typical specimens from the following pegmatites of different types containing carbonaceous matters were chosen for comparative investigation.

Rare metal granitic pegmatites are represented by specimens of sugar-like and lamellar albite from Viitaniemi, Finland containing spherical inclusions of thucholite (up to 1 cm in diameter), crystals of zircon, tantalite, pyrochlore (Figs 1, 2), fluorite, black tourmaline, amblygonite—montebrasite, lepidolite.

In **alkaline granitic amazonitic pegmatite** of the mountain Plaskaya (Western Keyvy, Kola Peninsula) organic matter is present in the form of microscopic inclusions in crystalline egg-yellow thorite. Thorite occurs as segregations up to 1 cm among sugar-like albite. This thorite is attributed to the late pegmatite minerals (Voloshin, Pakhomovsky, 1986).

Granitic pegmatites of mica type are represented by the specimen from muscovite deposit Lopatova Guba, Chupinsky region, Northern Karelia, Russia. Carbonaceous matter occurs as black fine-grained pseudomorphs after cubic crystals of uraninite (up to 3 mm in size) grown in massive quartz in the core of a big vein pegmatite body. Associated minerals are potassium feldspar, oligoclase, muscovite, biotite, schorl, almandine, fluorapatite, monazite-(Ce), xenotime-(Y), and zircon.

Associations with bitumenosic matters from agpaitic and ultraagpaitic pegmatites of Lovozero and Khibina massifs (Kola Peninsula) have been also investigated.

In the pegmatitic body "Nastrofitovoye" (mountain Alluayv, Lovozero) black tear-shaped segregations with resinous luster (up to 3 mm in size) of bituminous matter associate with natrolite, raite, vinogradovite, and catapleiite.

In the pegmatite "Palitra" (mountain Kedykverpakhk, Lovozero) organic matter occurs as films and segregations of irregular form (up to 1 mm in size) of dark-brown up to black color with dull luster as well as its micro-

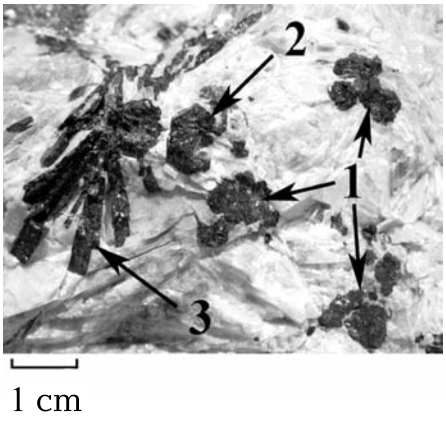


Fig. 1. Association of thucholite (1) with zircon (2) and tantalite (3) in albitite. Viitaniemi, Finland.

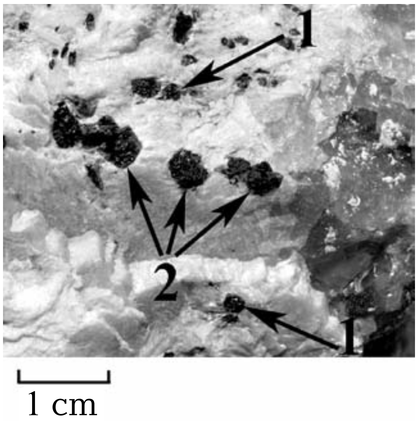


Fig. 2. Association of thucholite (1) with microlite (2) in albitite. Viitaniemi, Finland.

scopic inclusions in grains of X-ray amorphous Na,Th-silikate. The following minerals are tightly associated with organic matter: natrosilite and villiaumite as well as earlier ussingite, kapustinite, kazakovite, lomonosovite, vuonnemite, phosinaite-(Ce), steenstrupine-(Ce) and several high alkaline minerals.

In pegmatite "Koashva-2007/2" (mountain Koashva, Khibiny) big (up to 4 cm in size) spherical segregations of bituminous matter of coaly-black color with submetallic luster at the fracture occur in the hydrothermally altered core where they are intergrown in cavernous aegirine—natrolite aggregates. Associated minerals are astrophyllite, lorenzenite, titanite, burbankite, sphalerite, chlorbartonite and other.

Additionally, bituminous matter ("carbocer") with ingrowths of thorite forming structures of decay in the organic matrix (Chukanov *et al.*, 2006) has been used as a reference specimen. This specimen was collected by A.N. Labuntsov in 1930th in rinkite—natrolite vein on mountain Kukisvumchorr, Khibiny (see Labuntsov, 1937) and nowadays is kept in the Fersman Mineralogical Museum of the Russian Academy of Sciences (FMM № 41426).

Methods and results of investigations

Electron-microprobe analysis including obtaining of images of the investigated object in secondary and back-scattered electrons has been performed using the digital scanning electron microscope CamScan MV2300 equipped with YAG-detector of secondary and back-scattered electrons and energy-dispersive X-ray microanalyzer with semi-conductor (Si-Li) detector Link INCA Energy. Time of signal accumulation in every point amounted 500 ms. Investigations were performed under accelerating voltage of 20 kV, current of absorbed electrons at the standard Co specimen of 516 pA, diameter of electron beam at the surface of specimen of 0.157 μm.

All investigated specimens are fine intergrowths of different carbonaceous and mineral microphases. Such structures are characteristic to the products of decay of intermediate complexes of metal cations with organic matter (see Eakin, Gize, 1992).

Contents of elements with atomic number exceeding 10 determined by the microprobe method in the carbonaceous and mineral phases of the specimens under investigation are shown in Tables 1 and 2. In this case carbonaceous matter means homogenous matter where electron microscopy does not detect the presence of other phases, and semi-quantitative X-ray spectroscopic analysis reveals strong predominance (in atomic amounts) of carbon over other elements with atomic numbers exceeding 5. In spite of homogeneity of carbonaceous phases, microprobe analysis constantly reveals the presence of heavy elements (Table 1). In carbocer, calcium is the main trace element with atomic number exceeding 10 (analysis 8 in Table 1; see also Chukanov et. al, 2005, 2006). In other cases carbonaceous phase contains sodium (bituminous matters from granitic pegmatites), uranium and radiogenic (?) lead (carbonaceous matters from alkaline pegmatites), aluminium (thucholite), and other components. Carbonaceous phases of all investigated specimens regardless of their genesis contain sulfur (from 0.39 to 2.41 wt.%).

Table 1. **Chemical compositions of carbonaceous phases (wt.%)**

	Thucholite (Viitaniemi)		Carburan (Lopatova Guba)		Bitumen (Khibiny)		Bitumen (Lovozero)	"Carbocer" (Khibiny)
Number of analysis	1	2	3	4	5	6	7	8
Na	n.d.	n.d.	n.d.	n.d.	1.30	0.54	0.47	n.d.
Ca	3.58	3.86	n.d.	n.d.	n.d.	0.84	n.d.	13.96
Pb	1.02	0.76	11.76	10.39	n.d.	n.d.	n.d.	n.d.
Fe	0.27	0.32	n.d.	n.d.	n.d.	n.d.	n.d.	0.25
Al	3.64	4.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
La	0.10	0.11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ce	0.04	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
U	3.48	2.95	28.34	27.38	n.d.	n.d.	n.d.	n.d.
S	0.93	0.96	1.16	1.54	0.42	0.39	2.41	1.43
P	0.51	0.73	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	9.53	9.88	35.66	33.97	1.38	1.39	2.76	15.64

Note: n.d. — concentration of the component is below its detection limits by microprobe method

Carbonaceous matters from pegmatites of different types contain different types of mineral inclusions (Table 2). As a rule, mineral inclusions contain intergrowths of carbonaceous phase. The distances between inclusions of carbonaceous phase are often smaller than the size of area excited by electron beam. That leads to the lowering of sums of microprobe analyses.

Original "carbocer" contains inorganic phases presented mainly by thorite and carbonates including rare earth carbonates (Chukanov *et al*., 2006). Bituminous matters from other pegmatite bodies of the Khibina-Lovozersky complex are characterized by a variety of mineral phases (Figs. 3—5, Table 2).

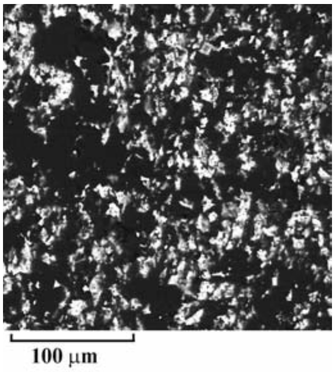
High-sulfur bitumen from the Lovozero (Fig. 3; analyses 11 and 12 in Table 2) contains numerous inclusions of imperfect isometric crystals (up to 5 μm in size). The habit of some crystals allows assuming tetrahedral symmetry of the mineral. Its composition may be approximately described by the idealized formula $(Th,Ca,Na)_4(Mn,Ti,Nb)_{1-2}(SiO_4)_4(PO_4) \cdot nH_2O$.

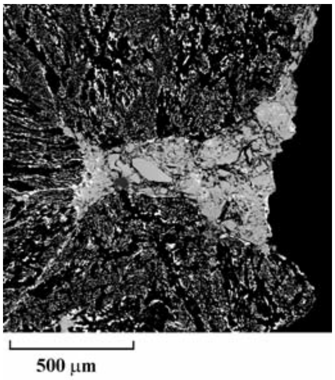
In low-sulfur bitumen from the Khibina (Figs. 4, 5) significant amount of inclusions is represented by thorium niobium-silicate (analyses 6—8 in Table 2). The composition of this mineral corresponds to the simplified formula $(Ca,Na)_2 REE Th_4(Nb,Ti)_{1+x}Si_{7-8}(O,OH)_y \cdot nH_2O$. Among the other mineral phases in this specimen of bitumen, one may mention high-niobium silicate with Nb:Si ≈ 2:1 (Fig. 4, analysis 9 in Table 2) and strontium-containing fluorite (analysis 10 in Table 2) covering rasvumite grains (Fig. 5).

In thucholite from lamellar albite from Viitaniemi, microprobe analysis shows the presence of very fine (less than 1 μm in size) isometric particles of a phase containing only uranium (presumably, uraninite). More big mineral inclusions (up to 30 μm) contain 62—67 wt.% of uranium and 4—10 wt.% of lead. Constant presence of sulfur (up to 1 wt.%) and low sums of analyses indicates on the possible presence of dissipated carbonaceous matter. In thucholite from the zone of sugar-like albite of the rare metal pegmatite Viitaniemi uranium is distributed between the carbonaceous matter and spherical aggregates of autunite or metaautunite (Fig. 6, analysis 1 in Table 2). Thorium is present only in the mineral phase belonging to the brockite—grayte series (Fig. 7, analysis 2 in Table 2). Carbonaceous matter of thucholite contains Al and Ca. According to the results of electron-microscopic investigation, these elements do not form their own mineral phases.

Contrary to the above mentioned specimens represented by globular aggregates of carbonaceous matter with mineral inclusions and signs of origin and crystallization within the early formed significantly organic phase (Eakin, Gize, 1992), carburan from the Lopatovaya Guba has sure signs of replacement of mineral phase (uraninite) by later introduced carbonaceous matter. Globular aggregates of the carbonaceous matter that do not contain mineral inclusions occur within the multiphase aggregate forming a pseudomorphs after cubic crystal of uraninite (Fig. 8). Mineral phases of carburan are oxides and/or carbonates of U and Pb, silicates of U as well as anglesite (analyses 3—5 in Table 2).

In order to reveal the nature of organic component of carbonaceous matters of peg-





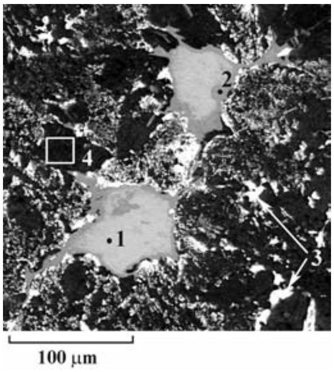


Fig. 3. Decay ingrowths of thorium-calcium silico-phosphate in bitumen. Pegmatite body "Nastrofitovoye", Lovozero, Russia. Image in back-scattered electrons.

Fig. 4. Intergrowth of high-niobium silicate (Nb:Si ≈ 2:1, gray phase in the center) with bitumen containing inclusions of thorium silicate (thorite? — numerous white areas). Khibiny, Russia. Image in back-scattered electrons.

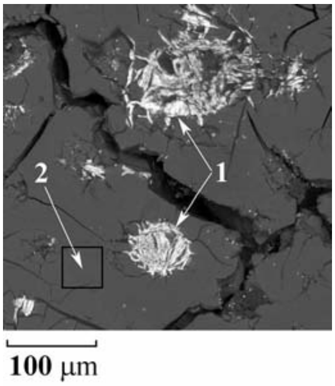
Fig. 5. Rasvumite (1) with edgings of Sr-containing fluorite (2) and ingrowths of thorium niobo-silicate (3) in high-sulfur bitumen (4). Khibiny, Russia. Image in back-scattered electrons.

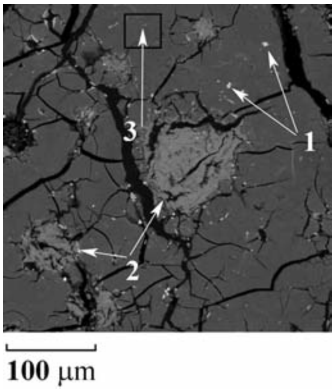
Table 2. **Chemical compositions of carbonaceous matters of pegmatites (wt.%)**

	Thucholite		Carburan			Bitumen					Bitumen		"Carbocer"	
	(Viitaniemi)		(Lopatova Guba)			(Khibiny)					(Lovozero)		(Khibiny)	
Number of analysis	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Na_2O	n.d.	n.d.	n.d.	n.d.	n.d.	0.47	n.d.	1.13	4.31	0.75	n.d.	1.21	n.d.	n.d.
CaO	5.39	7.40	n.d.	n.d.	n.d.	3.03	3.10	2.25	9.29	38.55	2.01	2.42	n.d.	1.18
PbO	0.34	9.68	17.54	6.84	71.33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	1.90	1.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.25	1.72	n.d.	n.d.	n.d.	n.d.
Al_2O_3	n.d.	2.62	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.45	0.96	n.d.	n.d.
La_2O_3	n.d.	0.25	n.d.	n.d.	n.d.	0.71	n.d.	0.48	0.55	n.d.	n.d.	n.d.	n.d.	n.d.
Ce_2O_3	n.d.	0.24	n.d.	1.63	n.d.	4.18	3.15	3.43	1.23	n.d.	n.d.	n.d.	n.d.	n.d.
ThO_2	n.d.	28.23	n.d.	7.61	n.d.	39.19	46.19	44.11	1.65	1.94	31.34	40.51	80.03	75.50
UO_3	64.35	2.98	69.01	41.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TiO_2	n.d.	n.d.	n.d.	n.d.	n.d.	1.31	1.23	1.72	5.60	n.d.	1.84	1.60	n.d.	n.d.
Nb_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	3.49	3.64	5.51	43.65	n.d.	2.75	1.82	n.d.	n.d.
SiO_2	n.d.	n.d.	n.d.	7.64	n.d.	17.47	18.14	16.94	11.08	n.d.	8.43	12.26	18.52	17.34
P_2O_5	15.34	19.60	n.d.	5.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.38	4.10	n.d.	n.d.
SO_3	n.d.	0.28	n.d.	n.d.	25.99	n.d.	n.d.	n.d.	n.d.	n.d.	0.80	0.45	n.d.	0.51
Total	90.42	74.55	86.55	72.68	97.32	72.13	78.47	77.65	79.22	73.72	97.05	98.25	98.55	94.53
Formula coefficients														
Na	–	–	–	–	–	0.42	–	1.03	0.74	0.03	–	0.65	–	–
Ca	0.89	0.48	–	–	–	1.48	1.55	1.15	0.90	0.85	0.93	0.71	–	0.07
Pb	0.02	0.16	0.98	0.15	0.98	–	–	–	–	–	–	–	–	–
Fe	0.25	0.06	–	–	–	–	–	–	–	–	–	–	–	–
Al	–	0.19	–	–	–	–	–	–	–	–	0.37	0.32	–	–
La	–	0.01	–	–	–	0.12	–	0.08	0.02	–	–	–	–	–
Ce	–	0.01	–	0.05	–	0.71	0.52	0.60	0.04	–	–	–	–	–
Th	–	0.39	–	0.14	–	4.09	4.63	4.73	0.04	0.01	3.07	2.57	0.98	0.99
U	2.08	0.04	3.00	0.69	–	–	–	–	–	–	–	–	–	–
Ti	–	–	–	–	–	0.45	0.41	0.62	0.39	–	0.75	0.33	–	–
Nb	–	–	–	–	–	0.72	0.74	1.17	1.79	–	0.54	0.23	–	–
Si	–	–	–	0.61	–	8.00	8.00	8.00	1.00	–	3.63	3.68	1.00	1.00
P	2.00	1.00	–	0.35	–	–	–	–	–	–	0.87	0.96	–	–
S	–	0.03	–	–	1.00	–	–	–	–	–	–	–	–	0.02
Method of calculation	P_2	P_1	U_3	$(Si,P,As)_1$	S_1	Si_8	Si_8	Si_8	Si_1	1 cation	$(Si,Al)_4$	$(Si,Al)_4$	Si_1	Si_1

Note: n.d. – concentration of the component is below its detection limits by microprobe method. Additionally detected: analysis 1 – SrO 1.23 % ($Sr_{0.11}$), ZrO_2 0.57 % ($Zr_{0.04}$), Sb_2O_5 1.30 % ($Sb_{0.07}$); analysis 2 – TiO_2 0.22 % ($Ti_{0.01}$), SrO 0.86 % ($Sr_{0.03}$), Y_2O_3 0.85 % ($Y_{0.03}$), ZrO_2 0.20 % ($Zr_{0.01}$); analysis 4 – As_2O_5 1.09 % ($As_{0.05}$), Dy_2O_3 1.09 % ($Dy_{0.03}$); analysis 6 – Pr_2O_3 0.80 % ($Pr_{0.12}$), Nd_2O_3 1.48 % ($Nd_{0.24}$); analysis 7 – K_2O 0.74 % ($K_{0.11}$), Nd_2O_3 2.28 % ($Nd_{0.36}$); analysis 8 – Nd_2O_3 2.08 % ($Nd_{0.35}$); analysis 9 – K_2O 0.61 % ($K_{0.07}$); analysis 10 – SrO 7.49 % ($Sr_{0.08}$), F 40.19 % ($F_{1.89}$), -O=F_2 -16.92 % ; analysis 11 – MnO 2.05 % ($Mn_{0.75}$), C 38 % , $O_{избыт}$ 7 % ; analysis 12 – MnO 1.92 % ($Mn_{0.46}$), C 26 % , $O_{surplus}$ 5 %

matites, infra-red (IR) spectroscopy has been used. All organic compounds show resonance absorption of IR radiation in the range 1300—3100 cm^{-1}. In this range silicates, oxides and phosphates do not give strong absorption bands. It makes possible to detect small amounts of organic compounds as admixtures to rock-forming and accessory minerals. IR spectra of carbonaceous matters and associated minerals pressed in the form of tablets with potassium bromide have been obtained using the two-beam spectrophotometer Specord 75 IR in the wavenumber range 400—4000 cm^{-1} with spectral width of slit no more than 2 cm^{-1} for the interval 400—1800 cm^{-1} and no more than 6 cm^{-1} for the interval 1800—3100 cm^{-1}.





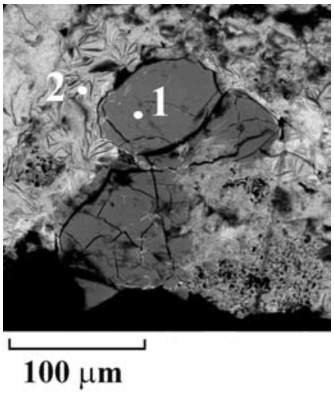


Fig. 6. Aggregates of autinite and/or meta-autinite (1) in thucholite (2). Viitaniemi, Finland. Image in back-scattered electrons.

Fig. 7. Inclusions of mineral grains of the series brockite—grayite (1) and aggregates of nontronite (2) in thucholite (3). Viitaniemi, Finland. Image in back-scattered electrons.

Fig. 8. Aggregates of carbonaceous matter (1) in the U and Pb hydroxide (carbonate?) aggregate (2) from carburan. Lopatova Guba, Russia. Image in back-scattered electrons.

During spectrum recording, analogous tablet of pure KBr was placed in the reference beam. NH_3 (gas) and polysterene were used as standards.

All investigated in the present work carbonaceous matters are characterized by high contents of water and/or hydroxyl groups that show strong wide bands in the frequency range 3100—3600 cm^{-1}. Bitumens from the ultraagpaitic pegmatites of the Khibino-Lovozersky complex (Fig. 9) are characterized by high contents of aliphatic hydrocarbon groups (corresponding C-H stretching vibrations correspond to a series of bands in the range 2800—3000 cm^{-1}) as well as unsaturated organic compounds giving series of bands in the frequency range 1200—1680 cm^{-1}. In the latter interval, bending vibrations of CH_2 and CH_3 groups, stretching vibrations of carboxylate groups and bending vibrations of water molecules are revealed. Their precise detection in this interval is difficult due to the overlapping of bands. High integral intensity of absorbance indicates on the presence of aromatic compounds. Band in the range 1680—1740 cm^{-1} characteristic to IR-spectra of bitumens from pegmatites is attributed to carbonyl groups (C=O stretching vibrations).

IR-spectrum of thucholite from Viitaniemi albitite (Fig. 10) is close to IR-spectra of "carbocers" with low contents of aliphatic hydrocarbon groups (Chukanov *et al.*, 2006): bands of C-H stretching vibrations are weak or are absent, and bands of absorption of aromatic and carboxylate groups are very strong. Spectrum of thucholite also contains bands of carbonyl and uranyl groups (corresponding ranges 1680—1740 and 900—950 cm^{-1}, Fig. 10).

IR-spectrum of carburan does not contain bands that may be for sure related with any organic groups. The strongest bands in the ranges 1400—1550 and 900—950 cm^{-1} presumably correspond to stretching vibrations of ions CO_3^{2-} and UO_2^{2+}, respectively. At the same time microprobe analyses show the presence of uranyl carbonate as well as significant amounts of carbonaceous matter. The latter is characterized by low sums of analyses on elements with atomic numbers exceeding 10 and high (more than 50%) contents of carbon. In total these facts show that significant share of carbon is present in the state characterized by low coefficients of absorption of IR-radiation. Taking into account that coefficient of extinction of stretching vibrations is proportional to the square of the bond-length partial derivative of dipole moment, one may make a conclusion that significant part of the carbonaceous matter of carburan is represented by pure carbon with nonpolar bonds C-C.

Earlier, as a result of investigation of modes of occurrence of bituminous matters in agpaitic pegmatites of the Lovozersky massif a conclusion was drawn that minerals of thorium crystallized at the later stages of pegmatites formation concentrated organic matters in the form of dispersed microscopic inclusions (Chukanov *et al.*, 2005, 2006; Ermolaeva *et al.*, 2007. 2008). Analogous observations were made by us during IR-spectroscopic investigation of minerals of amazonitic pegmatites from Western Keyvy. High concentrations of organic matters have been fixed only in the later thorite ("thorite-II" according to Voloshin, Pakhomovsky, 1986, see Fig. 11). At the Fig. 11, spectrum of Na,Th—silicate from ultraagpaitic

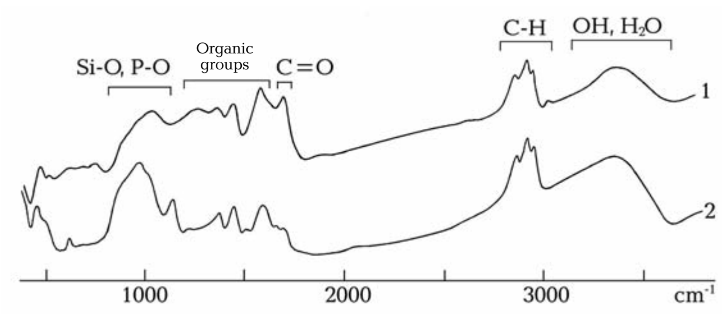


Fig. 9. IR-spectra of bitumens from the pegmatite body "Nastrofitovoye" (1) and from the pegmatite of the Koashva Mountain (2).

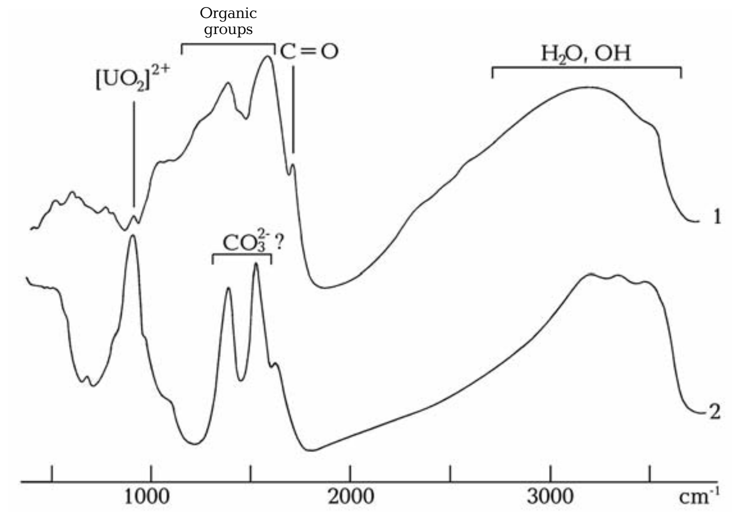


Fig. 10. IR-spectra of thucholite (1 — Viitaniemi) and carburan (2 — Lopatova Guba).

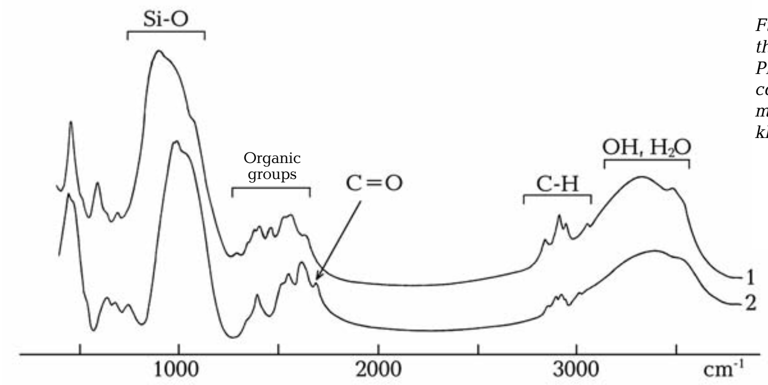


Fig. 11. IR-spectra of thorite (1) from the amazonitic pegmatite (Mountain Ploskaya) and sodium-thorium silicate (2) from the ultraagpaitic pegmatite "Palitra (Mountain Kedykverkhpahk, Lovozero).

pegmatite "Palitra" (mountain Kedykvarpakh, Lovozero) is shown for comparison.

Discussion

As a rule, carbonaceous matters from pegmatites and hydrothermal veins of different genetic types are heterogeneous matters in phase composition. In granitic pegmatites they are often enriched in uranium, thorium and/or rare earth elements. Thucholite (in the wide sense of this term) may contain inclusions of uraninite, or its core consists of uraninite (Spence, 1930; Zhirov, Bandurkin, 1968). Inclusions of thorite and thorianite occur in thucholite enriched in thorium (Parnell, 1988). Rare earth containing thucholite from pegmatite of the Parry Sound region (Canada) contains inclusions of phosphates of *REE* (with lanthanum maximum) and thorium (Parnell, 1990). Specimens investigated in this work were no exception and also were heterophase objects enriched in specific rare elements.

Comparing our results with the data from literary sources we may note that there is a stable general tendency to coexistence of carbonaceous matters and minerals of a row of characteristic incoherent elements (U, Th, *REE*, Zr, Hf, Nb, Ta, Ti, W, Sn). Uplifted concentrations of these elements are connected with definite mineral formation stage. For example, positive correlation of uranium with concentrations of Y, Zr, Nb, Ta, Hf, and *REE* has been revealed in the granitic massif Karkonosze (Poland) where this correlation occurred in miarolitic pegmatites, aplites and quartz veins (Mikulski, 2007). According to A.N. Labuntsov (1939), carburan formation in granitic pegmatites begins at the temperature about 700°C (almost simultaneously with the beginning of crystallization of accessory minerals: titanite, cyrtolite, xenotime-(Y), monazite-(Ce) and uraninite).

Investigation of solid bituminous matters (SBM) from agpaitic pegmatites (mainly by the example of pegmatites of the Khibino-Lovozersky complex) leads to the conclusion of a tight spatial connection of rare metal mineralization with organic matter in postmagmatic differentiates. First of all it concerns to Th, and also to *REE*, U, Ti, Nb, and Zr.

So, from the comparing of data on granitic and alkaline agpaitic pegmatites, one may make a conclusion of existing of a row of "bitumenphilic" elements including the following ones: U, Th, Y, Ln, Zr, Hf, Nb, Ta, Ti, W, Sn, Pb. It is notable that this row almost coincides with the set of coalphilic elements. These elements are distinguished on the basis of a great statistical material accumulated by now in the science of solid caustobioliths and generalized in the recently issued monographs (Yudovich, Ketris, 2006; Arbuzov, Ershov, 2007). In coals most of lithophile rare elements is firstly accumulated in the form of complexes with organic ligands and then partially occurs in concentrated form giving mineral phases. In mature coals mineral forms of these elements may predominate. They may originate authigenically during the decay of their carboxylate salts and other organic forms. It is notable that ash clarkes of lithophile rare elements, as a rule, exceed their concentration in clays from coals. Such elements in coals as Ta, Nb, Zr, Hf, and *REE* may reach industrially significant concentrations (Arbuzov, Ershov, 2007).

Earlier according to the analysis of data on paragenetic correlations between mineral and organic matter in the agpaitic pegmatites we have suggested the following genetical scheme (Chukanov *et al.*, 2005, 2006; Ermolaeva *et al.*, 2007, 2008; Chukanov *et al.*, 2008):

1. Mass crystallization of aegirine at the early stages of pegmatite formation binds greater part of iron in the form of Fe^{3+} that is favorable for the stabilization of the reduced forms of carbon in the residual fluid.
2. Sorption of small carbon-containing molecules (CO, CO_2, CH_4, C_2H_6, C_2H_4 etc.), their polymerization, transformation in aromatic compounds (process of reforming) and selective oxidation occurs at the microporous zeolite-like silicates of Ti, Nb, and Zr playing the role of sorbents and catalysts.
3. Oxygen-containing aromatic compounds with hydrophile functional groups (-OH, -C=O, -COOH, $-COO^-$) act as a complex-forming agents in relation to Th, *REE*, U, Zr, Ti, Nb, Ba, Sr, and Ca. They provide transportation of these ("bitumenphilic") elements in low-temperature hydrothermal conditions in the form of water-soluble macroassociates of the micelle type. Aliphatic bituminous matters, as a rule, are impoverished by oxygen and are less active as complex formation agents.
4. Concentration of Th, *REE* (and to a lesser degree, U, Zr, Ti, Nb) at the later stages of hydrothermal process occurs in the form of microphases that give abundant inclusions in segregations of SBM or in the form of macroscopic segregations of Th and *REE* minerals. In the latter case SBM are captured in the form of inclusions by growing crystal or on the contrary are crowd out to its surface forming outer zones enriched in SBM.
5. At the final stages occurs the decay of homogenous SBM onto organic (partly with Ca, Sr, Ba, and Pb) and mineral (with Th, Ln, Y, Ti, Nb, Ca, Na, K, and Si) microphases.

According to the literature data, tight association of uranium with organic matter may be a result of mobility of hydrocarbons and replacement of uranium minerals by them (Dubinchuk *et al.*, 1977) as well as due to the ability of oxygen ligands to form soluble organic complexes of U^{6+} or as a result of sedimentation of hydrocarbons at the surface of uranium minerals during processes of polymerization caused by radiation (Hoekstra, Fuchs, 1960). Further process at the same time is accompanied by the decay of uranium minerals as well as radiolythic decomposition of organic matters that lead to its dehydration and transformation into the carbonaceous matter of the anthraxolite type.

According to the microscopic investigation of textural peculiar features and electron-microprobe studies, the main genetic-morphology types of uranium-containing bituminous matters are distinguished. Two mechanisms of their formation have been suggested (Eakin, Gize, 1992). During the realization of the first mechanism, formed earlier mineral phases (uraninite, in particular) were later replaced by aggressive organic matter. During this process under the influence of radioactive decay, active organic particles (free radicals and other) may be formed and radiation-induced polymerization of organic molecules occurs. Bituminous matters of the second type were presumably formed in the process of generation of complex compounds of U^{6+} (in lesser degree, Th) with formed before organic matters, further reduction of uranium and decay of the homogenous metal-organic complex onto the organic and mineral (uraninite, coffinite) phases.

Supposition that prolonged radiation of bituminous matter leads to its dehydration, aromatization and polymerization has been repeatedly expressed in earlier publications (Abdel-Gawad, Kerr, 1961; Zumberge *et al.*, 1978; Landais *et al.*, 1987).

According to its mineralogy-morphological characteristics (globular segregations of carbonaceous matter with inclusions of U and Th minerals) and predominating modes of occurrence of carbon (aromatic and carboxylate compounds), thucholite from the Viitaniemi pegmatite is analogous to the Khibina "carbocer". The main differences reflecting geochemical specifity of two formations (rare metal granitic and agpaitic pegmatites) are in the nature of cations of carboxylate salts (alkaline-earth cations in "carbocer", and calcium and aluminium in thucholite) and in the composition of predominating mineral ingrowths (silicates of Th in "carbocer", phosphates and oxides of U and Th in thucholite).

The most likely predecessors of thucholite, as well as carbocer, are hydrocarbon gases primordially present in the residual portions of fluid forming the pegmatite body. In particular, this conclusion was made by authors of the work (Bushev *et al.*, 1997) as a result of investigation of organic compounds of rare metal granitic pegmatite of the Kukurt deposit (Eastern Pamir). According to the gas-chromatography and mass-spectrometer analyses of flying and extracted by chloroform compounds, this pegmatite contains 0.946 cm^3/kg alcans (up to C_8H_{18}), 0.731 cm^3/kg alcens (up to C_7H_{14}) and 44.7 ng/g aromatic hydrocarbons (including polycyclic). Presence of alcens is especially indicative because of their ability for polymerization at catalysts of the Zigler-Natta type under low temperatures. In comparison with thucholite, carburan from the ceramic pegmatites of Karelia is much more mineralized; according to S.M. Popov (1957), its average ash content accounts for more than 35%, and our observations confirm this conclusion.

Origin of carburan in contrast to the thucholite and bitumens of alkaline pegmatites obviously occurred by means of replacement of uraninite crystal by organic matter. Analogous process was reproduced in laboratory conditions (Dymkov *et al.*, 2002) when nasturan interacted with heavy oil under 300°C and 195 atmospheres during 72 hours. As a result, surface of nasturan particles were corroded, and they were overgrown by solid bitumen film.

During the comparison of carbonaceous matters from the granitic and agpaitic pegmatites one can observe that (in spite of the fact that bitumens from the granitic pegmatites were formed under significantly more high temperatures than bitumens from the alkaline pegmatites) in both cases specific mineralization with participation of Ti, Zr, and Nb (for granitic pegmatites also with Ta, Hf, and Sn) is directly preceded by sedimentation of carbonaceous matter. It once more confirms a hypothesis of the catalyst role of the mentioned high-valent transition elements in endogenic processes of formation of organic matters, their polymerization and partial oxidizing up to carbonyl, carboxyl and carboxylate compounds. We may remind that synthetic titanium-silicates and niobium-silicates find a wide application as catalysts of selective partial oxidizing of hydrocarbons in mild conditions (see the review: Chukanov *et al.*, 2004). The ability of transition metals to catalyse polymerization of unsaturated organic compounds in aqueous media and their copolymerization with CO in hydrothermal conditions are also well known (Mecking *et al.*, 2002). For one's turn high-molecular carbonyl, carboxyl and carboxylate compounds have a pronounced affinity with great high-valent cations such as Th^{4+}, U^{4+}, and REE^{3+} and form stable complexes with them. So, all chain of chemical transformations including catalyst formation of high-molecular organic compounds (with participation of Ti, Zr, Nb, Ta, Hf, and Sn), their selective oxidizing, formation of metal-organic complexes with Th^{4+},

U^{4+}, and REE^{3+}, radiolythic decomposition of organic matter and crystallization of minerals of the mentioned rare elements within the organic matrix is regular and caused by physicochemical features of carbon, hydrogen, oxygen and high-valent rare elements. As a result of these processes segregations of mineralized carbonaceous matters are formed. These segregations are natural microreactors with uplifted concentrations, from one side, of elements with high force characteristics (Ti, Zr, Nb, Ta, Hf, and/or Sn), and from the other side, with rare earth elements and/or radioactive elements (Th^{4+}, U^{4+}, *REE*). Mineral phases formed in such microreactors (with predominating silicates including titanium-silicates and niobium-silicates of thorium and lanthanides, see also Chukanov *et al.*, 2005, 2006; Ermolaeva *et al.*, 2007, 2008) are characterized by unique variety. Many of them are unknown in other conditions.

In conclusion let us consider the problem of carbon and carbonaceous matter sources in postmagmatic formations. Most of investigators consider carbonaceous matter of agpaitic magmatic rocks and related pegmatites as a product of natural evolution of magma and not as a result of contamination of enclosing rocks by organic matter (see Labuntsov, 1937; Petersilye *et al.*, 1969; Galimov, Petersilye, 1968; Florovskaya *et al.*, 1968; Loskutov, Polezhaeva, 1968; Nivin, 2002). In favor of this point of view witnesses the fact that in different pegmatite bodies bituminous matters occupy definite position and are connected with the same type paragenesises (and our observations confirm this). At the same time the sources of carbon remains debatable. At the earlier stages of magma evolution carbon is present mainly as a component of volatile components (CH_4, CO, and CO_2). Their mutual transformations are going during the following reactions: $CO + 3H_2 \leftrightarrow CH_4 + H_2O$, $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$, $2CO + 2H_2O \leftrightarrow CH_4 + CO_2$. Under the hypothesis that in these processes fractionation of carbon isotopes is limited, we have used the data on isotope composition of methane carbon from the rocks and minerals of the Khibiny and Lovozero (δC^{13} from -0.32 to -1.28) for the substantiation of the mantle origin of this carbon (Petersilye *et al.*, 1969). At the same time carbon of bitumens from agpaitic pegmatites was close in isotope composition (δC^{13} from -2.91 to -2.97) to the carbon of carbonaceous chondrites. Afterwards contradictions in the data on isotope composition of hydrocarbon gases from nepheline-syenitic complexes were repeatedly mentioned (Beeskow *et al.*, 2006; Potter, Longstaffe, 2007). On the basis of this it was made a supposition on the possible influx of organic matter (Nivin, 2008).

In our opinion, we ought to regard with great caution to the interpretation of isotope composition of bituminous matters of endogenic origin because such matters are products, as a rule, of catalyst reactions of radical polymerization, disproportioning, reforming and oxidizing (Rudenko, Kulakova, 1986; Chukanov *et al.*, 2005, 2006; Ermolaeva *et al.*, 2007, 2008). In presence of transition metals, free radical polymerization of unsaturated hydrocarbons is possible in conditions analogous to hydrothermal (see the review: Mecking *et al.*, 2002). All these processes may reveal strong spin selectivity that lead to the effective isotope fractionation of ^{12}C and ^{13}C (see the reviews of Buchachenko, 1995; Buchachenko, 2001). Constant tight association of pegmatitic bitumens with radioactive elements (uranium and thorium) results in the formation of radioactive-generated free radicals that is an additional source of spin-selective channels of processes with the participation of organic reagents. In particular, as a result of gamma irradiation, molecules of aromatic carbonyl compounds are transformed into the triplet state and decompose onto fragments forming radical pair. The nucleus of ^{13}C, unlike ^{12}C, has magnetic moment. Due to the hyperfine interaction with such nucleus, uncoupled electrons of the radical pare swiftly transform to the singlet state that makes possible recombination and, as a result, enrichment of original molecules by ^{13}C nuclei. ^{12}C nuclei accumulate in the products of recombination (CO and polycyclic aromatic compounds) (Buchachenko, 2001).

In case of granitic pegmatites the question of the origin of carbon and carbonaceous matter is treated ambiguous. In some works (Ellsworth, 1928a, 1932; Barthauer *et al.*, 1953; Mueller, 1969) hypothesis of magmatic origin of thucholite carbon is proved. But some works contain assumptions on the possibility of contamination of pegmatitic fluid by the bituminous matter of the enclosing rocks. For example, the pegmatite exposed at the Besner mine contains oil-like and asphalt-like bitumens in cross faults of veins, and thucholite occurred in these zones. It was treated as an indication of penetration of oil from above, from the sedimentary suite that is not present now (Spence, 1930). Afterwards this explanation was subjected to criticism (Fersman, 1931). Starting from the presence of a row of oil occurrences in the Lower Paleozoic of the Ontario region, it was admitted that oil fluid leaked below from the Lower Paleozoic rocks into the underlying Precambrian basement and became polymerized and hardened under the influence of radiation from the closely situated radioactive minerals in the pegmatite. Analogous conclusion was made in the work Steveson *et al*. (1990) based on the results of investigation of organic matter from quartz—calcite (with sulfides) veins of the uranium mine Panel, Canada. This matter practically does not contain Th and U (< 0.5 ppm) in spite of high concentration of uranium in enclosing strata. It was also supposed (Zhirov, Bandurkin, 1968) that graphite from the enclosing metamorphic (originally sedimentary) rocks may serve as the source of carbon for the carburan from the pegmatites of the northern Karelia and Kola Peninsula.

Modes of occurrences of these matters in pegmatites of different types, their microstructure, and connection of their segregations to the specific rare metal mineralization — all these facts are the indications that in most cases bitumens, thucholite and carbocer should be considered as matters formed as a result of natural evolution of pegmatite in tight connection with processes of mineral formation. The presence of carbonaceous matters itself indicates rather low activity of oxygen in the moment of their formation; otherwise, deposition of carbon only in the form of carbonates will occur. In the agpaitic rocks the main channel of oxygen evacuation from the fluid is obviously connected with crystallization of aegirine; as a result of this process iron is bonded mainly in the form of Fe^{3+} (Ermolaeva *et al*., 2008). In case of granitic pegmatites mechanisms of oxygen evacuation from fluid are less obvious. It is likely that definite role in this process may play crystallization of feldspars (in case of pegmatites from northern Karelia they contain 0.12—0.13 wt.% of Fe_2O_3) as well as muscovite with 1—7 wt.% of Fe_2O_3 and 0.3—0.4 wt.% of FeO (Labuntsov, 1939).

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