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## Genetic Aspects of the Formation of Carbonaceous Substances in the Minusa Basin

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The carbonaceous substances confined to both igneous and terrigenous rocks are widespread in the Minusa intermontane trough of the Altai–Sayan region [1]. The characteristics of bitumen from this region obtained with methods traditional for petroleum geochemistry are given in [2, 3]. According to [3], the formation of high-carbonic and high-molecular compounds is related to the thermal destruction of the dispersed organic matter (OM) as a result of the large-scale emplacement of basaltic magma in the Early Devonian and the subsequent condensation of sublimates in relatively cold areas. The OM of thin marine units in sequences mainly composed of volcanosedimentary and terrigenous rocks might have served as a source of bitumen.

In order to elucidate the origin of carbonaceous substances in this region, we carried out a comprehensive investigation based on the INAA and ICP-MS determination of microelement contents and isotopic compositions (Table 1).

One kerite occurrence located in the southwestern Chebakovo–Balakhta Basin is confined to amygdules in dolerites hosted in the Lower–Middle Devonian terrigenous rocks (Table 1, sample 1).

The Sokhochul bitumen occurrence is located in the Marchengash lava field at the southern wall of the North Minusa Basin [1]. Amygdules filled with kerite (sample 2) and asphalt (sample 4) are localized near the

roof of basaltic sills. In the eastern area, kerite (sample 3) was found in fractures in association with chalcedony-like quartz, prehnite, and carbonate. The kerite is also developed as cement of tectonic breccia within zones of transverse near-meridional reverse strike-slip faults. Vis-uous maltha (sample 5) is exposed as an asphaltlike bitumen cap on the bed-by-bed crush zone (1.0–1.5 m thick) with slickensides in massive basalt [2].

All these varieties of carbonaceous substances are characterized by significant contents of Sc, Cr, Ni, As, Se, Nb, Ta, Cd, Sb, Hf, Au, Hg, and PGE, i.e., of elements that are either atypical for biogenic organic matter or are subordinate in organic matter. The contents of virtually all minor elements in the studied asphaltenes considerably increase from high-carbonic bitumen to maltha. This is difficult to explain in terms of the concept of these materials as products of OM pyrolysis under the influence of basalts. According to the latter scenario, bituminous substances like maltha should be maximally depleted in metals, whereas the solid substances of the same class must be enriched in metals. Moreover, the contents of all microelements should be similar in line with their fugacities at similar thermodynamic parameters. However, kerites (samples 1–3) reveal appreciable variations in the concentration of metals: 4.5 times for Ni, 3.7 times for REE, 7.5 times for As, 12.8 times for Hg, and 24 times for Pb. The As, Zr, Ag, Pd, Hg, and Pb contents systematically increase, while REE concentrations decrease from the bitumen formed in closed systems (amygdules) to the variety condensed in fractures. Hence, the fluids responsible for the formation of carbonaceous matter in open dynamic systems underwent a certain geochemical differentiation.

Despite the enrichment of asphalt in practically all elements, the kerite–asphalt series is characterized by similar geochemical attributes. For example, the Pd/Pt ratio is always higher than unity, while the Th/U ratio is below unity. Maltha differs from solid bitumen not only by the higher concentrations of minor elements but also by the reverse character of the ratios mentioned above.

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**Table 1.** Contents of microelements in carbonaceous substances and basalt, mg/t

Element	Kerite	Kerite	Kerite	Asphalt	Asphaltene from maltha	Basalt	Asphaltene from oil
	1	2	3	4	5	6	7
Li	103.5	53.9	34.7	492.8	2871.1	15545.0	202.1
Be	11.2	3.4	1.9	93.2	209.1	1848.4	6.3
Sc	206.8	142.2	203.8	992.8	5640.5	21655.1	309.0
Ti	4538.5	3281.1	4319.6	47651.0	184250.4	9342916.9	11654.5
V	1508.8	824.6	832.5	6244.6	39676.0	205722.2	190915.1
Cr	1618.3	1068.5	1216.8	3938.6	67031.0	257455.9	7927.9
Mn	3930.1	30076.6	17339.1	52752.8	281462.2	1277119.5	2546.9
Fe <sub>2</sub> O <sub>3</sub> , %	0.03	0.05	0.02	0.59	5.43	10.06	0.21
Co	112.1	223.1	63.9	993.8	4250.2	38102.5	196.6
Ni	2810.7	12796.2	9866.0	6305.9	35945.8	114536.4	47968.9
Cu	1946.8	364.2	957197.5	4520.2	279201.5	34963.4	21474.0
Zn	237.3	635.4	237.3	2867.2	73474.1	100000.1	45023.5
Ga	42.1	44.1	34.5	652.0	2113.8	18582.2	63.9
As	195.1	116.3	873.2	338.3	7010.0	319.5	n.d.
Se	343.4	373.6	249.4	130.6	305.7	1336.0	n.d.
Rb	9.3	40.7	27.2	117.3	5471.0	13783.5	192.1
Sr	1447.9	2089.0	626.6	11326.0	136774.8	839495.9	7890.1
Y	231.2	90.2	24.8	1357.1	5358.0	33514.1	52.0
Zr	99.5	92.7	135.9	718.3	14807.9	231406.4	1814.5
Nb	9.7	5.7	7.4	59.8	322.2	13955.5	8.7
Mo	12.2	16.5	5.4	22.2	1379.1	837.9	118.1
Ru	2.2	1.0	1.2	1.0	<0.01	n.d.	1.0
Rh	0.5	0.2	12.1	0.7	<0.01	n.d.	0.8
Pd	13.3	6.1	31.1	79.6	<0.01	n.d.	45.6
Ag	<0.01	<0.01	62.4	106.7	1108.7	1140.0	80.2
Cd	1.2	13.7	1.9	41.1	574.2	910.9	69.3
Sb	13.3	8.6	7.5	61.6	13012.4	100.0	n.d.
Cs	0.6	3.1	6.4	12.3	364.0	3081.8	9.3
Ba	321.2	3915.4	670.2	8224.1	2599851.6	535917.4	13314.1
La	243.4	196.9	80.1	3044.0	9033.3	31469.5	106.4
Ce	318.6	234.1	122.7	6242.8	22101.0	69470.4	209.1
Pr	56.7	31.4	14.0	420.4	2122.4	8598.8	21.9
Nd	250.7	115.9	40.1	1765.2	8375.6	35222.0	77.7
Sm	44.0	22.4	5.3	309.2	1561.1	6972.9	11.5
Eu	18.28	13.1	0.7	233.7	677.4	2511.8	5.9
Gd	40.9	16.8	5.3	306.1	1245.4	5994.2	10.6
Tb	5.6	2.7	0.8	40.7	176.3	901.8	1.6
Dy	33.0	14.4	3.9	206.1	956.0	5328.6	10.7
Ho	7.1	3.0	0.9	43.2	185.9	1078.5	2.1
Er	19.6	9.1	2.1	106.1	485.9	2875.4	7.1
Tm	2.9	1.2	0.4	13.3	65.4	425.5	1.0
Yb	18.0	7.5	2.4	73.1	394.7	2739.3	6.9
Lu	3.0	1.1	0.4	10.9	62.9	401.8	1.3
Hf	2.2	2.3	2.5	20.7	327.8	4393.5	43.3
Ta	0.6	1.0	0.6	0.7	26.5	700.2	0.1
W	6.8	4.5	9.3	15.8	340.3	83.8	66.2

**Table 1.** (Contd.)

Element	Kerite	Kerite	Kerite	Asphalt	Asphaltene from maltha	Basalt	Asphaltene from oil
	1	2	3	4	5	6	7
Re	0.5	0.2	<0.1	0.3	0.9	21.9	1.6
Ir	0.4	0.2	0.2	0.3	<0.01	n.d.	0.3
Pt	0.6	<0.1	0.2	0.7	150.0	n.d.	0.6
Au	0.7	0.3	0.2	1.0	23.4	2.1	18.8
Hg	11.5	11.2	143.8	84.1	746.9	<0.01	80.3
Tl	0.4	1.5	0.4	2.3	29.8	42.4	2.8
Pb	29.1	458.3	700.7	545.9	2814621.9	4679.6	37068.2
Bi	7.0	8.8	4.4	12.3	191.0	11.7	83.0
Th	3.1	5.5	3.7	23.7	2554.6	1663.5	24.6
U	17.8	5.7	8.9	65.7	626.2	782.7	10.3
(La/Yb) <sub>N</sub>	9.9	19.3	24.6	8.4	16.8	8.4	11.4
(La/Sm) <sub>N</sub>	3.8	6.0	10.3	3.1	3.1	3.1	6.3
Eu/Eu*	1.3	2.0	0.4	1.2	1.2	1.2	1.6

Note: Bitumen from miaroles: (1) in dolerite, Krasnaya Gorka, (2, 4) in basalt, (3) in vein, (6) in basalt, Sokhochula; (5, 7) asphaltenes from maltha and oil, respectively; (n.d.) not detected.

Maltha is similar to oil in concentrations of V, Co, Ni, Cu, As, Mo, Ag, Cd, Sb, Pt, Au, and Hg draws. Relative to the clarke value, their concentrations are two times higher for Sb and Hg and 1.5 times higher for Ag and Mo. Se, Au, and As concentrations are one order of magnitude higher. V, Re, and Ni contents are also elevated.

Based on the carbon isotopic composition of bitumen from miarolic cavities ( $\delta^{13}\text{C} = -(33.9-36.9)\%$ , the authors of [3] suggest that aquagene OM is a source of C-bearing substances. However, this assumption should be approached with caution. As has been shown in [4, 5], the  $\delta^{13}\text{C}$  values of carbonaceous substances from diatremes in the Siberian Craton range from  $-5$  to  $-40.7\%$ . According to [6], this isotopic heterogeneity is caused by contemporaneous formation of calcite and hydrocarbons from a single source under conditions of extreme disequilibrium of the system.

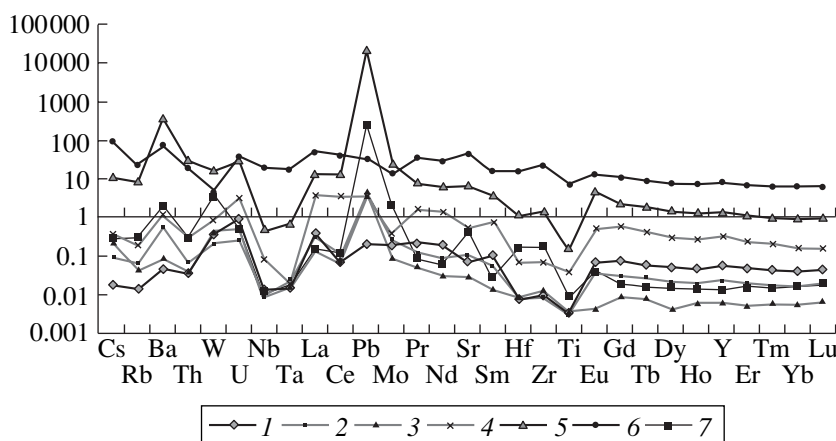
REE distribution is commonly used to ascertain sources of materials involved in natural processes. Despite the variable level of REE concentrations in the studied samples, their chondrite-normalized patterns, with few exceptions, are similar (Fig. 1). All of them are characterized by a positive Eu anomaly ( $\text{Eu}/\text{Eu}^* = 1.2-2.0$ ), which is atypical of OM from formational water and sedimentary rocks, in general. The LREE/MREE ratio is not contrasting ( $\text{La}_N/\text{Sm}_N = 3.1-3.8$  and  $6.0-6.3$ , respectively), although the general degree of REE fractionation is somewhat different. The  $\text{La}_N/\text{Yb}_N$  ratio is similar ( $8.4-9.9$ ) in the basalt, Krasnaya Gorka kerite, and Sokhochul River asphalt, but this ratio is higher in other samples. The veined bitu-

men with a high La/Yb ratio ( $\text{La}_N/\text{Sm}_N = 10.3$ ) and a negative Eu anomaly ( $\text{Eu}/\text{Eu}^* = 0.4$ ) is the only exception. The relatively low level of REE concentration in this substance and the elevated contents of other microelements, relative to other kerite samples, indicate an intense fractionation of fluids at the initial stage of their release from the source.

The sign of the Eu anomaly is related to the variation of redox conditions and the degree of fractionation of elements in the melt–crystal–fluid system. The elevated Eu content in the studied basalt, as compared with average values for mafic and ultramafic rocks, suggests that Eu was present in the melt in a bivalent form. The high Ti (9240 ppm) and Fe (10 wt %) contents in this basalt also indicate a reduced character of the source.

Thus, the character of the accumulation of microelements in carbonaceous substances and similar REE patterns in the studied samples show that basalts and bitumen were derived from cognate sources.

The rather complicated distribution of LILE and HFSE in these substances shown on the spidergram (Fig. 2) is related to different causes. Small negative Nb and Ta anomalies may be indications for a certain contamination of the melt with lithospheric material. At the same time, similar anomalies of these elements in bitumen and maltha reflect their fractionation pattern in the crystal–fluid system rather than their crustal source. According to [5], Nb, Ta, and Ti mainly concentrate in solid phases in the process of melt crystallization. The small minimum in the Th–W–U system of basalt is consistent with the behavior of these elements in mafic and



**Fig. 1.** Chondrite-normalized REE patterns [8] of carbonaceous substances and basalt. (1, 2) Kerite from amygdules, (3) kerite from vein, (4) asphalt, (5, 7) asphaltenes from maltha and oil, (6) basalt (see Table 1).

ultramafic rocks. Since W and U pass into the fluid phase during crystallization of mafic melts, their behavior differs from that of Th and Nb. The concentration of chalcophile W and lithophile U is related to their high fugacity in volcanic processes, whereas the sharp maximum in the content of Pb testifies to its crustal origin. The summary PM-normalized pattern of transitional elements displays fractionation of Sc, V, Mn, and Cu into the fluid phase and a low fugacity of Ti, Cr, Co, and Ni.

Thus, the formation of various classes of carbonaceous substances ranging from liquid maltha in basalts to country rocks of the Minusa Basin is related to the degassing of reduced and highly alkaline mafic magmas in the course of crystallization. However, the structure of carbonaceous substances and their geochemical characteristics allow us to suggest that they were formed asynchronously and under different thermodynamic conditions. Maltha was formed at the latest stage. The source of fluids responsible for this process was located deeper than the basalts exposed at the surface and the associated high-carbonaceous substances.

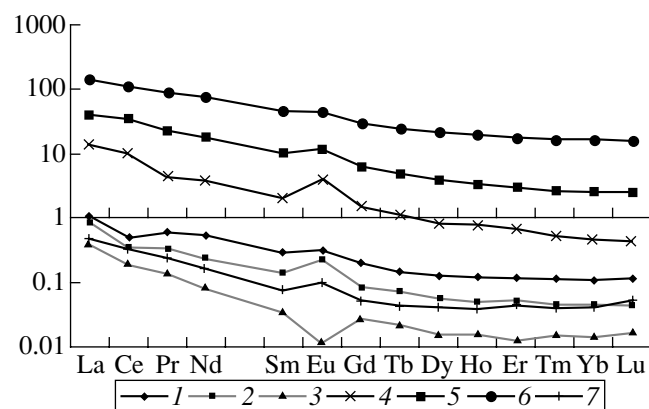
Table 1 shows the microelemental composition of asphaltenes from oil of the Maloich field in the southern West Siberian Plate (Figs. 1 and 2 are given for comparison). Hydrocarbon pools in this field are hosted in the Devonian rocks (Well 27, depth interval 2837–2857 m). The geochemical signature of maltha from the Minusa Intermontane Basin is quite comparable with the respective characteristics of oil.

This conclusion is valid from the concept of the polygenetic origin of naphtides. According to this concept, accumulation of oil pools requires not only the occurrence of source rocks but also a powerful source of energy in the form of emplacement of mafic-ultramafic melts into the lower consolidated crust and the injection of the fluids released from the crystallized melts into the upper crust. Transformation of the fluids on paths of their migration and interaction with sedi-

mentary rocks may result in the accumulation of hydrocarbons [7].

The PGE distribution in oils from various provinces [8] indicates that the geochemical signature of oil is determined by accumulation of the metals inherent to ultramafic rocks in combination with elements typical of alkaline rocks (REE, Th, U, Zr, and others). The alkaline trend of igneous activity serves as an indicator of structural evolution of the depressions favorable for oil formation and plays the role of an oxygen filter for transmagnetic fluids. Such an environment promotes the formation of reduced oil-forming systems [9].

To establish the genetic links of the C-bearing substances with intraplate alkaline magmatism, the analysis of the microelemental composition of veined kerite and maltha was supplemented with a study of their Sr and Nd isotopic compositions. As follows from Table 2, the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of kerite (0.70488) corresponds to the initial Sr isotopic composition of basalts from this region ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7036\text{--}0.7043$  [10]). The



**Fig. 2.** PM-normalized [14] distribution of HFSE and LILE in carbonaceous substances and basalt. See Fig. 1 and Table 1 for legend.

**Table 2.** Nd and Sr isotopic compositions of veined kerite and maltha

Sample	Rb	Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ (measured)	$^{87}\text{Sr}/^{86}\text{Sr}(0)$	$\epsilon_{\text{Sr}}(0)$
Kerite (sample 3)	0.091	1.038	0.2536	$0.70644 \pm 18$	0.70488	5.5
Asphaltene from maltha (sample 5)	5.33	95.96	0.1607	$0.707077 \pm 13$	0.70609	22.6
Sample	Sm	Nd	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ (measured)	$^{143}\text{Nd}/^{144}\text{Nd}(0)$	$\epsilon_{\text{Nd}}(0)$
Kerite (sample 3)	0.0053	0.0697	0.07604	$0.512545 \pm 19$	0.512351	4.2
Asphaltene from maltha (sample 5)	1.561	9.475	0.1647	$0.512541 \pm 11$	0.51212	-0.3

Sr isotopic composition of maltha ( $\epsilon_{\text{Nd}}(0) = 22.6$ ) also fits the values characteristic of the Early–Middle Devonian igneous rocks. The source of the Early–Middle Paleozoic magmatism is characterized by  $\epsilon_{\text{Nd}}(0)$  within a range of +(4.0–7.5) [11]. The Nd isotopic composition of the solid carbonaceous substance falls in the same range (Table 2). Maltha is slightly depleted in radiogenic Nd as a result of the younger age of the mantle source and its elevated alkalinity. This is also supported by the fact that the Sr isotopic composition of maltha remained almost unchanged over the last 400 Ma.

Thus, consideration of relationships between the mantle and crustal processes in the Altai–Sayan region shows that the occurrences of mantle magmatism of various ages and depths are juxtaposed in this region. They display a distinct trend of an increase in depth and alkalinity of mantle melts [11]. The reduced metalliferous fluids, which produce bitumen and hydrocarbon pools under certain conditions, may arise in a long-lived mantle fluid-magmatic system. Taking into consideration the factual data presented and the geological history of the region, which is characterized by a powerful source of heat and fluids, we believe that the Minusa Intermontane Trough can accommodate oil pools.

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