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ORGANIC MATTER AND GEOCHEMISTRY OF KUNGURIAN COALS FROM NORTHERN PREURAL FOREDEEP

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Abstract. The article presents the results of coal-petrographical and geochemical studies of Permian Kungurian coals from Northern Preural foredeep. According to their coal-petrographical composition the coals are divided into two- and three-component with the predominance of vitrinite group. The coals formed within lowland bogs. The distribution of n-alkanes and isoprenoids in the hydrocarbon fraction of the bitumen indicates the presence of three organic matter sources: sapropel, humus and mixed.

Key words: coals of Kungurian age, conditions of formation, coal-petrography, types of organic matter, bitumoid, n-alkanes

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Permian coal-bearing deposits contain a significant amount of organic matter (OM), the maximum concentration of which is characteristic for the regions of coal-bearing formation. The generation of Kungurian coals and rocks took place in various settings. The conditions of accumulation directly affect the composition of the initial OM of coals and determine its dominant type. Investigation of coals was carried out in 6 sections (Figure 1) of Kungurian deposits on rivers Vorkuta, Kozhym, stream Bokovoy and mines of the Vorkuta coal-bearing region (Vorkutinsky, Vorgashorsky, Yunyaginsky). In addition, published data on the coals of the Vorkutinsky and Vorgashorsky deposits were used (Korelsky, Margo, 1975). Carboniferous sediments, similar to the complex under consideration, are currently receiving much attention from many researchers. Evaluation of the properties of oil and gas rocks is inseparable from the determination of the initial OM type and the level of its catagenetic maturity. Determination of the OM composition and its accumulation conditions are the primary tasks for characterizing the type of initial matter of the rocks. In the present work, the main attention was paid to the composition of coals and their formation conditions, which directly influence the properties of carbonaceous matter and the products of its processing.

Research Methodology

The results of coal petrography studies in conjunction with data of organic geochemistry make it possible to determine the type of OM, its composition and conditions for the formation of coals. Carried out coal-petrographical studies characterize the composition of OM, the conditions for its accumulation and the level of catagenetic transformation. In addition to coal petrography, the results of pyrolysis using the Rock-Eval method (VNIGNI, Moscow) were used to determine the type of OM, its generation potential (HI, mg HC/g C_{org}) and the degree of catagenetic conversion (T_{max}, °C). Chemical-bituminological studies included determination of the content of organic carbon (C_{org}, %) and chloroform bitumen (%). Another of the methods used is gas chromatography (GC), the results of which also characterize the dominant type of OM,

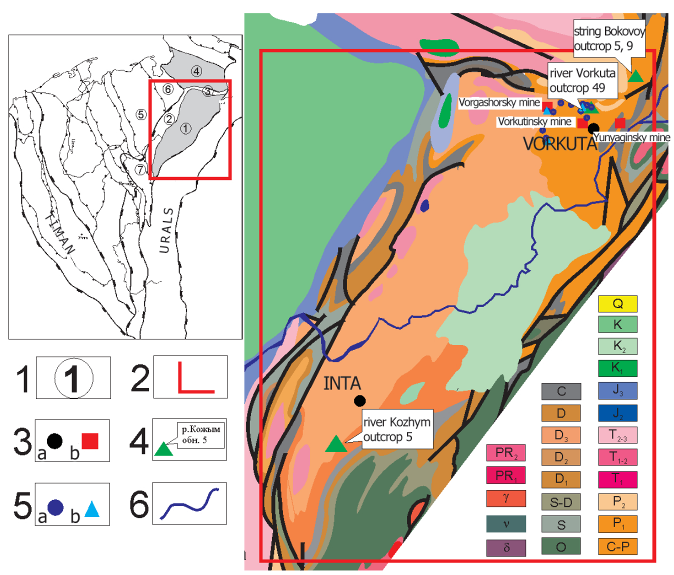


Fig. 1. Geological map of the research area: 1 – numbers of tectonic elements; 2 – boundary of the studied area; 3-5 – studied sections and their numbers: 3 – cities (a), mines (b); 4 – outcrop; 5 – finds of sapropel-humus coals: a – package p, b – package t (according to data (Korelsky, Margot, 1975)): 6 – rivers. Tectonic elements: 1 – Kosyu-Rogovsky depression, 2 – Chernyshev ridge, 3 – Chernov ridge, 4 – Korotaikhin depression, 5 – Khoreyversky depression, 6 Varandey-Adzvinsky structural zone, 7 – Bolshesyninsky depression

conditions for its accumulation and transformation during catagenesis. In general, the conducted complex of methods gives more complete information on the OM composition and its properties.

Coal petrography and formation conditions

The coals in question correspond to different grades – from long-flame (Kozhym river) to the gas (in the mines of the Vorkuta district). Changes in the grade composition and accordingly metamorphism intensity occurs in northeastern direction, which was repeatedly pointed out by many researchers (Coal-bearing formation..., 1990; Anischenko et al., 2004). The data of coal petrography studies, in particular the component composition, were plotted on the diagram of the OM microcomponents ratio (Fig. 2). The major part of coal concentrated in the upper corner and along the axis Vt-It of the diagram, characterized by inertinite-vitrinite (It-Vt) composition. Part of the coals displaced to the center of the diagram consist of three groups of components: liptinite, inertinite and vitrinite.

The most diverse composition is determined in coals of the lekvorkutskian suite of the outcrop No.49 of the Vorkuta River and Vorkutinsky mine. The spread of the components Vt and It of these sections is 60-100%. According to the composition of microcomponents, the coals are divided into two groups: two-component and three-component. Coals consisting of three groups: vitrinite (Vt), inertinite (It), and liptinite (Lt), with a different fraction (5-40%) of the latter, were found in all the sections studied (Figure 3).

The vitrinite group is represented by telinite, collotelinite, and helinite. All components are found in coals in different ratios. The greatest content of telinite is determined in the coals of the Komsomolsky mine of the Vorkuta District (Figure 3a, b). Telinite is often encountered in the form of lenses and non-retentive interlayers in collotelinite (Figure 4 e). Collotelinite

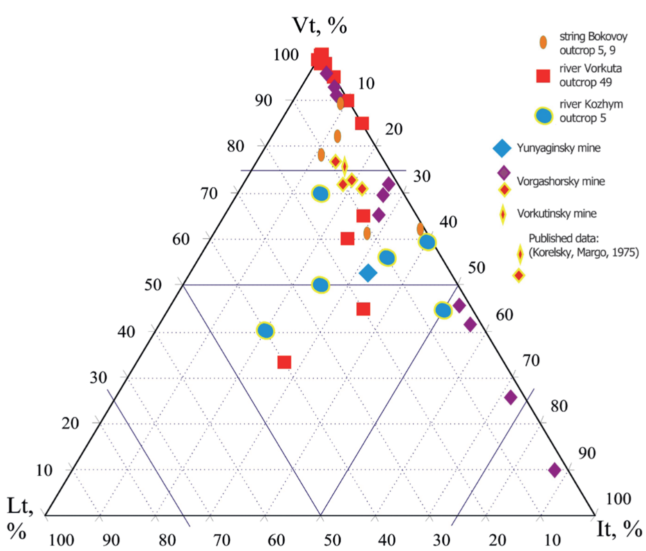


Fig. 2. Coal-petrographic composition of Kungurian coals of the Lower Permian

(Figure 3c, d; Figure 4c-e) and helinite (Figure 3a, b, Figure 4a, b) form lenses and entire interlayers.

Inertinite components are represented by fusinite (Figure 4a, c), inertodetrinite (Figure 4b, f), semifusinite (Figure 3d), mikrinite, macrinite and funtinite (Fig. 4g). The group of liptinite is found in various co-forms of lenses and inclusions of rubberite (Figure 3c, d) in the collinite base mass, as well as various inclusions – sporinite (Figure 4b), kutinite, and liptodetrinite (Figure 4 (a)), rarely alginite.

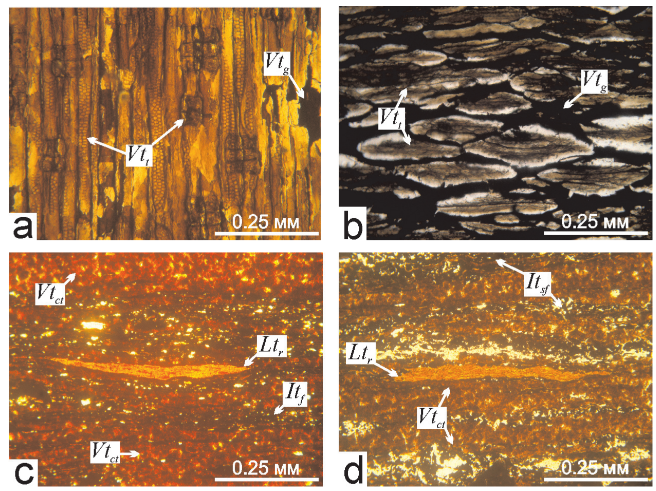


Fig. 3. Photo of coal thin sections in transmitted light; a – b – Mine Komsomolsky; c-d- Mine Vorgashorsky. The notation for Fig. 3, 4: Vt – vitrinite group, Vtt – telinite, Vtct – collotelinite, Vt_g – helinite, It – group of inertinite, It_f – fusinite, – semifusinite, Lt – group of liptinite, Lt_r – rubberite

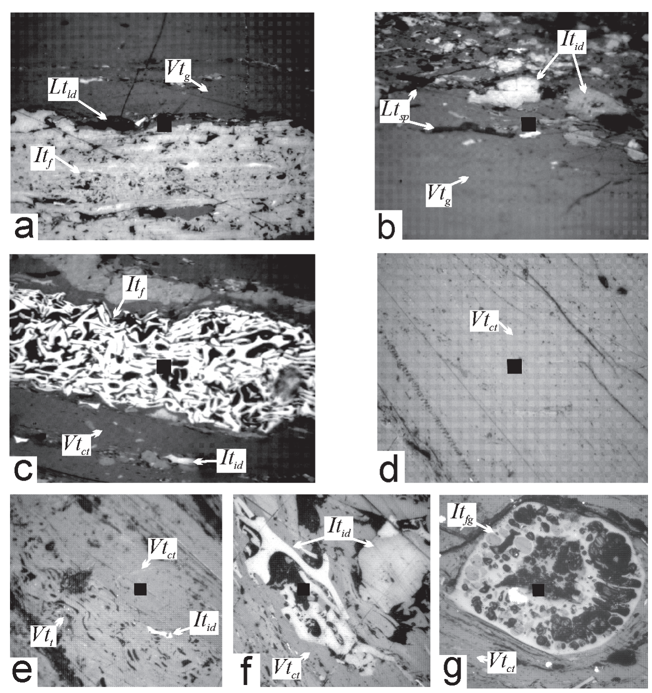


Fig. 4. Photo of polished thin sections of coal in reflected light, oil immersion, UVx50, mark at the center of the frame 5x5μm: a – c – sample 7.1.16, outcrop 49, Vorkuta River; d – f – sample 4, outcrop 9, Bokovoy Stream; g – sample 3, outcrop 5, Bokovoy River. Additions to the symbols in Fig. 4: It_{id} – inertodetrinite, It_{fg} – funginite, Lt_{sp} – sporinite, Lt_{ld} – lipodetrinite

The maximum contents of Lt are determined in coals of outcrop No. 49, where the greatest amount of cutinite, sporinite and, to a lesser extent, resinite were found. In the coals of the Vorkuta District, with small contents of liptinite group (up to 10%) and high ash content, the remains of algae (alginite) are found. The presence of mixed OM of the II-III type in these sections is confirmed by the data of pyrolytic studies, in particular the hydrogen index (HI). HI of mixed type coal varies from 150 to 400 mg HC/g of C_{org}. According to the dominant composition of OM in coals, there are III, II-III, III-IV and VI types. The predominance of one or another type of OM is due to differences in the conditions of accumulation and sources of organic material. The presence of a large variety of OM types indicates the presence of various sources of material supply and, ultimately, the difference in the properties of coals.

Conditions for the formation of coal beds play a primary role in the coal composition. At the present time, various indices are used, on the basis of which diagrams are constructed, where regions are distinguished with differences in conditions of coal accumulation. In this paper, we used the Diessel indices (Diessel, 1992), taking into account the constancy of humid conditions and the rate of burial of the sediment. TPI and GI are indicators of structural integrity and gelification, respectively (Figure 5). The structural integrity index (TPI) is estimated using a fraction, in the numerator of which the sum of structural components, and in the denominator, structureless:

TPI = (telovitrinite + semifusinite + fusinite) / (detritovetrinite + makrinite + inertertetrinite).

Under oxidation conditions (low water level or passing water), decomposition of OM and plant structure occurs. In anaerobic conditions with low bacterial activity, the structure is preserved.

The second index (GI) – the index of gelification (homogenization) – serves to determine water cut. It is determined by the ratio of the gelified components to ungelified ones and shows the geochemical conditions of peat accumulation. An increase in the GI index is an indication of the water level. The transition is from anhydrous forest conditions to lake ones:

GI = (vitrinite + macrinite) / (semifusinite + fusinite + inertertetrinite).

The greatest differences in the conditions of coal accumulation are characteristic for the section of the lekvorkutskian suite on the outcrop No. 49 (River Vorkuta), in view of selection of coals in various parts of the coal cycle. According to the calculated indices, ears were formed under various conditions from small dry bogs, to lowland and reed bogs, i.e. coastal areas with the influence of marine conditions. The ears of the deposits of the Vorkuta region gravitate toward the formation of lowland bogs, as well as the coals of the

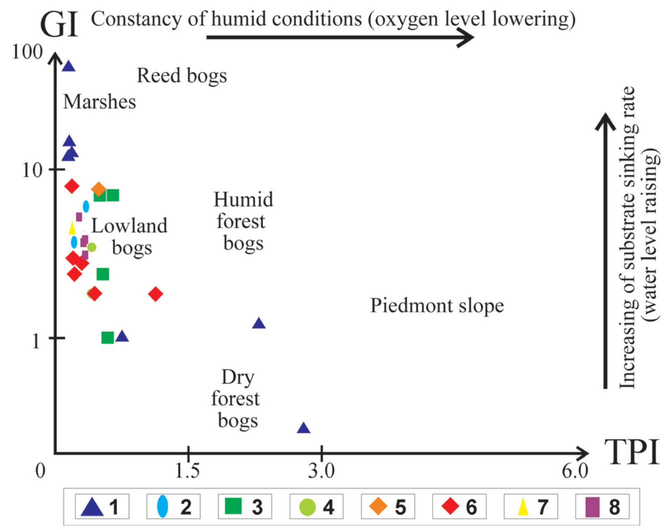


Fig. 5. Field of figurative points of coal samples of Kungurian age in the north of the Preural fore deep on the genetic diagram of Diessel. Sampling points: 1 – outcrop 49, Vorkuta River; 2 – outcrop 5, Kozhym River; 3 – outcrops 5, 9, Bokovoy Stream (numbering according to Pukhonto, 1998); 4 – Yunyaginsky Mine; 5 – Vorkutinsky Mine; 6 – Vorgashorsky Mine; 7 – Vorkutinsky field; 8 – Vorgashorsky field (7-8 finds of sapropelian-humus coals according to data (Korelsky, Margot, 1975))

Kungurian sediments on the river Kozhym and stream Bokovy. The vast majority of coals formed in coastal wetlands with the influence of marine conditions. Thus, the coals are characterized by the generality of formation conditions, but differ in the sources of the initial matter and in the composition of the OM.

Geochemistry of coals

The type of initial OM determines the differences in the geochemical indicators and products of its catagenetic transformation. Concentrations of organic carbon (C_{org}, %) and chloroform bitumen (CFB, %) vary over a wide range: C_{org} – 25-90%, CFB – 0,1 -1,4%. The maximum values are characteristic for less ash ears of the Vorkuta District. The bituminous factors (β_{x6}, %) calculated from the ratio of CFB to C_{org} do not exceed 3%.

According to the distribution of n-alkanes in bitumen (Figure 6), three groups can be distinguished among the examined coals. The first group of bitumen is characterized by a left-symmetric distribution with a predominance of low-molecular n-alkanes in the C_{13}-C_{18} area with a maximum distribution for n-C_{16}, which is characteristic of the sapropel component of OM. The concentration of high molecular alkanes of the normal structure of composition C_{25}-C_{33} is extremely insignificant (Table). It was possible to identify isoprenoids i-C_{15}, i-C_{16}, i-C_{18}, i-C_{19} (Pristan (Pr)) and i-C_{20} (phytane (Ph)). Moreover, the concentration of i-C_{19} is greater than i-C_{20}. Such a distribution is characteristic for bitumen of coal of lekvorkutiskian suite from the outcrop No. 49 on the river Vorkuta and coal from the Vorgashorsky Mine. The composition of coals predominantly consists of vitrinite, as well as inclusions of liptinite – resinite, kutinite and sporinite.

For the second group, characteristic for coals of the "thick" layer from the Vorkutinsky Mine, an increased content of medium-molecular n-alkanes of the composition Cl_9-C_{24} is observed, with a shift of the distribution maximum to the region of n-C_{18}, n-C_{20}. This group of bitumen is characterized by a very low content of alkanes of the isoprenoid structure in comparison with n-alkanes.

The first two types of distribution characterize the vast majority of ears, with predominance of low- and medium-molecular n-alkanes occurring in the northern sections. Each type of distribution is characterized by both 2-and 3-component composition of OM (Vt, It, Lt). Small differences in the ratio of n-alkanes are observed with a change in the composition of the microcomponents of the liptinite group, which is more pronounced in bitumen from the outcrops along the river Vorkuta and the stream Bokovoy (Figure 6).

The third group of bitumen is characterized by a high content of high-molecular n-alkanes of composition C_{25}-C_{33} C_{33} (responsible for the contribution of humic OM), the relative concentration of which reaches 31.9%,

Section		*Outcrop 5 riv. Kozhym*	*Vorgashorsky mine*	*Vorkutinsky mine*	*Outcrop 49 riv. Vorkuta*	*Yuniyaginsky mine*	*Outcrop 5 str. Bokovoy*
Catagenesis grades (Ro, %)		MC_1 (0,5–0,65)*	$MC_{2\text{-}3}$ (0,8–0,87)*	MC_3 (0,85–1,1)*	MC_3 (0,8–1)	$MC_{3\text{-}4}$ (1,15–1,4)*	MC_5 (1,87)
Geochemical parameters	C_{13}-C_{18}	16,1–28,3	45,99	25–33,95	28–74	48,4	18,9
	C_{19}-C_{24}	30,2–32,5	31,12	45,3–52	15,6–34,7	37,3	34,6
	$>C_{25}$	25,3–31,9	14,31	14,3–16	2,9–6,6	7,5	26,8
	** $K_{od}C_{17}$	1–1,1	0,96	0,55–1	0,7–1,5	0,27	1,23
	*** $K_{od}C_{29}$	2,65–2,9	1,14	1,48	0,5–1,2	-	0,6
	Pr/ Ph	4,1–4,75	3,79	0,4–2,6	1,7–6,5	1,7	6
	Pr/ nC_{17} Ph/nC_{18}	2,6–2,8 0,56–0,6	0,34 0,1	0,1–0,86 0,1-0,24	0,3–1,8 0,2–0,8	0,74 0,1	1,92 0,4
	Pr+Ph / nC_{17}+nC_{18}	0,9–1,2	0,2	0,2–0,3	0,5–1,2	0,23	1,24

*Table. Geochemical parameters of saturated hydrocarbons of Kungurian coals of different catagenesis grades in the north of the Preural fore deep. Note: * according to the data of Anishchenko et al., 2004, ** $K_{od}C_{17}$ = 2*n-C_{17}/(n-C_{16} + n-C_{18}), *** $K_{od}C_{29}$ = 2*n-C_{29}/ (n-C_{28} + n- C_{30})*

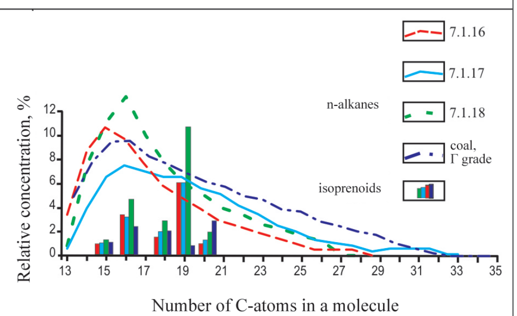
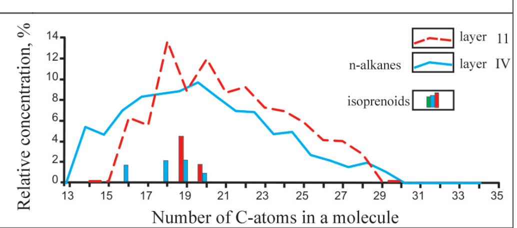
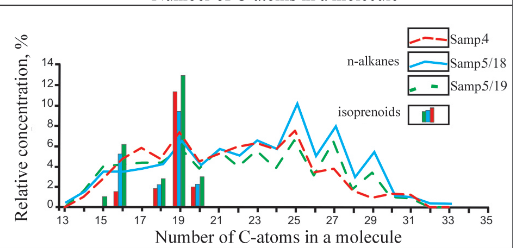
Group	Section (Sample No.)		CFB, %	β_{x6}, %	Distribution of n-alkanes and isoprenoids
I	Outcrop 49, riv. Vorkuta	7.1.18	1,35	1,74	
		7.1.16	0,88	1,55	
		7.1.17	0,78	1,26	
	Mines	Vorgashorsky, coal, Γ grade	0,036	0,9	
II		Vorkutinsky, 11 layer	0,8	1,0	
		Vorkutinsky, IV layer	0,13	0,18	
III	Outcrop 5, str. Bokovoy, sample 4		0,034	0,1	
	Outcrop 5, riv. Kozhym	5/18	0,068	0,12	
		5/19	0,123	0,44	

Fig. 6. Distribution groups of saturated hydrocarbon coal bitumen (compiled with the addition of Anishchenko et al., 2004)

and the bimodal distribution. The bimodal distribution of n-alkanes (Figure 6), characterizing the mixed type of OM (sapropel-humus), is noted in the bitumen from the outcrop No. 5 of the River Skin and along the stream Lateral to the north-east of the Vorkutinskian section. The change in the composition of OM is reflected in the geochemical parameters calculated from gas chromatography data (Table).

The greatest spread of oddness coefficients $K_{od}C_{17}$ – 0.7-1.5 and $K_{od}C_{29}$ – 0.5-1.2 is characteristic for coals from the outcrop No. 49 (Vorkuta River), which is due to differences in the composition and conditions of formation. The predominance of medium-molecular odd n-alkanes ($K_{od}C_{17}$> 1) reflects the participation of algal OM in the composition of the initial biomass (Hunt, 1982; Tissot, Welte, 1984). The value of the oddness coefficient of high-molecular n-alkanes ($2C_{29}/C_{28}+C_{30}$) for sapropelic OM, the formation of which took place under regenerative conditions, rarely exceeds 1. Humic OM, accumulation of which took place in weakly reducing and suboxidative conditions, is characterized by an increased value of the oddness coefficient (>>1).

The maximum values of $K_{od}C_{29}$ – 2,65-2,9 are noted in coals from the outcrop 5 (Kozhym River) of the third group of n-alkanes distribution. The ratio of isoprenoids is also characterized by a considerable spread of Pr/ Ph values from 0.39 to 6. Under the conditions of the Timan-Pechora basin, the value of the pristane/ phytane parameter depends on the facies of the OM accumulation(Anishchenko et al., 2004). Bitumen of coal accumulation zones (lake-marsh conditions) is characterized by high values of this parameter (2-4.5). In wetland plains with weak coal accumulation, the value of this indicator decreases to 1.5-2 (Anishchenko et al., 2004). An increase in the values of this coefficient is possible due to the growth of thermal maturity of OM. The ratios Pr/n-C_{17}- 0.1-2.8 and Ph/n-C_{18}- 0.1-0.8 generally indicate differences in the composition and conditions of coal accumulation. Values of the ratio (Pr+Ph)/(n-C_{17} + n-C_{18}) <1, with the exception of bitumen from outcrops along the stream Bokovoy.

Conclusions

In terms of the composition of coal-petrographic components, the coals are subdivided into two- and three-component coals with a predominance of the vitrinite group. The differences in coals are manifested in the presence and composition of the liptinite group components. Liptinite is distinguished into terrigenous and aquatic. The first one in coals is represented by cutinite, sporinite and resinite, and the second one – by alginite. The formation of coals of the main coal accumulation zones took place in the conditions of lowland bogs. The presence of alginite indicates the proximity of lake conditions.

Three types of alkanes distribution are distinguished in the saturated fraction of bitumen, reflecting differences in the composition of the initial OM. The predominance of low molecular weight alkanes of normal structure is characteristic to the sapropel component of OM, which is confirmed by the presence of alginite in the composition of these coals in the Vorkuta District. Significant concentrations of high-molecular n-alkanes responsible for the contribution of humic OM are characteristic for the southern part of the Kosyu-Rogovsky Depression (the Kozhym River). Minor differences in the composition of the initial biomass of coals allow us to say that there were different lake-marsh sedimentation conditions in the northern and southern sections of the Kosyu-Rogovsky Depression during the lekvorkutskian time.

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