

Geochemical features of bitumen shows in the Lower-Middle Devonian deposits of the Northern-Western part of Kotelny Island (Novosibirsk Island Archipelago)

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Abstract. The work presents the results of organic matter (OM) study of rocks, the composition, chemical structure of chloroform bitumen (CBH), their fractions and the nature of the hydrocarbon biomarkers distribution in samples taken from outcrops. The obtained results confirmed the existing idea of the domanicoid nature of OM and the high oil and gas potential of the studied deposits. According to our data, the aquagenic type of OM is indicated by a high content of C_{org} , a high yield of CBH, a high content of oils in the composition of synbitumoids, and the predominance of relatively low molecular weight n-alkanes with a maximum at nC_{15-18} . A sufficient maturity of bitumen can be judged by CPI coefficients close to unity and low absorption coefficients of oxygen-containing groups and bonds in the CBH, thus deposits entered the main oil generation zone and generated liquid hydrocarbons that could migrate and form pools. According to the data of Chromato Mass Spectrometry, it is shown that a feature of the composition of CBH from the Lower Devonian sediments is the presence of high concentrations of dibenzothiophenes, in contrast to the Middle Devonian, which may be associated with the formation of the initial OM in an environment with higher hydrogen sulfide contamination of sediments. It has been suggested that naphthides generated by aquagenic OM of the Lower Devonian deposits can be enriched with dibenzothiophenes. The studied bitumen shows are mainly syngenetic in nature and have been influenced by hypergenic oxidation (judging by the nature of the IR spectra of resinous components) and contact metamorphism. According to the characteristics of the distribution of saturated hydrocarbons, it was shown that, in the Middle Devonian, bitumen occurrences along with chemical oxidation were affected to a different degree of bacterial oxidation processes, in contrast to the Lower Devonian bitumen shows. The results can be used to assess the generation potential of oil source strata and to forecast the prospects of oil and gas potential in the shelf of the eastern sector of the Russian part of the Arctic.

Keywords: Kotelny Island, Lower and Middle Devonian, organic matter, bitumen shows, hydrocarbon biomarkers

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Introduction

Among the oil and gas-bearing Palaeozoic basins of the Arctic zone of the Russian Arctic Sector, the territory of the Novosibirsk Islands is interest. In the section of Lower-Middle Devonian sediments of the Kotelny bitumen shows of various nature from syngenetic dispersed differences of organic matter (OM) to secondary local of bitumen. According to a number of researchers sediments

of the Lower Middle Devonian of the Middle Paleozoic potentially oil and gas-bearing complex are related to the oil produced strata (Gramberg, 1976; Evdokimov et al., 2008; Ivanov, Clubov, 1979; Kosko, 1988; Polyakova et al., 2016; Safronov, 2002). The perspective of this complex of sediments along with syngenetic bitumens and high content of OM is confirmed by good collector properties of rocks (Gramberg, 1976).

At the same time, the analysis of publications on geochemistry of OM of rocks and bitumens of the Devonian sediments of the Kotelny island showed that the studies had been carried out mainly at the level of determination of organic carbon content (C_{org}), yield of chloroform bitumoid (CHB) and group composition.

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From a point of view of an assessment of oil source properties of rocks these data are not sufficiently detail.

In order to clear up oil source properties of the rocks and characteristics of nature of bitumen shows, there were studied the content of OM, the composition and chemical structure of CHB and the distribution of hydrocarbon biomarkers in samples from the outcrops of the Pshenicinskaya, Bysakh-Karginskaya, Shlyupochnaya suites of the Lower Devonian and Sokolovskaya suite of the Middle Devonian. The samples selected in the north-western part of the Kotelny island.

Material and methods

Analytical studies are made according to the generally accepted scheme of bituminous research (Guide to the analysis of bitumen..., 1966). The content of organic carbon in the rocks (C_{org}) was determined by burning method, the yield of CHB – by hot extraction with chloroform. After precipitation of asphaltens with excess petroleum ether, CHB were separated out by column chromatography (on ASK silica gel) resins and hydrocarbons (oil fractions). The structural-group composition of CHB and their fractions was determined by IR-Fourier spectroscopy. IR spectra were recorded on Nicolet Protégé 460 spectrometer in the region $4000-600\text{ cm}^{-1}$ in the cell with KBr windows, the thickness of the absorbing layer was $33 \times 10^{-6}\text{ m}$. The interpretation of the IR spectra was made according L. Bellamy (1963). The chromato-mass-spectrometric studies of saturated hydrocarbon fractions of the oil fractions were performed on the system including the gas chromatograph Agilent 6890 with interface and

high-performance mass-selective detector Agilent 5973N. The chromatograph is equipped with a quartz capillary column 25 m long, 0.25 mm diameter, impregnated phase HP-5MS. Carrier gas – helium, flow rate 1 ml/min. evaporator Temperature 320°C ; programming temperature rise – from 100 to 300°C at a speed of $4^\circ\text{C}/\text{min}$ followed by isotherm for 30 min. Ionizing voltage source 70 eV, source temperature 220°C . The mass chromatograms of hydrocarbons (oil fractions) were obtained from total ion current (TIC) and characteristic fragment ions. Identification of individual hydrocarbons was carried out by computer search in the library of the National Institute of Standards NIST-05 according to literature data and reconstruction of structures by the nature of ion fragmentation in electronic impact.

In general, there were analyzed 19 samples of rocks from deposits of the Lower-Middle Devonian, the contents of the C_{org} (19), the yield of CHB (19), group composition CHB (11) were defined. IR spectra of CHB were recorded for 11 samples as for 9-oil fractions, 8 – benzol and 8 – alcohol-benzol resins and the individual composition of saturated hydrocarbon oil fractions was determined for 11 samples.

Figures 1a and 1b show the geological scheme of the studied area, the stratigraphic section of the Lower-Middle Devonian sediments and the location of the samples. A detailed description of the stratigraphic section, the conditions of sedimentation and the nature of the bitumen of the studied area are discussed in detail in the works (Explanatory note..., 1985; 2016). The formation of the Lower-Middle Devonian sediments

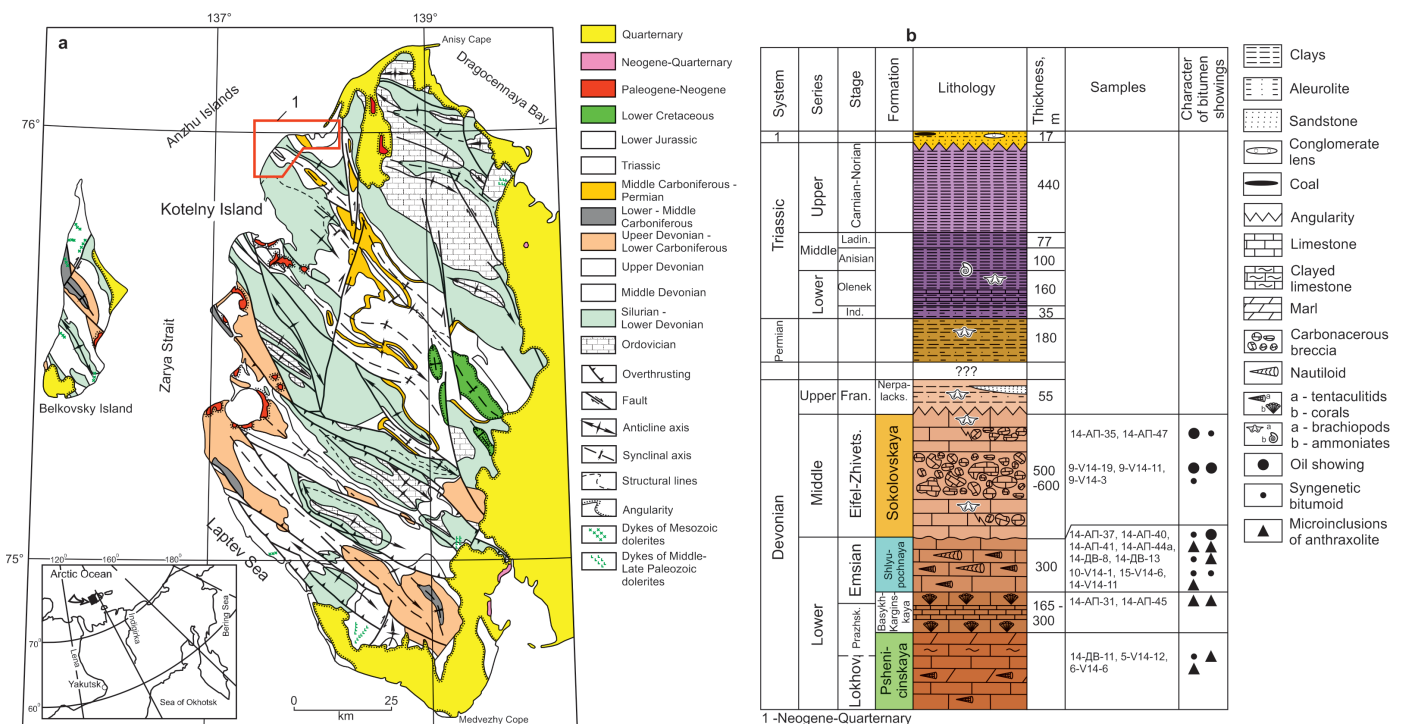


Fig. 1. a – The geological scheme of the studied area, the Polar Station, the Kotelny island (by (Tectonics, geodynamics and metallogeny..., 2001). b – The stratigraphic section of the Lower-Middle Devonian sediments and samples location.

occurred in the conditions of shallow-water marine facies with high sulphur-hydrogen contamination in a reducing environment favorable for the accumulation and preservation of the initial aquatic OM (Explanatory note..., 1985). In the studied section a variety of bitumen accumulations as syngenetic as epigenetic nature, local accumulation of bitumen, horizons saturated by anthraxolites with a thickness of up to 8-10 meters

(Ivanov, Clubov, 1979). The presence of anthraxolites and vein bitumens is an evidence that the processes of generation and migration of hydrocarbons were in these deposits (Safronov, 2002).

Research result

The results of the studies are given in Tables 1 and 2 and in Figures 2-4.

Age, suite	Number sample	Lithology	C _{org} , % on rock	CHB, % on rock	β _{x6} , %*	Group composition CHB, %		
						oils	resins	asphaltenes
D ₂ ^{sk}	14-АП-35	bituminous lime sandstone	2,06	0,239	11,6	70,3	27,2	2,6
D ₂ ^{sk}	14-АП-47	calcite with bitumen inclusions	0,35	0,063	18,1	43,5	43,5	13,0
D ₂ ^{sk}	9-в14-19	limestone	1,25	0,135	10,8	63,5	30,2	6,3
D ₂ ^{sk}	9-в14-11	limestone	1,25	0,119	9,5	59,9	37,4	2,6
D ₂ ^{sk}	9- в14-3	limestone	0,08	0,009	11,2	43,4	46,0	10,5
D ₂ ^{sk}	Mean		1,00	0,113	12,2	56,1	36,8	7,0
D ₁ ^{sh}	14-АП-37	limestone	0,55	0,032	5,8	16,3	73,8	9,8
D ₁ ^{sh}	14-АП-40	organogenic limestone	5,40	0,195	3,6	62,5	28,5	9,1
D ₁ ^{sh}	14-АП-41	calcite with bitumen inclusions	14,01**	not detect				
D ₁ ^{sh}	14-АП-44a	organogenic limestone	2,28	not detect				
D ₁ ^{sh}	14-ДВ-8	organogenic limestone	1,07	0,029	2,7	47,2	46,5	6,4
D ₁ ^{sh}	14 ДВ-13	calcite with bitumen inclusions	36,82**	not detect				
D ₁ ^{sh}	10-в14-1	organogenic limestone	0,82	0,017	2,1	49,4	48,3	2,2
D ₁ ^{sh}	15-в14-6	organogenic limestone	0,82	0,015	1,8	51,2	46,3	2,4
D ₁ ^{sh}	15-в14-11	limestone	0,23	not detect				
D ₁ ^{sh}	Average		1,60	0,058	2,7	45,3	48,7	6,9
D ₁ ^{bs}	14-АП-31	bitumen inclusions in carvernous dolomite	32,73	not detect				
D ₁ ^{bs}	14-АП-45	bitumen inclusions in carvernous dolomite	65,68	not detect				
D ₁ ^{psh}	14-ДВ-11	organogenic limestone	9,53	0,118	1,24	52,7	41,6	5,8
D ₁ ^{psh}	5-в14-12	limestone	0,10	not detect	0,00			
D ₁ ^{psh}	6-в14-6	limestone	0,10	not detect	0,00			

Table 1. Characteristic organic matter and chloroform bitumoids of rocks, the Devonian deposits, the Kotelny island, the Polar station. Signs: D₁^{psh} – the Pshenicinskaya suite, D₁^{bs} – the Bysakh-Karginskaya suite, D₁^{sh} – the Shlyupochnaya suite, D₂^{sk} – the Sokolovskaya suite; * β_{x6} % – bituminous coefficient = (CHB/C_{org})*100 %; ** – values didn't include at the calculation of mean significance of C_{org}.

Age, suite	Number sample	Σb.b.-nC ₂₀ ΣnC ₂₁ e.b.	Maximum n-alkanes	Isoprenoids n-alkanes	CPI	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈	Pr+Ph nC ₁₇ +nC ₁₈
D ₂ ^{sk}	14-АП-35	0,20	HC _{25,24}	0,15	1,02	0,49	2,39	3,58	3,08
D ₂ ^{sk}	14-АП-47	0,71	HC _{18,19,20}	0,12	0,99	0,58	0,34	0,49	0,64
D ₂ ^{sk}	9-В14-19	0,52	HC _{19,20}	0,17	0,95	0,68	0,83	0,78	0,80
D ₂ ^{sk}	9-В14-11	0,52	HC _{25,26} и HC ₁₅	0,19	0,97	0,13	1,61	1,65	1,63
D ₂ ^{sk}	9-В14-3	0,78	HC _{16,17}	0,31	0,94	1,26	1,26	1,18	1,22
D ₁ ^{sh}	14-АП-37	1,03	HC _{17,18}	0,08	1,03	1,23	0,36	0,29	0,33
D ₁ ^{sh}	14-АП-40	1,63	HC _{16,17}	0,05	0,94	1,49	0,20	0,13	0,16
D ₁ ^{sh}	14-ДВ-8	1,01	HC ₁₇	0,09	0,97	0,51	0,19	0,33	0,26
D ₁ ^{sh}	10-В14-1	0,52	HC _{16,17} и CH ₂₆	0,20	0,94	1,16	0,81	0,98	0,89
D ₁ ^{sh}	15-В14-6	0,67	HC ₁₇	0,29	0,98	1,32	0,86	0,95	0,90
D ₁ ^{psh}	14-ДВ-11	0,67	HC ₁₇	0,10	1,00	1,15	0,50	0,46	0,65

Table 2. Characteristic saturated hydrocarbons of chloroform bitumoids of rocks, the Devonian deposits, the Kotelny island, the Polar station. Signs: Pr – pristan (iC₁₉), Ph – phytan (iC₂₀), CPI = Σn-alkanes with even number of carbon atoms of molecule / Σn-alkанов с чётным number of carbon atoms of molecule.

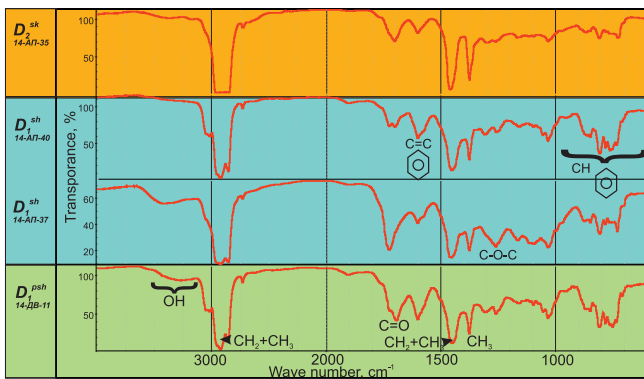


Fig. 2. IR spectra of chloroform bitumoids of rocks, the Lower-Middle Devonian deposits, the Kotelny island, the Polar station

Pshenicinskaya suite. In the suite the three samples were studied. Two of them have a low content C_{org} to 0.1 % and CHB was absent by hot extraction. The absence of CBH may be due to the effect of contact metamorphism on the bitumen of local character.

The third sample (14-DV-11) presented by organogenic limestone with a high content of C_{org} and an increased yield of CHB was analyzed in detail (Table 1). Due by the low value of the bitumoid coefficient of 1.24 %, we can assume the syngenetic character of the bitumoid. According to the group component composition it reveals a similarity with samples from the above-lying the Shlyupochnaya suite and is characterized by a high content of asphalt-resinous components (Table 1, Fig. 1b).

In the chemical structure of the CBH of the Pshencinskaya suite as well as the Shlyupochnayay suite aromatic cycles dominate as can see from the IR spectra in the region of 600-900 and 1600 cm^{-1} and the significant values of carbonyl (1700-1730 cm^{-1}) and hydroxyl (3300 cm^{-1}) groups (Fig. 2, 3).

From the Bysakh-Kargin'skaya suite two sample (14-DV-31 and 14-DV-45) with inclusions of bitumen in cavernous dolomites had been analyzed (Fig. 1b, Table 1). They characterized by the very high content C_{org} of 30.9 and 65.7 % and the absence of CHB. Most likely, they relate to local thermally highly transformed bitumen differences of anthraxolite type (Ivanov et al., 1979). Data on the presence of solid bitumen in the dolomite caverns are given in the paper (Explanatory note..., 1985), where the C_{org} content also reaches high values of 26.4 and 61.5 %, but they have a high yield of CHB – 0.120 and 0.269 %.

The Shlyupochnaya suite. The studied samples are organogenic limestones, limestones with interlayers of argillites, as well as limestones with inclusions of solid bitumen with a characteristic gloss over faults in calcite veins. Samples differ significantly in the content of C_{org} and yield of CHB (Table 1, Fig. 1B). The maximum content C_{org} from 14.0 to 36.8 % is detected in limestone samples with inclusions of solid bitumens, the chloroform-soluble bitumoids are absent (Table 1). These features are typical for thermally highly transformed bitumen differences of the anthraxolite class. The data about the filling out the pores in the limestones of the Shlyupochnay and the Sokolovskaya suites of solid bitumens type anthraxolites in the north-west coast of the Kotelny island are given in several papers (Ivanov et al., 1979; Clubov, 1983; Kosko et al., 1975).

In carbonate rocks C_{org} is much lower than in samples with inclusions of bitumen. In organogenic limestones C_{org} is almost an order higher compared to limestones. The group composition of CHB is represented by hydrocarbons and resinous components with a low content of asphaltenes (Table 1). Hydrocarbon

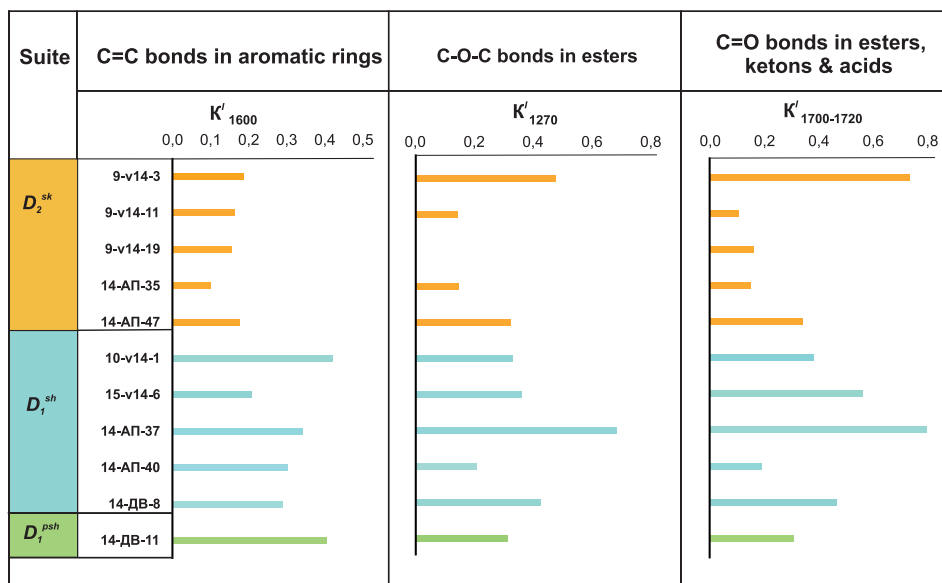


Fig. 3. Change of relative absorption coefficients in the IR spectra of chloroform bitumoids: K'_{1600} – aromatic rings, K'_{1270} – esters and $K'_{1700-1720}$ – carbonyl groups in samples from outcrops of the Lower-Middle Devonian deposits, the Kotelny island, the Polar station

compounds dominate in the chemical structure of CHB (Fig. 2, 3).

The absorption of carbonyl groups ($D_{1730-1700}$) relatively to the absorption of methyl and methylene groups (D_{1460}) is below (0.19-0.47), which can be considered as an indicator of the thermal maturity of the OM, which reached main oil generation phase.

The sample 14-AP-37 differs from above considered by very low hydrocarbons content (16.5 %) and high asphaltene – resinous components (83.5 %) as high absorption coefficients of oxygen-containing groups and bonds (Table 1, Fig. 1b). However, according to the character of the IR spectra of alcohol-benzene resins (for all the studied samples) it may be proposed that the samples were undergone to very strong oxidation in hypergenic zone, that relates to the sample 14-AP-37 to a greater extent. In the IR spectrum of alcohol-benzene resins of it the absorption of carbonyl groups is twice higher the absorption of methylene and methyl groups $D_{1700} > 2$.

The CHB of the Shlyupochnayay suite also differ in hydrocarbon composition – the content of aromatic carbon in hydrocarbons fraction varies in a wide range from 17 % to 44 %. According to the IR-Fourier spectrometry data in the composition of hydrocarbons fractions and unfractionated CHB the presence of a wide spectrum of aromatic hydrocarbons was found as in the sample of the Pshenicinskaya suite. This indicates the nontypical character of the IR spectra for naphthides with a large number of absorption bands in the region of 600-1000 cm^{-1} , due to deformation vibrations of unsubstituted hydrogen atoms in aromatic cycles – 708, 750, 762, 780, 808, 831, 848, 868 cm^{-1} and valence oscillations C=C bonds 1575, 1588, 1604 cm^{-1} (Fig. 3).

Among the studied samples of the Shlyupochnayay suite two samples sharply differ in geochemical parameters (Table. 1). Sample 14-AP-37 with the low yield of CHB, low hydrocarbons content (16 %) and dominance of asphalt-resin components, as well as high values of absorption of oxygen-containing groups and bonds can be considered as syngenetic or syngenetic residual bitumoid. While in the other (14-AP-40) – there are all the signs to relate it to paraautochthonous bitumoids $\beta=3,6$ %, which have already lost connection with the source rock, but have not left the generating strata. It is close to malta by hydrocarbons content (62 %), low – resins, low relative absorption coefficients of carbonyl and ether groups and bonds (Table 1; Fig. 2, 3).

The composition of saturated hydrocarbons of the Shlyupochnayay suite characterizes the high content of relatively low molecular weight n-alkanes ($\sum \text{b.b-nC}_{20} / \sum \text{nC}_{21-\text{e.b.}} = 1.01 - 1.63$), with maximum nC_{15-18} inherent marine OM (Table. 2, Fig. 4). Among the saturated hydrocarbons of the Pshenicinskaya suite n-alkanes make up 56 %, a high content of relatively

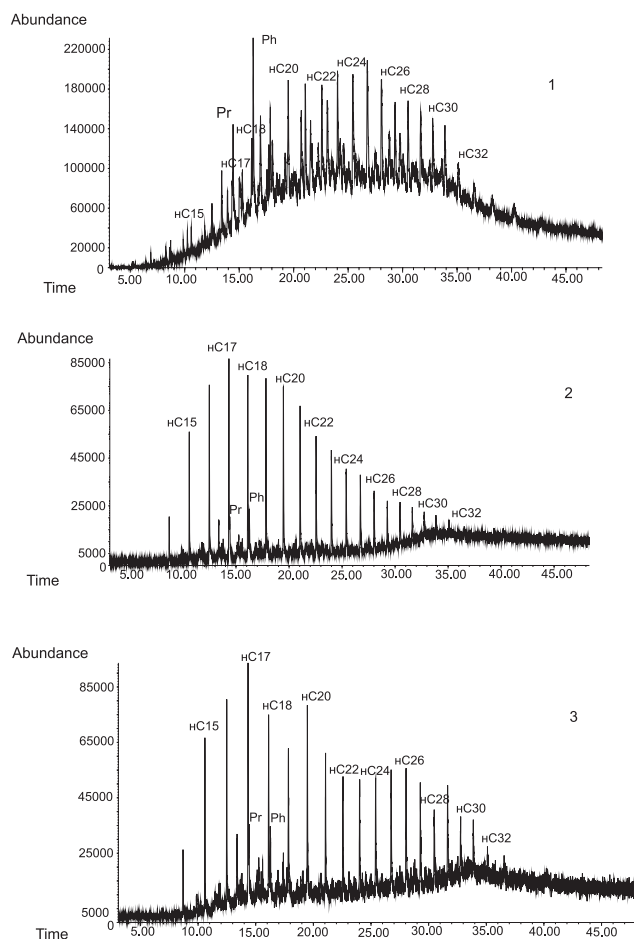


Fig. 4. Chromatograms ($m/z 57$) saturated hydrocarbons of organic matter of rocks: 1 – the Sokolovskaya suite (the Middle Devonian); 2 – the Shlyupochnayay and 3 – the Pshenicinskaya suites (the Lower Devonian). Signs: nC_{15} – nC_{30} – n-alkanes, Pr – pristane, Ph – phytane.

low-molecular homologues with a maximum of nC_{17} . In both suites alkane hydrocarbons are characterized by a low ratio of isoprenoids/n-alkanes. The values of the CPI coefficient are close to unit that indicates the thermal maturity of OM. 12-, 13-methylalkanes were not found in the composition of alkane hydrocarbons, which differs them from the Vend-Cambrian oils of the Siberian platform. Genesis of the latter is related with aquagenic OM which formed in the reducing medium in the absence of sulphur hydrogen contamination and mainly carbonate composition of the source sediments (Kashirtsev et al., 2015).

A specific feature of the hydrocarbons fractions of CHB of rocks in the Shlyupochnayay suite as the Pshenicinskaya is high content of dibenzothiophenes submitted by dibenzothiophenes, methyl-dibenzothiophenes, dimethyl-dibenzothiophenes, dimethylnaphthalenes. It shows the appearance of a number of intense peaks of these compounds in the chromatograms for total ion current. A complex character of the chromatograms complicates the identification of polycyclic hydrocarbon series hopanes and steranes carrying valuable genetic

information. In the IR spectra of hydrocarbons fractions intensive absorption bands of aromatic hydrocarbons “close” the absorption of alkanes with the number of methylene groups of more than 4 and causes a shift of the band maximum of 720 cm^{-1} in range $728\text{--}732\text{ cm}^{-1}$. Most likely the high concentration of dibenzothiophenes are due to the peculiarities of accumulation of initial OM in these suites in the environment of high sulphur hydrogen contamination of sediments in the north-west of the Kotelny island. Sulphur aromatic compounds of a number of benzothiophenes are purpose have no analogues in the alive matter of the biological predecessors. Their formation occurs in the process of diagenetic transformations of aqua OM in marine sediments with sulphur hydrogen contamination (Dakhnova, 2000; Kontorovich et al., 2004; Parfenova, 2017). The presence of dibenzothiophenes differs these samples from the Lower Devonian bitumen of the Indigiro-Zyryansky anticline (Zueva et al., 2016).

Sokolovskaya suite. The samples differ in lithological composition of the enclosing rocks, the character of bitumen saturation, the content and composition of CHB (Table. 1, Fig. 1B). The content of C_{org} characterized from low – 0.08 % to high values of 2.06 %, the difference in the yield of CHB is almost two orders. In the group composition of CHB hydrocarbons and resins dominate. The character of the distribution of saturated hydrocarbons with a maximum of n-alkanes in the relatively low molecular weight region of $nC_{16,17,19}$ indicates the aqua genic nature OM of studied bitumoids. OM characterizes high thermal maturity and reached main stage of oil generation, that can conclude by the coefficient CPI, close to unit.

Comparison the two samples shows (Table 1) different the nature of bitumen saturation: in one – to a type of the pore of the collector (*14-AP-35*) in another – a vein bitumen saturation in calcite (*14-AP-47*). They are contrast in composition that well correspond variable picture of bitumen saturation in the suite (Note..., 1985; 2016). In the composition of the sample *14-AP-35* hydrocarbons dominate 70.3 %, which allows to consider it as oil saturation. In the sample *14-AP-47* hydrocarbons content is only 43.5 % and therefor it is close to malta. Differences in the chemical structure of CHB by the IR spectra also show the proximity of one – (*14-AP-35*) to the lower content of oxygen-containing groups and bonds to oils, and the other (*14-AP-47*) – to malta. According to the values of the bitumoid coefficient (Table 1) both bitumens can most likely be relate to paraautochthonous. Data on presence in the suite of epibitumoids with high β ratios $>100\%$ are given in the works (Explanatory note..., 1985; 2016).

In the sample *14-AP-35* from the oil saturation rock a significant predominance of methane-naphthenic structures $MN/NA=1,83$ was defined, which differed

it from the studied samples from the lower-lying the Shlyupochnaya and the Pshenicinskaya suites. The content of n-alkanes from the amount of identified hydrocarbons is 40.7 %. The maximum distribution of n-alkanes shifted to the high molecular weight region on $nC_{24,25}$, which may was due not only to the nature of the initial OM (Table 2, Fig. 4). It is known that the predominance of relatively high molecular weight n-alkanes, and pristan and phytan over a number of eluting n-alkanes C_{17} and C_{18} may be due to the influence of biodegradation processes on the change in an initial composition of CHB. In result a decrease of content of relatively low molecular weight hydrocarbons had been occurred which were the most accessible for microorganisms. According by the values of the coefficients of pristan/ nC_{17} , phytane/ nC_{18} and the shift of the maximum in a relatively high molecular weight region, bitumoid from limestone (*sample 9-V-14-11*) was attacked by biodegradation processes to a lesser extent.

In the sample *14-AP-47*, related to malta, the content of alcohol-benzene resins is above almost twice and asphaltenes – five times as compared with to oil saturation sample. In the chemical structure of CHB content aromatic structures is of almost two times more. The high content of oxygen-containing groups and bonds in the chemical structure of resins and CHB is due to the processes of chemical oxidation in the hypergenesis zone. The maximum of n-alkanes is located in the region of $nC_{18}\text{--}nC_{20}$ (Table 2). The ratio pristan and phytane with a number eluted n-alkanes less than unit, which is characteristic for naphthides unchanged by the processes of biodegradation.

Thus in the Sokolovskaya suite against the background of syngenetic bitumen saturation, there were detected bitumen the formation of the composition of which was influenced to varying degrees by the processes of chemical and bacterial oxidation, which significantly changed the initial composition of naphthides.

According to the data of chromatomass-spectrometry in hydrocarbons fraction of CHB of the Sokolovskaya suite dibenzothiophene either not detected or their content is negligible for individual samples unlike from the Shlyupochnaya and the Pshenicinskaya suites. Probably it dues to differences in sedimentation and diagenesis conditions with less sulphur hydrogen contamination of waters and sediments in the Middle Devonian than in the Lower Devonian.

Conclusions

Thus, the obtained results confirmed the existing point of view on the Lower and Middle Devonian deposits of the Kotelny island as containing potentially oil source strata with a high content of aqua genic OM (Gramberg, 1976; Evdokimov et al., 2008; Ivanov, Klubov, 1979; Kosko, 1988; Polyakova et al., 2016; Safronov, 2002).

According to our data, this is indicated the high content C_{org} , a large yield of chloroform bitumoids, a high content of hydrocarbons in the composition of CHB, the predominance of relatively low molecular weight n-alkanes with maximum at nC_{15-18} . The sufficient maturity of the bitumoids can be proved by the values of CPI coefficients close to unite and the low values of the absorption coefficients of oxygen-containing groups and bonds in the CHB, i.e. the deposits entered at main oil generate zone and generated liquid hydrocarbons that could migrate and form oil accumulations.

The studied bitumoids are mainly syngenetic and have been undergone significant changes in the zones of catagenesis and hypergenesis. The data on IR spectra of the resinous components showed that all the studied samples had been underwent to strong hypergenic oxidation. According to the feature of the distribution of saturated hydrocarbons, it was found that in the Sokolovskaya suite of the Middle Devon, the bitumen along with chemical oxidation were affected to different degree by the processes of bacterial oxidation in contrast to the Lower Devonian bitumen.

According to the data of chromatomass-spectrometry it is shown that the feature of the composition of bitumen from the Lower Devonian deposits is the presence of high concentrations of dibenzothiophenes compared with the samples of the Middle Devonian. These differences may be related to the conditions of sedimentation and diagenesis of OM, which in the Lower Devonian were characterized by higher sulphur hydrogen contamination of sediments. This leads to the conclusion that naphthides generated aqua genic OM of the Lower Devonian marine sediments may be enriched with dibenzothiophene.

In the process of evolution shelf of the Laptev and East Siberian seas the Middle Paleozoic rocks reached the apocatagenesis zone and already realized their potential to a large extent (Gramberg, 1976; Polyakova et al., 2016; Safronov, 2002). May assume that in favorable geological conditions at the vertical migration initially generating Devonian oils could accumulate pools in the overlying strata. The obtained results can be used to estimate the generation potential of oil source strata and prospects the oil and gas bearing of the shelf of the Eastern sector of the Russian Arctic.

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References

- Bellami L. (1963). Infrakrasnye spektry molekul [Infrared spectra of molecules]. Moscow: IL, 590 p. (In Russ.)
- Dakhnova M.V. (2000). Geochemistry of organic sulfur compounds and its role in the prediction of oil and gas potential. *Geologiya, metody poiskov, razvedki i otsenki mestorozhdenii toplivno-energeticheskogo syr'ya. Obzornaya informatsiya* [Geology, methods of prospecting, exploration and evaluation of fuel and energy raw materials]. Moscow: Geoinformmark, is. 1, p. 52. (In Russ.)
- Explanatory note to the State Geological Map of the Russian Federation (1985). Scale 1:2 000 000. Novosibirsk Islands. Compiled by: Kosko M.K., Bondarenko N.S., Nepomiluev V.F. Moscow: Soyuzgeolfond, 160 p. (In Russ.)
- Explanatory note to the State Geological Map of the Russian Federation (2016). Scale 1:1 000 000. Laptev-Sibiromorsky Series. Scientific editors: M.K. Kosko, E.A. Gusev. St. Petersburg: VSEGEI, 317 p.
- Evdokimova N.K., Yashin D.S., Kim B.I. (2008). Hydrocarbon potential of sedimentary cover deposits of offshore East Arctic Seas of Russia (Laptev, East Siberian and Chukotsk). *Geologiya nefii i gaza = Oil and gas geology*, 2, pp. 3-12. (In Russ.)
- Gramberg I.S. (1976). Potential opportunities of oil and gas formation in sedimentary strata of the Laptev and East-Siberian seas. *Geologiya shel'fa Vostochnosibirskikh morei. Sb. nauchnykh trudov NIIGA* [The geology of the shelf of the East Siberian seas: Coll. papers]. 122 p. (In Russ.)
- Guide to the analysis of bitumen and scattered organic matter of rocks (1966). Ed. V.A. Uspensky, K.F. Rodionova, A.I. Gorskaya, A.P. Shishkina. Leningrad: "Nedra" Publ., 316 p. (In Russ.)
- Hughes W.B., Holba A.G.Dzou, L.I.P. (1995). The ratio of dibenzothiophene to phenanthrene and pristane to phetane as indicators of depositional environment and lithology of petroleum source rocks. *Geochem. And Cosmochem. Data*, 59, pp. 147-152. [https://doi.org/10.1016/0016-7037\(95\)00225-O](https://doi.org/10.1016/0016-7037(95)00225-O)
- Ivanov V.V., Klubov B.A. (1979). Naftidy i naftoidy Severo-Vostoka SSSR [Naphthides and naphthoids of the North-East of the USSR]. Moscow: "Nauka" Publ., 147 p. (In Russ.)
- Kashirtsev V.A., Kontorovich A.E., Kim N.S., Chalaya O.N., Zueva I.N. (2015). Steranes in neoproterozoic oils from the Nepa-Botuoba anteclise in the Siberian platform and the South Oman salt basin in the Arabian platform. *Neftekhimiya = Petroleum Chemistry*, 55(3), pp. 197-205. (In Russ.). <https://doi.org/10.7868/S0028242115020136>
- Kontorovich A.E., Melenevskii V.N., Ivanova E.N., Fomin A.N. (2004). Phenanthrenes, aromatic steranes and dibenzothiophenes in the Jurassic sediments of the West Siberian oil and gas basin and their significance for organic geochemistry. *Geologiya i geofizika = Russian Geology and Geophysics*, 45(7), pp. 873-883. (In Russ.)
- Kosko M.K. (1988). Sedimentatsionnye basseiny Vostochno-Sibirskogo i Chukotskogo morei [Sedimentation basins of the East Siberian and Chukchi seas]. *Geologiya morei i okeanov*, pp. 188-195. (In Russ.)
- Parfenova T.M. (2017). Geochemistry of Sulfur and Sulfur Compounds of the Cambrian Kuonamka Complex (Eastern Siberian Platform). *Georesursy = Georesources*, 19(1), pp. 45-51. DOI: <http://doi.org/10.18599/grs.19.1.8>
- Polyakova I.D., Borukaev G.Ch., Sidorenko S.A. (2016). Hydrocarbon potential of the Riphean-Lower Cretaceous complexes of the Laptev Sea region. *Arktika: ekologiya i ekonomika = Arctic: Ecology and Economy*, 1(21), pp. 56-65. (In Russ.)
- Radke M., Welte D.H., Willsch H. (1986). Maturity parameters based on aromatic hydrocarbons: Influence of the organic matter type. *Org. Geochemistry*, 10, pp. 51-63. [https://doi.org/10.1016/0146-6380\(86\)90008-2](https://doi.org/10.1016/0146-6380(86)90008-2)
- Safronov A.F. (2002). Perspektivy neftegazonosnosti arkticheskoi chasti territorii Zapadnoi Yakutii. Rossiiskaya Arktika (geologicheskaya istoriya, mineragiya, geokologiya) [Oil and gas potential in the Arctic part of the Western Yakutia. Russian Arctic (geological history, minerageny, geocology)]. St. Petersburg: VNIIOkangeologiya, 960 p. (In Russ.)
- Schou L., Myhr M.B. (1988). Sulfur aromatic compounds as maturity parameters. *Org. Geochemistry*, 13, pp. 61-66. [https://doi.org/10.1016/0146-6380\(88\)90025-3](https://doi.org/10.1016/0146-6380(88)90025-3)
- Tectonics, geodynamics and metallogeny of the Sakha Republic territory (Yakutia) (2001). Moscow: Maik "Nauka/Interperiodika", 571 p. (In Russ.)
- Vassoevich N.B. (1973). Osnovnye zakonomernosti, kharakterizuyushchie organicheskoe veshchestvo sovremennykh i iskopaemykh osadkov. Priroda organicheskogo veshchestva sovremennykh i iskopaemykh osadkov. [The main patterns that characterize the organic matter of modern and fossil sediments. The nature of the organic matter of modern and fossil sediments] Moscow: "Nauka" Publ., pp. 11-59. (In Russ.)

Zueva I.N., Chalaya O.N., Lifshits S.Kh., Glyaznetsova Yu.S. (2016). Naftides of the Lower Devonian sediments of the Selennyakhsky uplift (northeast of Yakutia). *Materialy VI Konf. «Geologiya i mineral'no-syr'evye resursy Severo-Vostoka Rossii»* [Proc. VI Conf.: Geology and mineral resources of the North-East of Russia]. Yakutsk: SVFU Publ., pp. 346-349. (In Russ.)

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