Geochemistry of organic matter of Devonian deposits in Kotelny island (New Siberian Islands) and Selennyakhsky uplift (Omulevsky terrain)

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Abstract. For the purpose of comparative study of oil source properties of Devonian deposits in the central part of Kotelny island (New Siberian Islands) and Selennyakhsky uplift (Omulevsky terrain), geochemical studies of the composition, chemical structure of chloroform-extracted bitumens of organic matter and relict hydrocarbons were conducted. In terms of bituminological parameters, naphthide manifestations are characterized by large variations in the content of organic matter, the yield of chloroform-extracted bitumens, group composition and chemical structure of chloroform-extracted bitumens, which indicates the presence of bituminous varieties as traces of generation, migration and accumulation of hydrocarbons. According to the composition and distribution features of relict hydrocarbons, naphthide manifestations in the central part of Kotelny island and Selennyakhsky uplift show great similarity, which is proved by their common type of aquagenic initial organic matter, its high degree of maturity and a sufficiently high generation potential of Devonian deposits, which entered main oil formation stage and could generate liquid hydrocarbons, and in deeper subsidence zones they reached main gas formation stage. The obtained results on the geochemistry of organic matter confirm the existing viewpoint on general history of geological development and similarity of the formation conditions for oil and gas potential in offshore territories of the Laptev and East Siberian seas as well as in continental part of the East Siberian platform. This allows estimating oil generation potential of organic matter in rocks and oil-and-gas content in offshore Devonian deposits based on the results of a better known continental part of the territory.

1. Introduction

When assessing the oil-and-gas potential in the Russian Federation, it becomes clear that northeastern part of the country is insufficiently studied. Middle Paleozoic offshore deposits of the East Siberian basin largely contain bitumen varieties through the section as indirect signs of oil content and evidence of generation and accumulation of hydrocarbons (HC) in the geological past (pre-Upper Paleozoic). It is assumed that Middle Paleozoic sediments, fragments of the section of which are currently exposed on the New Siberian Islands, in the Early Mesozoic could still be in the thermobaric conditions of main oil formation (MOF) and main gas formation (MGF) stages. As the offshore of the East Siberian Sea evolved, the Middle Paleozoic rocks reached the apocatagenesis zone and, to a large extent, have already fulfilled their potential. In case of vertical fluid migration, Devonian oils could primarily form deposits in Mesozoic sediments in favorable geological conditions [1–6].
For the purpose of comparative study of oil source properties of Devonian deposits in the central part of Kotelny island (New Siberian Islands) and Selennyakhsky uplift of Omulevsky terrain (OT), geochemical studies of the composition, chemical structure of chloroform-extracted bitumens (CB) of organic matter (OM) and relict HC were conducted. Samples of carbonate rocks were taken from the outcrops of river Balyktakh in Lower Devonian deposits of Shlyupochnaya formation (5 samples) of Kotelny island and from deposits of Nelichenskaya, Sagyrskaya and Datninskaya formations (26 samples) of Selennyakhsky uplift of OT (river Sakyndzha and creeks Gon, Medvezhy and Chyatlyun). Bituminological studies were carried out using rock samples delivered to the laboratory by K. I. Mikulenko and V. V. Gaiduk, the geologists of our Institute.

The set of analytical studies included hot extraction of CB from rocks, determination of group composition by column chromatography, structural and group composition of CB and their fractions by IR-Fourier spectroscopy, as well as chromatography-mass spectrometric studies of saturated hydrocarbons.

In the central part of Kotelny island and Indigiro-Zyryansk trough, Lower Devonian sediments deposited in similar conditions of shallow marine facies in a reducing environment favorable for the accumulation and preservation of aquagenic initial OM.

2. Central part of Kotelny island

According to the data of chemical and bituminological studies carried out by VNIGRI (Saint Petersburg), in the western part of Kotelny island, the content of organic carbon in limestones and dolomites of Shlyupochnaya suite is 0.28–1.39%, the yield of CB ranges from the low (0.01%) to increased (0.13 %) values [7]. Low values of the bitumen coefficient (less than 10%) indicate the syngenetic nature of bitumen manifestations in limestones and dolomites. At an increased organic carbon content of 0.66-4.68%, clayey limestones are characterized by lower CB yields, which also indicates the syngenetic nature of bitumen manifestation. Individual bitumen manifestations with a high coefficient (up to 38%) are apparently paraautochthonous, which testifies to HC migration through the section of a formation.

The results obtained for the central part of Kotelny island are presented in Table 1. The studied samples of CB yield in carbonate rocks differ by an order more and reach high values. Bitumens differ significantly in group composition—almost twice in the content of oils, resins and asphaltenes.

It should be noted that the feature of bitumens is a very high content of asphaltenes up to 40%. According to IR spectroscopy, the chemical structure of CB is dominated by hydrocarbon structures with a low amount of oxygen-containing groups and bonds. The absorption of carbonyl groups (D1730-1700) relative to the absorption of methyl and methylene groups (D1460) is significantly lower than unity and is equal to 0.18-0.58. This indicates a rather high thermal maturity of OM, since catagenesis is accompanied by destruction of the initial material with separation of peripheral groups and bonds and an increase in the content of HC structures. Bitumens differ fundamentally (from 0.72 to 2.07) in the ratio of carbonyl (D1700) to aromatic (D1600) cycle absorption per averaged molecule, which can be considered as a presence of bituminous varieties in the section of Shlyupochnaya formation: syngenetic, syngenetic residual and migrational (including paraautochthonous). This assumption is consistent with the above data on large variations in the group composition of CB, as well as in the hydrocarbon composition of CB, according to which methane-naphthenic hydrocarbons dominate in some samples (up to 74.1%), and in others—naphthenic-aromatic hydrocarbons (71.9%). For the fractions of CB oils, completely different types of spectra were obtained: typical aliphatic with intense absorption of long methylene chains in the region of 720 cm−1 for some samples and aromatic spectra with intense absorption bands of unsubstituted hydrogen atoms in aromatic cycles —750, 810, 880 and absorption of C = C bonds in the region of 1600 cm−1 in aromatic cycles—for others. This is confirmed by large variations in the content of aromatic carbon in oils from 17.9 to 31.7%. Calculations of aromatic carbon per averaged molecule of naphthenic-aromatic HC showed that they are characterized by rather high hybridity, in individual samples up to 66.2% of carbon in them is associated with aliphatic fragments, which is typical of naphthides generated by OM of marine genesis.
Oil fractions of CB differ significantly in the distribution of relatively low- and high-molecular n-alkanes ($\sum_{ibp-nC_{20}} / \sum_{nC_{21}-ebp} = 0.40 - 1.12$) and position of maximum ($nC_{18}$ and $nC_{22}$). At the same time, the differences are less pronounced in the ratios of n-alkanes and isoprenoids (Table 2).

Table 1. Geochemical parameters of naphthide manifestations on outcrops from Devonian deposits in Kotelny island (New Siberian Islands) and Selennyakhsky uplift of OT.

| Parameter value | Group composition of CB,% | Hydrocarbon composition of CB, per $\sum HC$ | *Ratio |
|-----------------|---------------------------|-----------------------------------------------|--------|
|                 | oils | $\Sigma$resins | $\Sigma$asph. | M-H | H-A |
| Lower Devonian, Shlyupochnaya formation, Kotelny island | | | | | |
| Minimum | 1.71 | 0.066 | 2.6 | 20.8 | 18.5 | 16.4 | 10.4 | 43.7 | 1.07 |
| Maximum | 9.95 | 0.463 | 16.8 | 49.4 | 52.5 | 49.7 | 56.3 | 89.6 | 3.47 |
| Average | 4.1 | 0.277 | 8.5 | 31.4 | 35.7 | 32.9 | 25.0 | 75.0 | 2.16 |
| Lower Devonian, Nelichenskaya formation, Selennyakhsky uplift | | | | | |
| Minimum | 0.14 | 0.024 | 11.6 | 19.0 | 33.1 | 10.8 | 30.8 | 36.6 | 1.64 |
| Maximum | 0.72 | 0.146 | 25.7 | 41.3 | 54.9 | 48.0 | 63.4 | 69.3 | 4.97 |
| Average | 0.46 | 0.097 | 18.9 | 30.7 | 39.4 | 29.9 | 47.1 | 52.9 | 3.69 |
| Lower Devonian, Sagyrskaya formation, Selennyakhsky uplift | | | | | |
| Minimum | 0.12 | 0.000 | 0.0 | 24.4 | 45.1 | 14.8 | | | 2.51 |
| Maximum | 1.02 | 0.052 | 18.4 | 37.1 | 59.6 | 23.7 | | | 9.37 |
| Average | 0.43 | 0.032 | 8.0 | 31.0 | 50.3 | 18.7 | | | 6.78 |
| Lower Devonian, Datninskaya formation, Selennyakhsky uplift | | | | | |
| Minimum | 0.22 | 0.027 | 12.1 | 34.0 | 42.4 | 23.6 | | | 1.98 |

*alcohol-benzene to benzene resins ratio

They are characterized by relatively high values of the isoprenoid/n-alkanes ratio (0.11-0.25), predominance of phytane over prystane ($p/f = 0.67-0.71$) and n-alkanes $C_{17}$ and $C_{18}$ over eluted isoprenoids (Table 2). A similar nature of the composition of saturated hydrocarbons is inherent in naphthides, the genesis of which is associated with the initial OM of marine facies. At the same time, it should be noted that the feature of studied CB of Devonian deposits is the absence of 12- and 13-methylacans in their composition, which distinguishes them from Vendian-Cambrian oils of the Siberian platform, the genesis of which is associated with aquagenic OM that formed in a reducing environment in the absence of hydrosulfuric contamination and with predominantly carbonate composition of source rocks [8, 9].

In Selennyakhsky uplift of OT, Lower Devonian sediments are represented mainly by normal shallow marine carbonate and clay-carbonate organogenic strata [9]. According to [3], the degree of OM...
catagenetic transformation reached the MC2 (metacatagenesis) stage, i.e., these sediments entered the MOF stage.

One sample with a low OM content and an average CB yield (Table 1) from Datninskaya formation was analyzed, which is close to the samples from Sagyrskaya formation in terms of the composition of relict HC (Table 2).

**Table 2.** Individual composition of saturated hydrocarbons in naphthide manifestations on the outcrops from Devonian deposits in Kotelny island (New Siberian Islands) and Selennyakhsky uplift of OT

| Parameter value | $\sum \frac{ibp - nC_{20}}{nC_{20} - ibp}$ | Maximum of n-alkanes | Odd-even ratio | isoprenoids \(\frac{nC_{19}}{nC_{17}}\) | prystane \(\frac{nC_{20}}{nC_{18}}\) | phytane \(\frac{nC_{19} + nC_{20}}{nC_{17} + nC_{18}}\) |
|-----------------|---------------------------------|------------------|----------------|----------------|----------------|----------------|
| **Lower Devonian, Shlyupochnaya formation, Kotelny island** |
| Minimum | 0.40 | C\(_{18}\) | 0.86 | 0.11 | 0.67 | 0.37 | 0.45 | 0.42 |
| Maximum | 1.12 | C\(_{22}\) | 1.02 | 0.25 | 0.71 | 0.71 | 0.78 | 0.75 |
| Average | 0.78 | C\(_{18,22}\) | 0.96 | 0.19 | 0.69 | 0.50 | 0.58 | 0.55 |
| **Lower Devonian, Nelichenskaya formation, Selennyakhsky uplift** |
| Minimum | 0.75 | C\(_{15}\) | 0.82 | 0.12 | 0.37 | 0.16 | 0.32 | 0.30 |
| Maximum | 1.78 | C\(_{18}\) | 1.16 | 0.25 | 1.58 | 0.72 | 0.70 | 0.65 |
| Average | 1.27 | C\(_{15-18}\) | 1.03 | 0.19 | 1.09 | 0.46 | 0.46 | 0.45 |
| Minimum | 0.32 | C\(_{16}\) | 0.72 | 0.08 | 0.63 | 0.30 | 0.23 | 0.34 |
| Maximum | 1.57 | C\(_{18}\) and C\(_{29}\) | 1.46 | 0.21 | 1.67 | 0.66 | 0.50 | 0.48 |
| Average | 1.00 | C\(_{16-18}\) and C\(_{29}\) | 1.03 | 0.16 | 1.03 | 0.45 | 0.40 | 0.41 |
| **Lower Devonian, Sagyrskaya formation, Selennyakhsky uplift** |
| Minimum | 0.56 | C\(_{16}\) | 0.92 | 0.14 | 0.86 | 0.46 | 0.31 | 0.46 |
| Maximum | 1.54 | C\(_{18}\) | 1.10 | 0.27 | 2.13 | 0.88 | 0.63 | 0.75 |
| Average | 0.82 | C\(_{16,18}\) | 1.02 | 0.22 | 1.48 | 0.70 | 0.50 | 0.60 |
| **Lower Devonian, Datninskaya formation, Selennyakhsky uplift** |
| Minimum | 0.57 | C\(_{17}\) | 1.01 | 0.31 | 1.27 | 0.67 | 0.55 | 0.61 |

In the overlying Sagyrskaya formation, bitumen manifestations are common in brown bituminous organogenic limestones that are rhythmically interbedded with clayey coral-shell limestones at the base of the formation. Bituminological characteristics are given in Table 1. The samples are characterized by a low content of organic carbon in rocks (0.43% on average) and a low CB yield from 0.022 to 0.052%.

Low values of the bitumen coefficient from 4.4 to 7.7% for the MC2 stage of OM catagenesis can be considered as evidence of the syngenetic-residual character of bitumen manifestations. This is consistent with the low content of oils in the group composition of CB (31% on average) and high content of the amount of resinous components (up to 59%) with a predominance of alcohol-benzene resins (6-8 times). In CB chemical structure of these samples, aromatic cycles dominate over compounds with long methylene chains, while oxygen-containing groups and bonds play a significant part. An increase in the
values of bitumen coefficient up to 10.0-18.4% is most likely due to the presence of syngenetic and paraautochthonous bitumens in the section of Sagyrskaya formation.

In the overlying Nelichenskaya formation, host rocks are represented by rhythmically alternating black, gray, dark gray, and clayey bituminous limestones.

Compared to Sagyrskaya formation, the organic carbon content in rocks is characterized by a wider range of values and reaches high values (Table 1). Two groups can be distinguished in the studied samples of this formation: one, as in Sagyrskaya formation, with a low average organic carbon content of 0.46% and the other with an increased and high content of 1.71-9.95%. In samples of the first group, an increased CB yield is observed—0.097%. In the second group, maximum CB content reaches very high values—0.463% and averages 0.277%. The values of the bitumen coefficient are higher than in Sagyrskaya formation. At the same time, the samples of these formations differ less significantly in terms of group composition. According to the IR-Fourier spectroscopy data, a more pronounced aromatic character and a lower participation of oxygen-containing groups and bonds (K_1700/K_1600=0.62-0.81 compared to 1.15-1.39 in Sagyrskaya formation) is determined for the CB of this formation.

In terms of composition, individual saturated HC for oily CB fractions of rocks from Datninskaya, Sagyrskaya, and Nelichenskaya formations are very similar (Table 2). In both syngenetic and paraautochthonous CB, almost uniform unimodal distribution of n-alkanes with a high content of relatively low-molecular homologs and a distribution maximum in the nC_{15}-nC_{18} region was determined. The isoprenoids/n-alkanes ratio is 0.12-0.31, which is typical for aquagenic OM. The prystane/phytane ratios vary within a wide range of 0.37-2.13. In most of the samples, phytane predominates over prystane. Low values of the isoprenoids/n-alkanes, as well as prystane/n-heptadecane and phytane/n-octadecane ratios indicate good OM preservation. A feature of polycyclic hydrocarbons is the presence of tricyclic alkanes. Pentacyclic saturated HC (hopanes) are characterized by an increased content of trisnorhopanes, a low proportion of morethanes, a high content of homohopane homologs relative to hopane, and increased values of C_{35}/C_{34} homohopane ratios.

The aforementioned features of the composition and distribution of biomarkers in the bitumens of Lower Devonian deposits are inherent in aquagenic OM, which accumulated in reducing conditions of diagenesis. Low values of isoprenoid/n-alkanes, as well as prystane/n-heptadecane and phytane/n-octadecane ratios indicate a good preservation of OM. This is confirmed by the data on high content of vanadyl (2837 mg/100 g) and nickel (469 mg/100 g) porphyrins in CB. The catagenetic maturity of OM rocks can be judged by the odd-even ratio that is close to unity, and the prevalence of S-isomers over R-isomers among homohopanes. Thus, the bituminous strata of Nelichenskaya formation with favorable oil source properties can be considered as typically domanikoid formations.

As can be seen from the data presented, the studied bitumen manifestations of Lower Devonian deposits in the central part of Kotelnny island and the deposits in Selennyakhsky uplift of OT demonstrate great similarities in terms of bituminological and lithological parameters. Geothermal history of regional development is different, but these deposits are characterized by similar facies conditions of OM sedimentation and rock lithological composition. New data indicate similar composition and distribution of relic HC of the studied naphthide manifestations in Lower Devonian deposits in the central part of Kotelnny island and Selennyakhsky uplift of OT, which proves a single aquagenic type of the initial OM and its high degree of maturity. Increased and high values of the bitumen yield in Shlyupochnaya formation of Kotelnny island, comparable to Nelichenskaya formation of Selennyakhsky uplift considered as domanikoid, indicate a fairly high generation potential of Devonian sediments that entered the MOF stage and could generate liquid HC, and in deeper subsidence zones they reached the MGF stage and generated gaseous HC.

3. Conclusions
Investigations have shown that naphthide manifestations in Lower Devonian deposits in the central part of Kotelnny island and sediments in Selennyakhsky uplift of Omulevsky terrane are very similar in terms of some bituminological parameters. At the same time, large variations in the content of organic matter, yield of chloroform-extracted bitumens, their group composition and chemical structure are
traced in naphthide manifestations of both regions, which is due to the presence of bituminous varieties in the section of these deposits. Although the geological history of regional development is different, some researchers believe that facies conditions of sedimentation and organic matter transformation were similar for these deposits at the initial pre-inversion stage. This is confirmed by our results of geochemical studies on the composition and distribution of relict hydrocarbons in the studied naphthide manifestations in Lower Devonian deposits of the central part of Kotelny island and Selenyakhsky uplift of Omulevsky terrane. The type of initial aquegenic organic matter and its high degree of maturity were the same for the above-mentioned deposits. Increased and high values of the bitumen yield in Shlyupochnaya formation of Kotelny island, comparable with Nelichenskaya formation of Selenyakhsky uplift considered as domanikoid, indicate a fairly high generation potential of Devonian deposits in Kotelny island that entered main oil formation stage and could generate liquid hydrocarbons, and in deeper subsidence zones they reached main gas formation stage. New data on the geochemistry of organic matter confirm the existing viewpoint on the general history of geological development and similarity of conditions for the formation of oil-and-gas bearing capacity in offshore territories of the Laptev and East Siberian seas and continental part of the East Siberian Platform. This allows estimating oil generation potential of organic matter in rocks and oil-and-gas content in offshore Devonian deposits based on the results of a better known continental part of the territory.

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