# ABOUT OIL-BEARING FORMATION OF ROMASHKINSKOE OIL FIELD – EVIDENCE FROM BEREZOVSKAYA AREA

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# Abstract

This paper is devoted to the geochemical study of the oils of the South Tatar arch and their possible generation sources. The connection between the OM of the Domanik formation and oils and bitumen from the same age-old sediments was found. The relationship between bitumen from the basement rocks and the oils of the productive Devonian terrigenous strata was determined on the basis of their close component and biomarker composition. The generality of the reducing conditions for their sedimentation indicate the presence of a deep fluid component in the formation of the oil-bearing capacity of the sedimentary strata in the Beryozovskaya area of the Romashkinskoye oil field.

**Keywords**: oil, organic matter, composition, biomarkers, genesis, Romashkinskoe oil field

# **1 INTRODUCTION**

Despite the high exploration degree of the Volga-Ural oil and gas province, in particular the territory of Tatarstan, the question of the origin of the oil of the South Tatar arch (STA) and the adjacent territories remains extremely controversial (Kayukova et al., 2009). Regardless of the fact that the Domanik formation is a proven highly productive oil-bearing stratum (OBS) of most deposits in the overlying carbonate sediments of the Volga-Ural basin (Stoupakova et al., 2015; Nosova & Pronin, 2010; Fadeeva et al., 2015; Deniz & Karaaslan, 2017; McMillan et al., 1988; Maciel et al., 2016), this statement causes certain doubts in a number of cases in respect of large Devonian



deposits. The paper (Rodionova, 1967), excludes the possibility of migration of hydrocarbons (HC) from the Pre-Urals trough and the Caspian depression. The calculation of the syngenetic HC of Devonian deposits showed that their maximum amounts are concentrated in the ancient depressions flanking the largest oil deposits in the STA and their initial amount was quite sufficient for the formation of oil deposits in the territory of the Volga-Urals region, even with a relatively low accumulation coefficient.

The paper (Kiseleva & Mozhegova, 2012) suggests that possible OBS are the terrigenous deposits of the Timansky and Pashiysky horizons of the Buzuluk depression, as well as clay terrigenous rocks of the underlying horizons. However, they contain much less organic matter (OM) than the deposits of the Domanik formation. Among other ideas, the possibility of HC coming from the basement is also discussed (Kayukova et al., 2009; Gatiiatullin et al., 2015; Shital & Mirza, 2018). Interest in the crystalline basement is due to the fact that according to some data (Muslimov et al., 1976), it may contain oil deposits; moreover, faults in the basement may serve as migration routes for HC to the overlying sediments. In (Shirokova et al., 1976), it was suggested about the ongoing possible replenishment of oil-bearing complexes of the sedimentation mass of the STA with HC from the basement rocks at the present time.

Objective of this paper was geochemical study of the oils from STA and their possible generation sources by reconstructing the original type and facies conditions of accumulation of OM, determining the degree of its catagenetic maturity and detecting the secondary migration processes.

#### **2 MATERIALS AND METHODS**

Objects of research were the samples of crude oil and cores from Devonian (D<sub>3</sub>sm  $\mu$  D<sub>3</sub>mnd, D<sub>3</sub>tm, D<sub>3</sub>ps, D<sub>2</sub>zv) deposits of the Berezovskaya area of the Romashkinskoe oil field, as well as core samples from the basement rocks of this deposit (Fig. 1, table). A particular focus is placed on this territory, as Berezovskaya area adjoins the Altunino-Shunaksky depression, which separates the two largest deposits of the Volga-Urals oil and gas basin.

At the base of this depression there is a large tectonic fault developed in the body of the crystalline base. The relief of the crystalline basement has a complex block structure, is complicated by faults of the north-eastern and north-western strikes. The crystalline basement during the genesis process could repeatedly be a permeable zone during the periods of tectonic activation ((Kayukova et al., 2009; Gatiiatullin et al., 2015; Muslimov et al., 1976; Zonouzirad et al., 2016).

Bitumen (CSB) were extracted from core samples on the Soxhlet instrument using a mixture of solvents containing chloroform, benzene and isopropyl alcohol in equal proportions. Determination of the component composition of CSB from rocks and oils was carried out by column liquid-adsorption chromatography on ASA silica gel with the separation of the hydrocarbon part (oils) and two groups of resins: benzene and alcohol-benzene. Before adsorption separation from the CSB and oils, asphaltenes were precipitated in 40-multiple hexane according to a standard procedure.





**Fig. 1.** Objects of investigation on the map of the Romashkinskoe field: 1) Altunino-Shunaksky depression, 2) basement faults, 3) wells of oil sampling, 4) wells of core sampling



Nº	Area	Geological	Sampling interval,	Lithology
		age	М	
1	Berezovskaya	D <sub>3</sub> sm	1769-1773	Carbonate
2	Berezovskaya	D <sub>3</sub> mnd	1808-1826.6	Carbonate
3	Berezovskaya	D <sub>3</sub> tm	1780.3-1782.2	Sandstone
4	Berezovskaya	D <sub>3</sub> tm+ps	1763.2-1765.2	Sandstone
			1766.0-1767.6	
5	Berezovskaya	D <sub>3</sub> ps	1832.1-1839.6	Sandstone
6	Berezovskaya	D <sub>2</sub> zv	1803.8-1806.0	Sandstone
Bitumen extracted from sedimentary rocks				
7	Berezovskaya	D <sub>3</sub> sm	1759.0-1760.5	Marlstone
8	Berezovskaya	D <sub>3</sub> sm	1805-1808	Carbonate
9	Berezovskaya	D <sub>3</sub> ps	1761.0-1762.6	Sandstone
10	Berezovskaya	D <sub>3</sub> ps	1766.8-1770.0	Argillite
11	Berezovskaya	D <sub>3</sub> ps	1852-1860	Sandstone
12	Berezovskaya	D <sub>2</sub> zv	1869-1876	Sandstone
Bitumen extracted from crystalline basement rocks				
13	Alkeevskaya	AR-PR	1809.5-1810.0	Gneissose granite
14	Almetevskaya	AR-PR	1827.0-1827.8	Gneissose granite
15	Pavlovskaya	AR-PR	1838.0-1838.6	Gneissose granite
16	Abdrakhmanovskaya	AR-PR	1886.0-1886.8	Gneissose granite
17	Zelenogorskaya	AR-PR	1936.2-1937.0	Gneissose granite

**Table 1:** General characteristics of oils and bitumen (CBA) from Berezovskaya arearocks and rocks of the Romashkinskoye oil field crystalline basement

The individual hydrocarbon composition of bituminoids and oils was studied by chromatography-mass spectrometry using a DFS Thermo Electron Corporation (Germany). The energy of the ionizing electrons was 70 eV, the temperature of the ion source was 280°C. A capillary column with a length of 50 m and a diameter of 0.32 mm was used. The layer thickness of the stationary phase ID-BP5X (analog DB-5MS) - 0.25  $\mu$ m. The carrier gas - helium. Chromatography was carried out in a linear temperature programming mode: from 60 to 280°C with a temperature rise rate of 10°C/min. Mass spectrometric recording was performed using the total ion current (TIC), in the selective monitoring mode, recording mass-fragmentograms for characteristic ions m/z 71 (n-alkanes), m/z 191, 177 (gopans) and m / z 217, 218 (sterans). The results were processed in the TurboChrom/Geochemistry Navigator system. The identification of hydrocarbons was carried out using literature and library data.

#### **3 RESULTS AND DISCUSSION**

The investigated oils and bitumen from the rocks of various productive complexes of the Berezovskaya area are heterogeneous by their component composition (Fig. 2). Some features of their composition were revealed: the oils from the Semiluki deposits are quite close in their composition to the same of the oils from the terrigenous Devonian deposits, but both differ significantly from the CSBs of sedimentary cover and basement rocks. The oils are characterized by a high content of hydrocarbon compounds (61-78%), low resin content (20-37%) and very low content of asphaltenes (less than 5%). CSBs contain 1.5-3 times less HC compounds, but 2-3 times more asphaltenes. The CSBs of the Domanik formation contain 53% of asphaltenes. It is important to note the close composition of bitumen from the terrigenous Devonian deposits and basement.







For genetic judgments, gas-chromatographic coefficients commonly used in geochemical studies, which are the ratio of pristane/phytane (Pr/Ph), Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub>, were applied to assess the redox environment in early diagenesis and the catagenetic and migration processes at subsequent stages of deposit formation (Buryakovsky et al., 2005; Peters et al., 2007). In addition, the study involved examination of the indicators reflecting the nature of higher polycyclic biomarkers - steranes and terpans. Hemofossils are widely used as correlation parameters for revealing the initial genotype of OM, the facial conditions of sedimentogenesis, for determining the diagenesis conditions, the degree of catagenetic transformation and maturity of the OM of the OBS (Buryakovsky et al., 2005; Peters et al., 2007; Tissot & Welte, 1978).

In terms of the parameters  $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  (Kennon-Kessow diagram), all samples of oils and CSB fall into the region of strongly reducing shallow marine sedimentation environments of OM, mature by the level of catagenetic transformation. CSBs from the rocks of the crystalline basement fall into the post-ripe zone (Fig. 3). Values of the indicator Pr/Ph (0.3-0.77) of oils and CSBs of the sedimentary Devonian stratum indicate the marine genesis of the initial OM under strongly reducing conditions. The ratio of Pr/Ph for the basement CRBs is characterized by somewhat larger values (0.8-1.03).



#### Página | 6



Fig. 3. Relative distribution of Pr/n-C<sub>17</sub> and Ph/n-C<sub>18</sub>

Geochemical parameters responsible for the genotype of OM and the conditions of its sedimentation include C<sub>27</sub>, C<sub>28</sub>, C<sub>29</sub>-steranes. A high proportion of C<sub>27</sub>-steranes indicates OB associated with plankton, whereas the predominance of C<sub>29</sub>-steranes is due to the participation of higher-plant lipids, so the composition of steranes can be used to identify sources of organic matter (Peters & Moldowan, 1993; Seifert & Moldowan, 1978; Huang & Meinschein, 1979). The investigated fluids contain from 32 to 47% of C<sub>27</sub>-sterane, from 28 to 44% of C<sub>29</sub>-sterane and from 16 to 26% of C<sub>28</sub>-sterane, which indicates predominance of the sapropelic material (algae and bacteria) in the initial OM with a significant admixture of humic organics. That is, in terms of the relative content of C<sub>27</sub>, C<sub>28</sub> and C<sub>29</sub>-steranes shown in a triangular diagram (Fig. 4), one or another type of generating formation cannot be clearly distinguished. However, it is important to note that the terrigenous Devonian oil falls into the region of mixed humus-sapropel OM, while the Domanic oil and bitumen are closer to the area of pure sapropelic OM. The ratio of steranes C<sub>28</sub>/C<sub>29</sub> = 0.55 indicates the formation of a sediment, containing the initial OM, in the Devonian time.





Fig. 4. Ternary diagram of 20R 22 -steranes (C27, C28, C29): I – land plants, II – planktonic/land plants, III – planktonic/algal, IV – planktonic/bacterial, V – diatoms/bryophytes.

The diagram shown in Fig. 5 allows us to note a certain differentiation of the investigated objects in terms of their content of tricyclic terpanes, steranes and pentacyclic terpanes. There is a tendency to increase in the content of tricyclic terpanes up the section of the sedimentary strata from the basement rocks to the Pashiysky and Timansky deposits, and the content of steranes in the CSB is less than in the investigated oils, which may result from fractionation of the composition of biomarker hydrocarbons in migration processes (Seifert & Moldowan, 1978).





**Fig. 5.** Diagram of distribution of tricyclic terpanes, tetracyclic steranes and pentacyclic terpanes.

The ratio of steranes to pentacyclic triterpanes (STER/PENT = 0.24-0.51) indicates a high contribution of bacterial material to the original organic matter or its significant bacterial processing during diagenesis (Kiseleva & Mozhegova, 2012).

Against the background of the assertion about the migratory character of the Domanic oil, attention is drawn to the existing connection between the CSB of rocks and the oils of the Semiluki horizon according to the genetic parameters DIA/REG and  $T_s/T_m$  (Fig. 6), Ph/n-C<sub>18</sub> $\mu$  Pr/n-C<sub>17</sub> (Kennon-Kessow diagram) (Fig. 3).



**Fig. 6.** Distribution of DIA/REG and Ts/Tm parameters, characterizing the lithological composition of the source rocks.



The objects investigated by the DIA/REG parameters (the ratio of rearranged diasterane C<sub>27</sub>20S<sup>[2]</sup> to the regular sterane C<sub>29</sub>20R) and T<sub>s</sub>/T<sub>m</sub> (the ratio of the more stable trisporogane C<sub>27</sub>18<sup>[2]</sup> (H) to the less stable C<sub>27</sub>17<sup>[2]</sup>) are conditionally divided into two groups. The values of these parameters for the fluids of the Semiluki deposits indicate their connection with the carbonate sedimentation basin, while the genesis of the CSBs from the basement rocks and some of the CSB samples from the terrigenous Pashiysky deposits is associated with clay minerals. This is due to the fact that the regrouped steranes are mainly formed in clay sediments. However, the separation into two groups is not sufficiently clear, which allowed us to distinguish in (Kayukova et al., 2009) an intermediate group with ambiguous parameters at the Romashkinskoe oil field. According to the authors of (Kayukova et al., 2009), this indicates a mixed type of oil due to the processes of ascending and descending migration. The results of the conducted studies indicate that similar processes took place during the formation of the oil presence in the territory of the Berezovskaya area located in the zone of development of major tectonic basement faults. In this area, separate oils and CSBs from the rocks of regionally productive deposits of the Pashiysky horizon can be combined into the intermediate group.

#### **4 SUMMARY**

The examined oils of the Semiluki horizon are syngenetic to the host sediments. The deposits of the Semiluki horizon in the territory of the STA are at the stage of late protocatagenesis with the transition to the early stages of mesocatalagenesis (Fadeeva et al., 2016). According to Bazhenova (Bazhenova, 2012), OM-rich silicic-carbonate deposits are already capable of generating "immature" oil at this stage. The low degree of maturity of the fluids of the Domanik formations is confirmed by the values of the geochemical parameters considered in the study.

• Oil-bearing rocks were formed in highly reducing marine conditions. The source of OM was marine microorganisms (algae and bacteria), as well as considerable quantities of the remains of higher plants. The latter is especially characteristic for terrigenous Devonian oils and bituminoids.

• The close values of the geochemical parameters for the terrigenous Devonian and the crystalline basement oils and CSBs, and their difference from similar parameters for the Domanik formation oils and CSBs indicate the presence of various sources of their generation. The values of the indicators: Pr/Ph, DIA/REG and  $T_s/T_m$ , indicate the relationship of the basement CSB with the fluids of terrigenous deposits. The possibility of the existence of several sources of oil generation differing in the lithologic composition of the oil-bearing rocks was indicated in (Kiseleva & Mozhegova, 2012). The data given in (Kayukova et al., 2009), according to which carbonate and terrigenous petroleum rocks took part in the generation of oils of Pashiysky and Timansky productive beds, were confirmed.

•The relative distribution of steranes and gopanes confirms the existence of migratory processes, which also occur in the crystalline basement. The possible processes of hydrocarbon migration in the basement rocks and sedimentary strata during the formation of the oil bearing capacity in the STA in the territory of Tatarstan were also indicated in (Burova & Zhuze, 1976).



#### **5 CONCLUSION**

Thus, the distinctintions of the composition of petroleum and bitumen formations of the Domanic formations from the oils of sub-Domanic sediments and basement bitumen were revealed. A close component and biomarker composition of bitumen from the basement rocks and terrigenous Devonian stratum is shown, and a generality of the reducing conditions for their sedimentation is revealed, which indicates the influence of crystalline base fluids on the formation of the oil bearing capacity of the Berezovskaya area.

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