

## The role of Domanik deposits in the formation of oil pools in the central areas of the Volga–Ural petroleum province (*Buzuluk depression*)

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### Abstract

The results of genetic typification of oils and bitumens from oil source rocks (OSR) of the Buzuluk depression are presented. Crude oils within the study area were divided into five genetic types, which differ both in organic-matter composition and in the conditions of its accumulation. Characteristic of the potential source rock was given for each oil type. Oil-to-source rock bitumen correlation studies were performed using biomarker distribution. The studies have shown that only oils from the Upper Devonian–Middle Carboniferous deposits (oils of Types I and II) were generated by Domanik rocks. Middle Devonian oils (Types III–V) are not related to the Domanik strata. The identified relationships between oils and organic matter of different facies-genetic types of Domanikoid–Domanikite OSR can be used to refine the stratigraphic volume and geographic distribution boundaries of Domanik deposits in the study area.

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**Keywords:** Domanik deposits; genetic typification of oils; source rock bitumens; biomarkers; steranes; triterpanes; alkanes; Buzuluk depression

### Introduction

For the last years, a large amount of factual data on the genetic characteristics of oils and bitumens of the South Tatar arch (STA) has been obtained using modern geochemical techniques (Aref'ev et al., 1994; Gordadze and Tikhomirov, 2005, 2007; Kiseleva and Mozhegova, 2012). At the same time, much less attention has been paid to the Buzuluk depression, one of the most perspective areas of the Volga–Ural petroleum province (Ablya, 2001; Gordadze and Tikhomirov, 2005; Kiseleva, 2012).

In this paper, the results of detailed geochemical studies of source rock bitumens and oils from productive horizons of this area are presented. Their aim is to give genetic characterization of hydrocarbon sources and identify the role of Domanik source rocks in the formation of oil accumulations in the Buzuluk depression.

### Materials and methods

Thirty-nine samples from 12 oil fields occurring at depths of 1100–5400 m in the Samara and Orenburg regions were

used in this study for the genetic typification of oils from the Buzuluk depression. Reservoir ages range from the Eifelian Stage of the Middle Devonian to the Moscow Stage of the Middle Carboniferous. The oils were studied by gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS) methods. In addition to the detailed characteristics of the oils, we determined their bulk properties—density and sulfur content.

To study the geochemical characteristics of source rocks from the Buzuluk depression by the Rock-Eval method, we analyzed more than 120 core samples of Upper Devonian rocks (from the Timan to the Zavolzh'e Horizons) from sections of four parametric wells located in different zones of the Mukhanovo–Erokhovka depression. The rock sampling interval was from 2800 to 3100 m. From the results of pyrolysis, 28 rock samples having potential oil-source characteristics were selected for detailed studies. Chloroform extracts isolated from the rocks were analyzed by gas chromatography and gas chromatography-mass spectrometry.

The following analytical methods were used to determine the geochemical characteristics of oils and bitumens.

**Determination of the density** of oils was performed using a Densito 30P portable density and concentration analyzer. The determination accuracy is  $\pm 0.001 \text{ g/cm}^3$ .

**Determination of sulfur** in oil samples was carried out by energy dispersive X-ray fluorescence spectrometry on a

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SLFA-20 oil sulfur analyzer in accordance with the State Standard GOST R 51947-2002. The reproducibility is 0.015 wt.%.

**Isolation of oil and bitumen fractions** was performed by a rapid method using a Fisher Scientific PrepTorr apparatus after precipitation of asphaltenes and their subsequent separation. Saturated and aromatic hydrocarbons were eluted from the resulting maltene fractions with isooctane and a (3:1) isooctane–benzene mixture, respectively, on serially connected plastic columns filled with alumina and silica. Separation was carried out under vacuum.

**Gas chromatographic analysis** of the saturated fractions of oils and bitumens was conducted on an Agilent Technologies 7890A chromatograph using a flame ionization detector (FID) and a DB-1 quartz capillary column (60 m × 0.32 mm, a stationary liquid layer phase 0.25 μm thick). The conditions of the analysis were as follows: initial and final temperatures of the column heating oven 100 °C and 320 °C, respectively; injector temperature 320 °C; detector temperature 320 °C; temperature programming rate 4 °C/min.

**Gas chromatography-mass spectrometry analysis** of saturated, aromatic and maltene fractions of oils and bitumens was carried out on a CLARUS 500 (PerkinElmer) gas chromatography-mass spectrometer. The gas chromatography (GC) conditions were as follows. The samples were injected with an autosampler using helium as the carrier gas at an inlet pressure of  $20.7 \times 10^4$  Pa and a helium rate of 2 ml/min at 100 °C. A 60 m × 0.32 mm HP-1701 column with a stationary phase layer 0.25 μm thick was used. The column oven temperature was programmed as follows: isothermal at 100 °C for 2 min; an increase from 100 °C to 150 °C at a rate of 12.5 °C/min; an increase from 150 to 300 °C at a rate of 3 °C/min; isothermal at 300 °C for 14 min; split/splitless injector operation was used. The gas chromatography-mass spectrometry (GC/MS) interface: the column is directly introduced into the MS ion source; the transfer-line temperature is 300 °C. Mass spectrometric analysis was carried out in the SIR mode.

All analyses were performed at the All-Russian Research Geological Oil Institute (VNIGNI). The obtained geochemical characteristics of oils and bitumens are given in Tables 1 and 2.

## Research results for oils

The oils studied vary greatly in their bulk characteristics (density, sulfur content), which in the study area depend mainly on the depth of their occurrence. Most of the oils from the northern regions of the Buzuluk depression (the Mukhanovo–Erokhovka depression and the Sidorovka–Zemlyansk swell) occurring at depths from 1100 to 3000 m are light to moderate in density and sulfurous to high-sulfur in sulfur content. In turn, deep (4300–5400 m) oils from the Eifelian and Givetian deposits of the southern regions of the depression (Kamelik–Chagan zone of uplifts and the Chinarev basement high) and the Givetian oil from the Mikhailovsko-Kokhanskoe

field (well 350) (depth 3100 m) of the Mukhanovo–Erokhovka depression are very light and low-sulfur (Table 1).

In view of the greater depths of oils within the southern plunge of the Buzuluk depression and, consequently, the greater maturity of probable source rocks, it is reasonable to consider separately oils from the Kamelik–Chagan uplift zone and the Chinarev high of the southern part of the Buzuluk depression and oils from its northern part (the Mukhanovo–Erokhovka trough and the Sidorovka–Zemlyansk swell).

**Genetic characterization of oils from the northern part of the Buzuluk depression.** Three genetic types of oils were identified in the northern part of the Buzuluk depression by studying the composition and distribution of hydrocarbon biomarkers in the oils. The obtained data were analyzed using a multivariate statistical method (cluster analysis) based on a set of parameters that characterize the facies-genetic types of the source organic matter (OM), the conditions of its accumulation, the OM maturity, and the lithological composition of the source rocks. Oils from Lower–Middle Carboniferous deposits were classified as Type I, oils mainly from Upper Devonian deposits and single samples from Lower–Middle Carboniferous deposits were identified as Type II (see Table 1), and oil from the Mikhailovsko-Kokhanskoe field, well 350 in Givetian deposits as Type III.

Analysis of the composition and distribution of biomarkers in Type I, II, and III oils shows that all of them are genetically related to OM of marine origin. This is indicated by the distribution of *n*-alkanes in them with a predominance of low-molecular-weight homologues, low pristane/phytane ratios (<1) (Table 1), as well as the presence of C<sub>30</sub> sterane in all samples, which is a highly specific marker of marine organic matter (Peters et al., 2005). At the same time, the studied oils are clearly differentiated.

In particular, oils of the identified types differ in the ratio of *iso*-alkanes and *n*-alkanes (Ph/*n*C<sub>18</sub> and Pr/*n*C<sub>17</sub>) (Table 1). In Type II oils, the ratio of isoprenoids to *n*-alkanes is higher than in Type I and III oils. The low values of the above parameters for Givetian oil may also be due to the higher thermal maturity of the source OM of this oil (Lijmbach, 1975; Tissot et al., 1971).

In addition, Type I, II, and III oils differ in the composition and distribution of polycyclic hydrocarbon biomarkers.

The differentiation of the studied oils in the source OM composition is shown in a correlation diagram of the Ster/Pent and C<sub>27</sub>/C<sub>29</sub> biomarker parameters (Fig. 1a). According to existing concepts (Andrusevich et al., 2000; Chakhmakhchev et al., 1996; Connan et al., 1986; Tissot and Welte, 1984), most of triterpanes (and predominantly pentacyclic ones) in oil are derived from lipids making up the membrane of bacteria (prokaryotes), so that a higher ratio of pentacyclic triterpanes to steranes in oil indicates a significant bacterial contribution to their source OM or of its intense microbial reworking during diagenesis. The ratio of the  $\alpha\alpha\alpha$  20R C<sub>27</sub> and C<sub>29</sub> regular steranes also characterizes the facies composition of the source OM (Moldowan et al., 1985). Moreover, the higher proportion of the C<sub>29</sub> homologue in oils may be due to the activities of specific bacteria capable to synthesize

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