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ScienceDirect

Russian Geology and Geophysics 58 (2017) 332–342

RUSSIAN GEOLOGY AND GEOPHYSICS

www.elsevier.com/locate/rgg

Geochemistry of Late Devonian oils of the Timan–Pechora basin

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Received 20 July 2016; accepted 1 September 2016

Abstract

The composition of biomarkers and aromatic hydrocarbons of Late Devonian oils of the Timan–Pechora Basin has been studied. It shows that the organic matter of oil-generating deposits is at the close stages of thermal maturity, which are within the early and middle stages of the oil window. Five groups of oils have been recognized, three of which were generated by organic matter of Domanik deposits and the other two formed from organic matter of another source. Most of the studied oil samples contain derivates of isorenieratene indicating that the organic matter of oil source rocks formed in the photic-zone anoxia of the paleobasin.

Keywords: Timan–Pechora basin oil; biomarkers; domanikites; alkylbenzenes; carbon isotope composition of oils

Introduction

Geochemical study of oils in a particular area and at a particular stratigraphic stage is aimed at answering several principal questions:

(1) Are the basin oils of the same genesis or were they generated in different oil source rocks?

(2) Is it possible to judge the relationship between the oils under study and the regional oil source rocks, based on the known data on the latter?

(3) Is it possible to assess the location of hydrocarbon (HC) kitchen area and the directions of oil migration, using a set of geochemical indices?

Geochemistry of oils of the Pechora basin has been the subject of long intenseand intensive study (Bazhenova et al., 2008; Bushnev, 1998; Matveeva et al., 1994; Pankina et al., 1986; Prischepa et al., 2011). Earlier investigations showed the presence of several types of oil of different genesis in various petroliferous rock complexes (Kiryukhina, 1995). As for Late Devonian oils, there are few research works on the directions of oil migration (Bushnev and Valyaeva, 2000) and on the carbon isotope composition of alkanes of typical Domanik oils (Bushnev and Burdel'naya, 2015). The goal of this work is to elucidate how the compositional diversity of HC biomarkers and the carbon isotope composition of Late Devonian oils of the Timan–Pechora basin are related to the varying composition of organic matter (OM) of the oil source rocks.

The object of study

The history of investigation and exploration of the Timan–Pechora basin (TPB) covers 150 years. The field studies in the Timan area, guided by Academician F.N. Chernyshev (1889–1890), revealed Devonian deposits. In 1918, I.M. Gubkin published the article "Ukhta oil-bearing district", in which he recommended a careful examination of its petroleum potential (Gubkin, 1918). He also mentioned Domanik deposits of the Ukhta area in his book "The Doctrine of Oil" (Gubkin, 1975). The scientific works of Academician A.A. Trofimuk on the development of oil fields in Bashkortostan (Volga–Ural basin) and, particularly, the discovery of Devonian (i.e., Domanik) oil there (Kontorovich, 2011) are logically related to the geology and petroleum potential of the TPB. The Timan–Pechora and the Volga–Ural basins of the East European Platform are similar in the presence of Late Devonian Domanik deposits in depressions, which are oil sources in both basins.

The TPB lies in the northeast of the East European Platform and borders upon the Timan Ridge in the west and upon the Ural–Paikhoi Fold Belt in the east. The northern boundary of

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1068-7971/$ - see front matter © 2017, V.S. Sobolev IGM, Siberian Branch of the RAS. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.rgg.2016.09.009

the TPB is the Barents Sea coast, though today there is a new concept that the TPB structures extend to the water area of the Pechora Sea (Malyshev, 2002; Prischepa et al., 2011). Structurally, the TPB is located within the epi-Baikalian Pechora marginal plate.

The TPB includes part of the Timan Ridge, Pechora syneclise, Urals foredeep, and Novaya Zemlya foredeep (Danilov et al., 1999). The tectonic structure of the TPB platform cover includes the following alternating mobile and stable geoblocks (in passing from west to east): the mobile Timan, Pechora–Kolva, and Varandei–Adz'va blocks separated by the stable Izhma–Pechora and Bol'shaya Zemlya blocks (Danilov et al., 1999). The basement of the basin is formed mainly by Riphean deposits (Bazhenova et al., 2008). The sedimentary cover is composed of Ordovician–Permian and Triassic–Cretaceous sediments. Its thickness increases from west to east, from 1 km in the Timan area to 10–12 km in the Urals foredeep, and averages 3–7 km.

The Domanik–Tournaisian petroliferous complex is among the most important ones in the TPB. Its domanik–domanikite strata are the main oil source including the Domanik deposits of the Middle Frasnian Semiluk Horizon and Late Frasnian and even Famennian domanikites (Bazhenova et al., 2008; Prischepa et al., 2011). Lithologically, the Domanik Horizon is composed of mudstones (mostly siliceous ones), siliceous marls, argillaceous limestones, and oil shales (Bazhenova et al., 2008). All rocks are enriched in OM to a particularcertain degree. The content of organic carbon in the Domanik deposits varies from hundredths of percent to tens of percents (averaging ~3%), and the thickness of OM-richest deposits is 20–40 m (Kiryukhina et al., 2013). The Domanik horizon is developed almost ubiquitously within the TPB. It is characterized by strong facies variability (Parmuzina, 2005): Deep-water (depression) facies prevail in the east and are changed by back-reef shallow-water shelf and coastal facies in the west. In the west and northwest, the area with the Domanik facies of the Semiluk Horizon is bounded by organogenic barrier structures (reef deposits) (Bazhenova et al., 2008). The Domanik deposits accumulated at different shelf depths. Fine-layered OM-rich sediments enriched in SiO_2 (Kiryukhina et al., 2013) accumulated in shelf depressions, and bioherm structures and banks (sometimes large) formed by OM-poorest organogenic limestones are localized on local shelf rises (Bazhenova et al., 2008). The ubiquitous formation of the Timan–Pechora and Volga–Ural Domanik deposits is explained by the Frasnian active transgression of the sea basin from the Paleouralian Ocean to the adjacent platform areas of the East European Platform (Kiryukhina et al., 2013).

Methods

Fractionation of oil with separation of aliphatic and aromatic fractions. Asphaltenes were separated from a weighted oil sample through precipitation by *n*-hexane (oil and *n*-hexane were used in the volume proportion of 1:40). The obtained maltene fraction was separated into apolar (50 ml of 20% chloroform solution in *n*-hexane) and polar (resins, 50 ml of ethanol–chloroform mixture (1:1)) fractions on a column filled with alumina (14 × 80 mm). The apolar fraction was separated into fractions of saturated HCs (5 ml of *n*-hexane) and aromatic HCs (5 ml of benzene) on a column (60 × 5 mm) filled with silica gel.

Gas chromatography (GH) analysis was made on a Kristall-2000M chromatograph (30 m × 0.25 mm column HP-5, 0.25 μm thick stationary phase). Temperature was programmed from 110 to 300 ºC at a rate of 5 ºC/min. The injector and detector temperatures were 300 ºC.

Gas chromatography–mass spectrometry (GC–MS) analysis was carried out on a Shimadzu 2010 Ultra GC/MS (30 m × 0.25 mm column HP-5, 0.25 μm thick stationary phase). Temperature was programmed from 110 to 300 ºC at a rate of 5 ºC/min. The injector temperature was 300 ºC, and the detector temperature was 250 ºC.

The carbon isotope composition of oil fractions was studied on a Delta V Advantage (Thermo) mass spectrometer equipped with a Flash EA elemental analyzer. The error of isotope measurements was 0.15‰.

Study of the carbon isotope composition of individual alkanes.

Separation of paraffins from the aliphatic fraction of the oil was made by adduction with urea in ethanol. For this purpose, 3 g urea was mixed with 10 ml ethanol and 1 ml benzene solution of the aliphatic fraction (30–50 mg), and the mixture was brought to a boil. After a slow cooling to the room temperature, the solution with precipitated crystals was cooled to –18 ºC. After 12 h, the supernatant was removed, and the urea crystals were washed with cooled (–18 ºC) ethanol (3–10 ml) and dissolved in distilled water (50 ml). Then, the solution was extracted with *n*-hexane (3–20 ml). The extract was dehexanized to 0.7–1.2 ml, diluted with *n*-hexane to 1.5 ml, and analyzed by GC–IRMS and GC (control analysis).

Gas chromatography–isotope ratio mass spectrometry (GC-IRMS) analysis was carried out on a Delta V Advantage (Thermo Fisher) isotope ratio mass spectrometer connected with a Trace GC Ultra gas chromatograph via an oxidation reactor and a GC IsoLink unit. To control the validity of isotope measurements, analysis of 3-methyl-6,6-dideuteriotricosane (laboratory standard) was periodically made. The standard deviation $\delta^{13}C$ did not exceed 0.5‰ for carbon of the laboratory standard and 0.7‰ for carbon of individual alkanes in the paraffin fraction of the oil.

Geologic characteristics of the studied oils

The oils for study were sampled from Upper Devonian reservoirs penetrated by deep drilling throughout the TPB. These are oil fields of the northern Varandei–Adz'va zone, Khoreyver depression, Pechora–Kolva aulacogene, Izhma–Pechora syneclise, and Timan Ridge (Prischepa et al., 2011). A total of 40 oil samples from 32 fields were studied (Tables 1 and 2).