

Biomarkers and adamantanes in crude oils from Cenomanian deposits of northern West Siberia

V.A. Kashirtsev^{a,*}, I.I. Nesterov^a, V.N. Melenevskii^a, E.A. Fursenko^a,
M.O. Kazakov^b, A.V. Lavrenov^b

^a A.A. Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences,
pr. Akademika Koptuyga 3, Novosibirsk, 630090, Russia

^b Institute of Hydrocarbon Refining Problems, Siberian Branch of the Russian Academy of Sciences, ul. Neftzavodskaya 54, Omsk, 664040, Russia

Received 12 February 2013; accepted 10 April 2013

Abstract

Chromato-mass-spectrometric studies made it possible to identify a wide spectrum of hydrocarbon biomarkers in crude oils from Cenomanian pools of northern West Siberia (Russkoe, Pangodinskoe, Van-Eganskoe, Severo-Komsomol'skoe). The distribution pattern of the main hydrocarbon components (*n*-alkanes, acyclic isoprenanes, steranes, terpanes) shows that most of the oils underwent intense microbial oxidation. We have established high concentrations of 25-norhopanes typical of high-degree degradation; demethylated hopanes are also revealed in "alkane" crude oils. Among low-molecular chemofossils, bi- and tricyclic mono- and sesquiterpanes have been recognized, whose precursors are usually biomolecules synthesized by plants. Unsaturated precursors of mono- and sesquiterpanes might have been the starting material for thermocatalytical synthesis of framework adamantanoid structures, whose high concentrations have been found in alkane-free crude oils.

© 2013, V.S. Sobolev IGM, Siberian Branch of the RAS. Published by Elsevier B.V. All rights reserved.

Keywords: crude oil; geochemistry; hydrocarbon biomarkers; adamantanes; Cenomanian; West Siberia

Introduction

Crude oils from Cenomanian deposits, commercial pools, discovered in the Russkoe, Van-Eganskoe, Severo-Komsomol'skoe, Tazovskoe, Ai-Yaunskoe, and other fields in the northern petroliferous areas of the West Siberian province have specific group and hydrocarbon compositions. By physicochemical properties and composition, these are heavy naphthene oils. Their geochemical characteristics are discussed in the works of Goncharov (1987); Kontorovich et al. (1975); Petrov (1984). Study of heavy naphthene oils has encountered many problems. First, their high viscosity in reservoir conditions, being hundreds of times higher than that of reservoir waters, hinders expulsion of oil by water. Second, all known Cenomanian oil pools, except for the Ai-Yaunskoe, contain massive gas caps, and the oil effective thickness is 15–25 m in height, reaching 60–70 m in the Russkoe field. The latter field is predicted to include several petroleum pools in sand reservoirs localized beneath the same clay cap and pinching out toward the erosion surface (Kuznetsov Formation) (Ne-

strov et al., 2011). There is no single viewpoint of the genesis of oils from Cenomanian deposits. Therefore, any new data on the composition and distribution of biomarker and other hydrocarbons in these oils provide additional information for genetic reconstructions.

Materials and methods

We studied oils from several Cenomanian pools in northern West Siberia: Van-Eganskoe (borehole BH-112, test interval ranging from 972 to 974 m), Severo-Komsomol'skoe (BH-R-453, 1116–1120 m), Russkoe (BH-34, 902–910 m), and Pangodinskoe (BH-65, 1268–1272 m). According to the results of studies and the physicochemical composition (density 814 kg/m³, yield of the fraction with a boiling point of <200 °C is 79%, resins and asphaltenes are lacking), the latter sample should be considered a condensate.

Chromato-mass-spectral (GC-MS) analysis of nonfractionated oils was performed on a setup including an HP 6890 gas chromatograph with an HP-5MS column (30 m long, 0.25 mm i.d., impregnated-phase thickness 0.25 μm) and an MSD 5975C mass-selective detector. Temperature program:

* Corresponding author.

E-mail address: Kashirtcev@ipgg.sbras.ru (V.A. Kashirtsev)

initial temperature 40 °C (4 min), heating to 290 °C with a rate of 5 °C/min, and keeping at this temperature (10 min). Mass-spectrometer operation conditions: ionizing voltage 70 eV, ion source temperature 230 °C, quadrupole temperature 150 °C, and interface temperature 300 °C. A pyrolytic cell (CDS 1500, Valved interface) was used as an evaporator. It was attached to the injector of an HP 6890 gas chromatograph, which made it possible to perform the analysis in the pyr-GC-MS regime. The temperature was programmed by a Pyroprobe 5000, CDS Analytical Inc. instrument. Oils were applied onto a platinum tape and were subjected to thermal desorption at 350 °C for 20 s. Chromatograms were recorded in the TIC (total ion current) and SIM (selected-ion monitoring) regimes. The individual composition of hydrocarbons was identified using the NIST05 mass spectrum database (including ~150,000 mass spectra of organic compounds) as well as literature data and information derived from organic-compound fragmentation by electron impact.

Discussion

According to the results of chromato-mass-spectral study of the hydrocarbon (HC) distribution (TIC chromatograms), all investigated oils are divided into three groups (Fig. 1).

Group 1 includes one of the oils from the Van-Eganskoe field, containing both normal and branched alkanes. Its TIC chromatogram has a well-defined “naphthene hump” (Fig. 1a), which suggests a partial bacterial oxidation of HCs nonresistant to biodegradation (Petrov, 1984).

Group 2 is condensate from the Pangodinskoe field (Fig. 1d), which lacks *n*-alkanes but has preserved isoprenoid HCs, including pristane and phytane, as well as saturated cyclic HCs, mainly decaline and its homologues. Hydrocarbons C₅–C₈ are also dominated by cyclanes (cyclopentanes and cyclohexanes, adding up to 91.10%), whereas the contents of alkanes and arenes are an order of magnitude lower (8.19 and 0.71% of all C₅–C₈, respectively). High-molecular terpanes and steranes are not identified in the condensate.

Group 3 includes heavy oils from the Russkoe and Severo-Komsomol'skoe fields (Fig. 1b, c), containing light HCs (ethylbenzene, xylenes, trisubstituted monoaromatic HCs, bi- and tricyclic naphthenes) and framework adamantanes. The identified high-molecular HCs are hopanes and, to a smaller extent, steranes, whereas normal and branched alkanes are absent or present as traces. In the early 1980s, 4-normethylhopanes (structurally altered hopanes lacking a methyl substituent in the cyclic part of the structure) were identified in Cenomanian oil from the Russkoe field (Kayukova et al., 1981). Later on, NMR studies (Rullkotter and Wendisch, 1982) showed that a methyl substituent was missing from the tenth rather than the fourth angular atom of hopanes, and their homologous series was called 25-norhopanes (in accordance with the number of an absent methyl substituent). The presence of demethylated hopanes indicates the high degree of bacterial oxidation of oils (Kashirtsev et al., 2001; Peters et al., 2007; Petrov, 1984). It was established that bacteria first

consume *n*-alkanes and then branched structures, including isoprenoids. At the final stages, polycyclic naphthenes are subjected to microbial oxidation, losing methyl and alkyl substituents around the rings. In particular, oil biodegradation at the last stages results in demethylated (25-nor)hopanes (Fig. 2) (Kashirtsev et al., 2001; Kontorovich et al., 1991; Peters et al., 2007; Seifert and Moldowan, 1982).

According to TIC chromatography data (the presence of normal and isoprenoid alkanes), oil from the Van-Eganskoe field is bacterially weakly altered. But detailed mass-spectrometric studies of the distribution of high-molecular HCs, mainly hopanoids (fragmentary ions *m/z* 177 and 191), showed the presence of demethylated (25-nor)hopane structures (Fig. 2). This means that the oil was bacterially oxidized no less intensely than the oils from the Russkoe and Severo-Komsomol'skoe fields, which lack alkanes (Fig. 1). Note that 25-norhopanes were also detected in Cenomanian alkane-free oil from the Van-Eganskoe field (BH-110, 960–963 m) during earlier research (Kontorovich et al., 1991). This paradox consisting in the “nonbiodegraded” oil (containing alkanes and isoprenanes) from BH-112 (972–974 m) and the presence of 25-norhopanes in it is most likely due to the secondary (following the biodegradation) filling of the reservoir with “fresh” oil. Mixing of biodegraded (with 25-norhopanes) and “fresh” (with alkanes) oils was described by Philp (1983) for the San Jorges Basin, Argentina. Possibly, the alkane composition of the studied oil from the Van-Eganskoe field is due to the inflow of HCs from the underlying pools.

Of special interest is the set of low-molecular biomarkers (chemofossils). The condensate from the Pangodinskoe field contains only decaline derivatives, whereas the rest studied samples include bicyclic monoterpanes (bicyclooctanes and bicyclononanes) and sesquiterpanes of the drimane series (Figs. 3 and 4). The precursors of these HCs are usually biomolecules synthesized by higher land plants (Peters et al., 2007; Semenov and Kartsev, 2009). For example, protonation of limonene (component of plant's essential oils) yields cations capable for different kinds of cyclization and formation of a wide spectrum of monoterpenes. Cyclization of farnesene leads to the formation of the carbon skeleton of drimane or bicyclofarnesane. These compounds were named after tropical plants of the *Drimys* genus growing in the Pacific basin (Semenov and Kartsev, 2009).

On the TIC mass-chromatograms of the oils from the Severo-Komsomol'skoe and Russkoe fields, extremely high concentrations of HCs with a diamond-like structure, adamantanes, have been identified. Earlier, in West Siberia and other regions of Russia, adamantonoids were studied in naphthene oils (Petrov, 1984) and condensates (Sokolova et al., 1989). In the oils studied in this work, residual concentration of cyclanes and adamantanes probably took place as a result of the biodestruction of the most labile HC components (Gordadze, 2008; Nesterov et al., 2011; Petrov, 1984). Fragmentary-ion scanning (*m/z* 135, 136, 149, 163, 177, and 188) yields a distribution pattern typical of adamantane methyl derivatives (Fig. 5, Table 1). Scanning by fragmentary ions *m/z* 188 and 187 of the intensely biodegraded oils showed the

Download English Version:

<https://daneshyari.com/en/article/4739175>

Download Persian Version:

<https://daneshyari.com/article/4739175>

[Daneshyari.com](https://daneshyari.com)